

FCCat 3
2022

**May 30th – June 3rd
2022**

*Ronce-les-Bains
(France)*

Congress Book

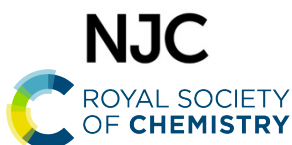


**FCCat 2022:
French Conference on
Catalysis 2022**



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Exhibitors





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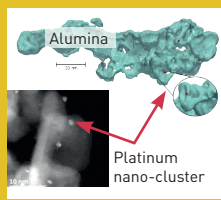
This dynamics is based on **fundamental research** that is essential to accelerate the acquisition of knowledge and feed the innovation process.

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SCIENTIFIC SKILLS

- Homogeneous catalysis
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- Organic & organometallic synthesis
- Synthesis of materials and scale-up
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- Genetic and enzymatic engineering
- Separation techniques and adsorption
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- Computational chemistry



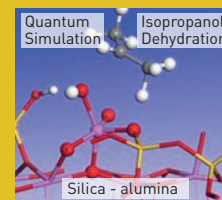
Electron microscopy and tomography. ACS Catal. 10 (2020) 4193



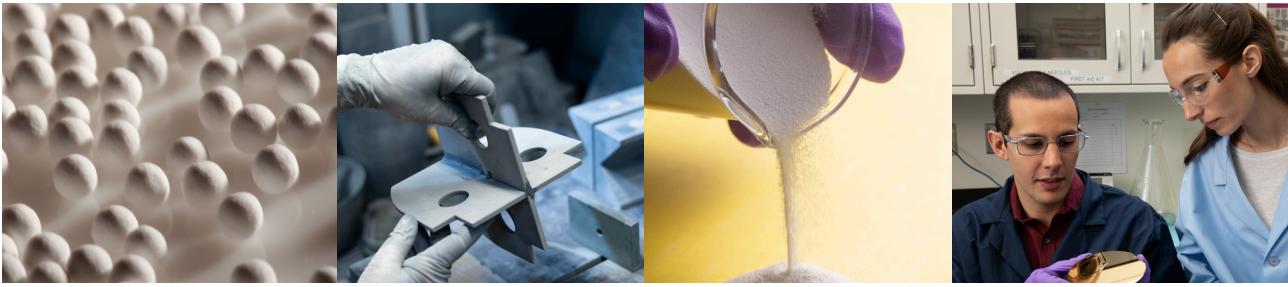
Small scale bioreactors for strain performance screening

SCIENTIFIC ISSUES

- From the molecular description of active sites to performance
- Catalysis and separation in oxygenated environments
- Substitution of expensive or toxic metals
- Activation of small molecules
- Identification of new catalytic materials and biocatalysts



Angew. Chem. Int. Ed. 56 (2017) 230



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	Monday, May 30th	Tuesday, May 31st	Wednesday, June 1st	Thursday, June 2nd	Friday, June 3rd
08:30		Lecture D. Debecker	Lecture T. Cantat	Lecture F. Epron	Lecture G. Costentin
09:00		Flash session 1 L. Desmurs; R. Raachini; B. Farah; P. Arango Ponton; D. Bourbiaux; T. Bahry; C. Squarzoni	Flash session 2 S. Zafeiratos; M. Obeid; A. Mesnier; H. Bekkali; F. Goc; J-D. Comparot; M. Tannous; N. Mediouni	Keynote A. Fortunelli	Keynote P. de Jongh
10:00		Coffee break	Coffee Break	Industrial Session / Round table	Coffee Break
10:30		Porous materials (OC1) S. Palencia Ruiz A. Ait Blal C. Chizallet J. Schneider A. Beuque	CO ₂ Valorization (OC5) H. Petitjean L. Christ P. Brédy R. Djettene T. Len	Coffee Break	Bifunctional / acid-base (OC9) S. Loridant A. Batista J. Sierra Cantor R. Ben Salem J. Marsouin
11:00		Sugars and cellulose (OC2) B. Yeskendir I. Abdouli P. Fongarland I. Bonnin H. Bensalem	H(D)S (OC6) N. Montroussier C. Cottrez B. Barata D. Ryaboshapka K. Sandoval	Industrial Session / Round table	Depollution (OC10) L. Pirault-Roy M. Morales V. Deboos S. de Araujo
12:00		Keynote S. Baudron	Keynote JR. Gonzalez Velasco		Conclusions
12:30		Lunch	Lunch	Lunch	Lunch box + Departures
14:00		Atom economy (OC3) M. Lions C. Thieuleux A. Ropp C. Godard J. Canivet L. K/bibi	Hydrogen (OC4) A. Poater M. König P. Hazemann C. Qasmi C. Molinet L. Oliviero	Metals, carbides (OC7) H. Guesmi F. Cadete S. Aires Y. Yan S. Carenco A. Beuque	HDO - CO ₂ /CH ₄ (OC8) G. Jeantelot R. Azevedo Rafael M. Magalhaes M. Barreau N. Gholampour E. Fourré
15:00	Arrival		Free afternoon / Social activities		
16:00		Coffee Break		Coffee Break	
17:00	Opening	J. Deng Y. Zan D. Hu		J. Rabeah V. Maslova	DivCat Prizes + Lectures (2x 45' + 20')
17:30	Lecture S. Scott				
18:00	Exhibitors	Keynote M. Tromp			
19:00	Keynote J. Luterbacher	Chemistry Europe (Wiley-VCH GmbH)	Poster Session 2	ICC 2024	
20:00	Welcome Party	Poster Session 1		Gala Dinner	
	Diner	Diner	Diner		



Please click on the name of the speaker to directly get the summary of the work

Monday, May 30th

16h30 **Opening**

16h50 **Plenary Lecture: Susannah SCOTT**

Department of Chemical Engineering, and Department of Chemistry & Biochemistry, University of California, Santa Barbara, USA

Catalysis for a Circular Carbon Economy: Valorizing Renewable and Recycled Feedstocks

17h30 **Exhibitors**

18h30 **Keynote: Jeremy LUTERBACHER**

Laboratory of Sustainable and Catalytic Processing, EPFL, Lausanne, Switzerland

Simplifying and controlling the catalytic upgrading of biomass through functionalization

Tuesday, May 31st

8h30 **Plenary Lecture: Damien DEBECKER**

Institute of Condensed Matter and Nanosciences (ICMN), Université Catholique de Louvain, Belgium

Preparation of Tailored Porous Metallosilicate Catalysts

Flash session 1 (9h15 – 10h10)

Mesoporous Zeolites to Solve Diffusion Limitations for Alkylation of Aromatics into para-Isomers

Lucie DESMURS, Anne GALARNEAU, Claudia CAMMARANO, Vasile HULEA

Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France

Towards Silica Supported Bimetallic Ni/Rh Catalysts for the Optimization of Phenols Production through Lignin Hydrogenolysis

Rita RAACHINI^{1,2}, Maya BOUTROS², Franck LAUNAY¹

¹Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France

²Laboratoire de Chimie Physique des Matériaux (LCPM/PR2N), Lebanese University, Jdeideh, Lebanon

Supported Mixed Valence Molybdenum Oxide Catalysts for the Hydrodeoxygenation of Lignin Derived m-Cresol

Bertha FARAH¹, Carole LAMONIER¹, Christine LANCELOT¹, Frédéric RICHARD²

¹Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France

²Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

Investigation of the Effect of the Commercial ZSM-5 Catalyst and their Modified Forms in the Pyrolysis Reaction of Plastic Waste

Paola ARANGO PONTON, Sophie DUQUESNE, Jean-François LAMONIER

Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France

Synthesis of Metallic Nanoparticles in Continuous Flow and Catalytic Applications in Hydrosilylation

Dolorès BOURBIAUX, Yousef SWESI, Anna SLADE, Anthony VIVIEN, Laurent VEYRE, Clément CAMP, Chloé THIEULEUX, Régis PHILIPPE, Claude DE BELLEFON

Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France

Sonocatalytic Oxidation of Benzyl Alcohol to Phenol over a Sonochemically Synthesized CuO Catalyst

Teseer BAHRY, Prince Nana AMANIAMPONG

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

Chemical Transformations of Alcohols Using Nanostructured Ceria for the Synthesis of Specialty Chemicals

Claire SQUARZONI¹, Anne PONCHEL¹, Marc PERA-TITUS²

¹*Unité de Catalyse et Chimie du Solide, Université d'Artois, Lens, France*

²*Eco-Efficient Products and Processes Laboratory, Shanghai, China*

Coffee Break

Oral Communications 1 (OC1): Porous Materials

10h30 Template Removal Processes of Mesophase MCM-41: Revealing the Effect of Gas Atmosphere on Detemplation Mechanism at High Sample Loads

Santiago PALENCIA RUIZ¹, Alexander SACHSE¹, Canan GUCUYENER², Nicolas BATS², Nuno ROCHA-BATLHA³, Ludovic PINARD¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Johnson Matthey, Cleveland, United Kingdom*

³*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

10h50 Investigation of Diffusion Properties of Zeolite-Based Catalysts by Inversion Methods: Principle and First Applications

Abdelhafid AIT BLAL¹, Luz ZAVALA-SANCHEZ^{1,2}, Reda ABOULAYT¹, Philippe BAZIN¹, Alexandre VIMONT¹, Sylvie LACOMBE², Souad RAFIK-CLEMENT², Mickaël RIVALLAN², Françoise MAUGE¹, Arnaud TRAVERT¹

¹*Laboratoire Catalyse et Spectrochimie (LCS), CNRS, ENSICAEN, Caen, France*

²*IFP Energies nouvelles, Solaize, France*

11h10 Multi-Scale Modeling as a Tool for the Prediction of Catalytic Performances: The Case of n-Heptane Hydroconversion in a Large Pore Zeolite

Jean-Marc SCHWEITZER¹, Jérôme REY¹, Charles BIGNAUD^{1,2}, Tomas BUCKO^{3,4}, Pascal RAYBAUD¹, Maïlys MOSCOVICI-MIRANDE¹, Frédéric PORTEJOIE¹, Christophe JAMES¹, Christophe BOUCHY¹, Céline CHIZALLET¹

¹*IFP Energies nouvelles, Solaize, France*

²*Département de chimie, École Normale Supérieure, PSL University, Paris, France*

³*Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, Slovakia*

11h30 Synthesis of a New Polyacid-Functionalized Mesoporous Material and Evaluation of Its Performance in Heterogeneous Catalysis

Julien SCHNEIDER¹, Jason RICHARD¹, Anthony PHIMPACHANH^{1,2}, Patrick LACROIX-DESMAZES¹, Martin IN², Corine GERARDIN¹, Nathalie MARCOTTE¹, Nathalie TANCHOUX¹

¹*Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France*

²*Laboratoire Charles Coulomb, Université de Montpellier, Montpellier, France*

11h50 3D Printing as Innovative Strategy to Enhance Catalytic Performance in the Methane Dehydroaromatization Process

Antoine BEUQUE¹, Ludovic PINARD¹, Vesna MIDDELKOOP², Santiago PALENCIA¹, Ben SUTENS², Alexander SACHSE¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Vito NV, Boeretang, Belgium*

Oral Communications 2 (OC2): Sugars and Cellulose

10h30 Green and Scalable Synthesis of UiO-66-SO₃H Metal-Organic Framework and its Catalytic Activity in Dehydration of Fructose

Bakytzhan YESKENDIR^{1,2}, Priscilla MAGALHAES DE SOUZA¹, Robert WOJCIESZAK¹, Yannick LORGOUILLOUX², Christian COURTOIS², Jean-Philippe DACQUIN¹, Jérémy DHAINAUT¹, Sébastien ROYER¹

¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

²*Laboratoire de Matériaux Céramiques et Procédés Associés, Université Polytechnique Hauts-de-France, Maubeuge, France*

10h50 Glucose Transformation into Levulinic Acid by Hydrothermal Process Assisted by Photocatalysis in Absence of Added Brønsted Acids Catalysts

Insaf ABDOULI, Frederic DAPPOZZE, Marion ETERNOT, Nadine ESSAYEM, Chantal GUILLARD

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

11h10 Development of an Innovative and Compartmented Fixed-Bed Reactor for Hemicelluloses Valorization into Sugar Alcohol

Victoria DIAS DA SILVA FREITAS, Maxime PICHOU, Léa VILCOQ, Régis PHILIPPE, Pascal FONGARLAND

Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France

11h30 Recyclable Ru/Alumina for the Catalytic Water-Mediated Hydrogenation of Glucose to Sorbitol: Process Optimization Study and Mechanistic Insights by in Operando Spectroscopy

Isaline BONNIN^{1,2}, Raphaël MEREAU², Thierry TASSAING², Karine DE OLIVEIRA VIGIER¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Institut des Sciences Moléculaires, UMR 5255 CNRS-Université de Bordeaux, Talence, France*

11h50 Selective Amination of Sugars in the Presence of a Recyclable Ru-Based Catalyst

Hana BENSALÉM, Sophie HAMEURY, Karine DE OLIVEIRA VIGIER

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

12h15 Keynote: Stéphane BAUDRON

Laboratoire de Synthèse et Fonctions des Architectures Moléculaires, CNRS, Université de Strasbourg, Strasbourg, France

Impact of Deep Eutectic Solvents on the Synthesis and Properties of Metal-Organic Frameworks

Lunch

Oral Communications 3 (OC3): Atom Economy in synthetic chemistry

14h00 Immobilization of Metal Complexes in Hydrophobic Zeolites for Ethylene Dimerization

Mathieu LIONS, Alain TUEL, David FARRUSSENG

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

14h20 Developing a Highly Active Catalytic System Based on Metal Nanoparticles for Alkene Hydrosilylation

Martin JAKOUBI¹, Clément CAMP¹, Valérie MEILLE², Chloé THIEULEUX¹

¹*Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

14h40 Tuning the Cobalt:Nickel Ratio of Nickel-Cobalt Nanoparticles for Phosphine-Modulated Catalytic Silane Activation

Anthony ROPP, Sophie CARENCO

Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), CNRS, Sorbonne Université, Paris, France

15h00 Rhodium Catalysed Asymmetric Hydroaminomethylation of α -Substituted Acrylates and Acrylamides

Cyril GODARD

Universitat Rovira i Virgili, Tarragona, Spain

15h20 Heterogenized Molecular Ni-Catalyst for the Sustainable Direct C-H Arylation of Heteroarenes

Yorck MOHR, Elsje QUADRELLI, JEROME CANIVET

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

15h40 Hydrogen Peroxide Decomposition over Titanium-Siloxanes

Ludivine K/BIDI, Geoffroy GUILLEMOT

Institut Parisien de Chimie Moléculaire (IPCM), CNRS, Sorbonne Université, Paris, France

Coffee Break

16h30 TEMPO Immobilized on Ru-BEA Catalyzed Oxidation of alcohols under Mild and Base-Free Conditions

Jianying DENG¹, Karima BEN TAYEB MEZIANE², Wenjuan ZHOU³, Vitaly V. ORDOMSKY¹, Mickael CAPRON¹

¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

²*Laboratoire Avancé de Spectroscopie pour les Interactions la Réactivité et l'Environnement (LASIRE), CNRS, Centrale Lille, ENSCL, Université de Lille, Univ. Artois, Lille, France*

³*Eco-Efficient Products and Processes Laboratory (E2P2L), CNRS-Solvay, Shanghai, China*

16h50 CuO/Cu(OH)₂ Supported on ZIF-8 as Nanocomposite Catalyst for Aerobic Alcohol Oxidation under Mild Reaction Conditions Using TEMPO as Co-Catalyst

Yifan ZAN, Julien REBOUL, Claude JOLIVALT

Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France

17h10 Combined Photo- and Thermally Activated Catalytic Process for Direct and Highly Selective CH₄ Oxidation to Formic Acid at Ambient Conditions

Di HU^{1,2}, Vitaly V ORDOMSKY^{1,2}, Andrei Y KHODAKOV^{1,2}

¹University of Lille, Villeneuve D'Ascq, France

²Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France

Oral Communications 4 (OC4): Production of H₂ and H₂ Vectors

14h00 Predictive Catalysis by DFT: Generation of H₂ and Fixation CO₂, N₂O

Albert POATER

Universitat de Girona, Girona, Spain

14h20 Electrodeposited Metal Oxide Thin Films and their Application in Alkaline Water Oxidation

Maximilian KÖNIG, Wim DE SCHEPPER, Jan VAES

VITO, Mol, Belgium

14h40 Photocatalysis vs Photovoltaics: Why not Make it a Symbiosis?

Paul HAZEMANN¹, Cédric BROCHIER¹, Laure PERUCHON¹, Eric PUZENAT²

¹Brochier Technologies, Villeurbanne, France

²Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

15h00 Hydrogen Storage by Innovative Liquid Organic Hydrogen Carriers (LOHCs)

Chaimae QASMI^{1,2}, Robin MOCHEL², Vincent GAUTIER¹, Isabelle CHAMPON¹, Sébastien THOMAS², Alban CHAPPAZ¹, Anne-Cécile ROGER²

¹Alternative Energies and Atomic Energy Commission (CEA), Grenoble, France

²Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), CNRS, Université de Strasbourg, Strasbourg, France

15h20 Tuning the Structural Dynamics of Pt/CeO₂ Catalysts for Accelerating the Water Gas Shift Reaction

Clément MOLINET, Mimoun AOUINE, Luis CARDENAS, Philippe VERNOUX, Laurent PICCOLO, Stéphane LORIDANT

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

15h40 Supported (Co)MoS₂ Catalysts for Production of H₂ through Water Gas Shift Reaction: Active Sites-Mechanism-Stability

Laetitia OLIVIERO, Weitao ZHAO, Françoise MAUGE

Laboratoire Catalyse et Spectrochimie (LCS), CNRS, ENSICAEN, Caen, France

Coffee Break

16h30 The Origin of High Activity of Cu Single Atoms on CeO₂-TiO₂ During CO Oxidation and PROX Reactions: An Operando Spectroscopic Study

Jawaher MOSRATI, Ali M. ABDEL-MAGEED, Thanh HUYEN VUONG, Haydar ABED, Angelika BRÜCKNER, Jabor RABEAH

Leibniz Institute for Catalysis (LIKAT), Rostock, Germany

16h50 Ammonia Decomposition in Electric Field over CeO₂-based Catalysts

Catherine BATIOU-DUPEYRAT¹, Elodie FOURRÉ¹, Valeriia MASLOVA¹, Gleb VERYASOV², Nikolai NESTERENKO²

¹Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

²Total Research and Technology Feluy (TRTF), Zone Industrielle Feluy C, Seneffe, Belgium

17h30 **Keynote: Moniek TROMP**

Chair of Materials Chemistry, University of Groningen, Groningen, The Netherlands

Novel Catalysis via Insights in Dynamic Structures and Electronics

18h00 Charlotte GERS PANTHER (Wiley-VCH GmbH)

Chemistry Europe

18h20 Poster Session 1

Wednesday, June 1st

8h30 **Plenary Lecture Thibault CANTAT**

LCMCE, CEA, Université Paris Saclay, Paris, France

Catalytic Strategies for the Reduction of C-O Bonds and their Utilization in the Conversion of CO₂ and Other Small Molecules

Flash session 2 (9h15 – 10h15)

Comparative NAP-XPS Study of the Surface Oxidation of Ni-Cermet Electrodes in CO₂ and H₂O Atmospheres

Dingkai CHEN¹, Mathias BARREAU¹, Fabrice BOURNEL^{2,3}, Jean-Jacques GALLET^{2,3}, Spyridon ZAFEIRATOS¹

¹Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), CNRS, Université de Strasbourg, Strasbourg, France

²Laboratoire de Chimie Physique-Matière et Rayonnement, Sorbonne Université, Paris, France

³Synchrotron SOLEIL, Gif-sur-Yvette, France

The Effect of Fe Presence in NiMgAl Catalysts on the CO₂ Methanation Reaction

Michel OBEID^{1,2,3}, Christophe POUPIN¹, Samer AOUAD³, Madona LABAKI², Edmond ABI-AAD¹

¹Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), CNRS, Université du Littoral Côte d'Opale, Dunkerque, France

²Lebanese University, Fanar, Lebanon

³University of Balamand, Koura, Lebanon

Design of an Innovative Continuous Process for Recycling Catalysts Supported on Magnetic Particles

Aline MESNIER, Frederic BORNETTE, Clémence NIKITINE, Marie-Line ZANOTA, Régis PHILIPPE, David EDOUARD, Pascal FONGARLAND

Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France

A Comparison of Layered Materials Used as Catalysts for Diols Conversion

Hamza BEKKALI¹, Philippe BOULLAY², Guillaume CLET¹

¹Laboratoire Catalyse et Spectrochimie (LCS), CNRS, ENSICAEN, Caen, France

²Laboratoire de Cristallographie et Sciences des Matériaux (CRISMAT), CNRS, ENSICAEN, Caen, France

Supported Carbides for Bifunctional Hydrogenolysis of Wood into Glycols

Firat GOC, Franck RATABOUL, Noémie PERRET

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

In-Situ FTIR to Unravel the Bifunctional Nature of Aromatics Hydrogenation Synergy on Zeolite/Metal Catalysts

Nuno BATALHA, Jean-Dominique COMPAROT, Anthony LEVALANT, Ludovic PINARD

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

Interest of Co Based Mixed Oxide in Total Catalytic Oxidation of VOCs Mixture

Mariebelle TANNOUS, Caroline PARIS, Christophe POUPIN, Stéphane SIFFERT, Renaud COUSIN

Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), CNRS, Université du Littoral Côte d'Opale, Dunkerque, France

Elaboration, Characterization and Photocatalytic Properties of Zinc Oxide: Impact of Structural Defects

Nouha MEDIOUNI^{1,2}, Chantal GUILLARD¹, Frederic DAPPOZZE¹, Abdesslem BEN HAJ AMARA², Hafsia BEN RHALEM², Lhoussain KHROUZ³, Stephane PAROLA³, Philippe NAMOUR⁴

¹*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*Laboratoire Ressource Matériaux et Ecosystème de Carthage, Faculté des Sciences de Bizerte, Bizerte, Tunisia*

³*Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, CNRS, Université Lyon 1, Lyon, France*

Coffee Break

Oral Communications 5 (OC5): CO₂ Valorization

10h30 Activating CO₂ on Amphoteric Catalysts: A Molecular Insight on Monoclinic Zirconia

Mathilde IACHELLA, Remi FAVRE, Maxime RIVIERE, Nicola SCAFURI, Nathalie TANCHOUX, Hugo PETITJEAN

Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France

10h50 Pyrrole-Containing Zinc Complexes as Robust Catalysts for the Valorization of CO₂ into Cyclic Carbonates

Lorraine CHRIST, Miguel ALONSO DE LA PEÑA, Alain TUEL

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

11h10 CO₂ Conversion by Low-Temperature Fischer-Tropsch

Pauline BREDY, Yves SCHUURMAN, David FARRUSSENG

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

11h30 Study of the CO₂ Conversion into Methanol: Catalytic Process Innovation and Optimization

Rania DJETTENE, Lionel DUBOIS, Diane THOMAS, Guy DE WEIRELD

University of Mons, Mons, Belgium

11h50 Investigation of Molybdenum and Rhenium Ultradispersed Over Titania as Catalysts for Carbon Dioxide Hydrogenation

Thomas LEN, Pavel AFANASIEV, Luis CARDENAS, Franck MORFIN, Laurent PICCOLO

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

Oral Communications 6 (OC6): Hydro(de)sulfurization

10h30 Mo loading and Alkali Ion Optimizations of Zirconia Supported Catalysts for the Direct Synthesis of Methanethiol

Nicolas MONTROUSSIER^{1,2}, Pascal BLANCHARD², Christine LANCELOT², Georges FRÉMY¹, Hélori SALEMBIER¹, Carole LAMONIER²

¹Arkema, Lacq, France

²Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France

10h50 Influence of the Synthesis Steps of a CoMoP/Gamma-Al₂O₃ Catalyst onto the Multiscale Mo Organization in the Active Phase by ASAXS Technique

Candice COTTREZ¹, Séverine HUMBERT¹, Anne-Sophie GAY¹, Elodie DEVERS¹, Frédéric DE GEUSER², Xavier CARRIER³, Alexandra CHAUMONNOT¹

¹IFP Energies Nouvelles, Solaize, France

²ESRF, Grenoble, France

³Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France

11h10 Innovative Chemical Imaging Speciation Methodology for Studying the Impact of the Impregnation and Drying of Supported CoMoP/Al₂O₃ Hydrotreating Catalysts by Quick-XAS and Raman Spectroscopies

Beatriz BARATA^{1,2}, Christèle LEGENS¹, Elodie DEVERS¹, Olivier DELPOUX¹, Laurent BARTHE², Camille LA FONTAINE², Olga ROUDENKO², Valérie BRIOIS²

¹IFP Energies Nouvelles, Solaize, France

²Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, France

11h30 High Specific HDS Activity of Ultradispersed Mo Species: Influence of Metal-Support Interaction

Daria Ryaboshapka¹, Laurent Piccolo,¹ Thomas Len,¹ Valérie Briois,² Mimoun Aouine,¹ Christophe Geantet,¹ Pavel Afanasiev¹

¹IRCELYON, Lyon, France

²Synchrotron SOLEIL, Gif-sur-Yvette, France

11h50 Evaluation of Catalysts in the Gas Phase Oxidative Desulfurization Reaction of a Model Scrap Tires Rubber Oil

Karol SANDOVAL¹, Paola GAUTHIER-MARADEI¹, Claudia TAVERA², Humberto ESCALANTE¹

¹Universidad Industrial de Santander, Bucaramanga, Colombia

²Universidad de Investigación y Desarrollo, Bucaramanga, Colombia

12h15 Keynote Juan Ramon GONZALEZ VELASCO

Department of Chemical Engineering, Chemical Technologies for Environmental Sustainability Group, Faculty of Science and Technology, University of the Basque Country UPV/EHU, Bizkaia, Spain

Double Function Materials for Integrated CO₂ Capture and Conversion Towards Synthetic Natural Gas

Lunch

14h00 Free afternoon / Social activities

18h00 Poster Session 2

Thursday, June 2nd

8h30 **Plenary Lecture: Florence EPRON**

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

Supported Bimetallic Catalysts for Sustainable Chemistry

9h20 **Keynote: Alessandro FORTUNELLI**

Istituto di Chimica dei Composti Organometallici, Italian National Research Council CNR, Pisa, Italy

Theoretical Approaches to Pt-based ORR Catalysts

9h50 **Industrial Session / Round table (45 min)**

Coffee Break

11h00 **Industrial Session / Round table**

Lunch

Oral Communications 7 (OC7): Metals, Carbides

14h00 **First Atomic Scale Evidence of Hydrogen-Inducing Size Dependent Structural Transition in Gold Nanoparticles: Toward a Realistic Picture of Reactive Surface**

Qing WANG¹, Abdallah NASSEREDDINE², David LOFFREDA³, Christian RICOLLEAU², Damien ALLOYEAU², Catherine LOUIS⁴, Laurent DELANNOY⁴, Jaysen NELAYAH², Hazar GUESMI¹

¹*Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France*

²*Laboratoire Matériaux et Phénomènes Quantiques, Université de Paris, France*

³*Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, CNRS, Université Lyon 1, Lyon, France*

⁴*Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France*

14h20 **Networks of Au_xPd_{1-x} Model Catalysts Obtained by the Di-Block Copolymer Inverse Micelle Method: Insights on Nanoparticle Formation and Network Stability at High Temperature Under Gas Pressure Within the Environmental TEM**

Francisco J. CADETE SANTOS AIRES^{1,2}, Eric EHRET¹, Bruno DOMENICHINI³, Laurence BUREL¹, Thierry EPICIER¹

¹*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*LCR/TSU, Tomsk, Russian Federation*

³*Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), CNRS, UTMB, Université de Bourgogne, Dijon, France*

14h40 **MXene-Supported Single-Atom and Nano Catalysts for Butadiene Hydrogenation**

Yilong YAN¹, Djibril SALL¹, Lola LOUPIAS², Stéphane CELERIER², Matthieu BUGNET^{3,4}, Quentin M. RAMASSE⁴, Mathieu PREVOT¹, Franck MORFIN¹, Laurent PICCOLO¹

¹*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

³*Matériaux : Ingénierie et Science (MATEIS), Université Lyon 1, Villeurbanne, France*

⁴*SuperSTEM Laboratory, Daresbury, United Kingdom*

15h00 Nickel Carbide Nanoparticles for Hydrogenation Reactions in Colloidal Suspension
Rémi F. ANDRE, Léna MEYNIEL, Sophie CARENCO
Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), CNRS, Sorbonne Université, Paris, France

15h20 How the Products in Methane Dehydroaromatization Process Impact Its Stability?
Antoine BEUQUE¹, Ludovic PINARD¹, Jean-François PAUL², Elise BERRIER², Alexander SACHSE¹, Hao HU²
¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*
²*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

Oral Communications 8 (OC8): HDO - CO₂/CH₄

14h00 Mechanism Investigation and Support Optimization for the Iridium-Catalyzed Hydrodeoxygenation of Phenols
Gabriel JEANTELOT, Morten G. INGEBRIGTSEN, Vidar R. JENSEN, Erwan LE ROUX
Chemistry Department, University of Bergen, Bergen, Norway

14h20 Catalytic Hydrodeoxygenation of Benzyl Phenyl Ether as a Model Molecule for Lignin
Raphaëla AZEVEDO RAFAEL¹, Eric MARCEAU¹, Robert WOJCIESZAK¹, Fabio BELLOT NORONHA²
¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*
²*National Institute of Technology, Rio de Janeiro, Brazil*

14h40 Hydrotreatment of HTL Micro-Algal Bio-Oil Over Sulfide, Nitride, and Phosphide Catalysts
Bruno MAGALHAES, Ruben CHECA, Chantal LORENTZ, Pavel AFANASIEV, Dorothée LAURENTI, Christophe GEANTET
Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

15h00 Operando Investigation of Ni Exsolution from LaNiO₃ Perovskites for Improved CO₂ Methanation Catalysts
Mathias BARREAU¹, Xuan THANH NGUYEN¹, Corinne PETIT¹, Sana LABIDI¹, Michael HAEVECKER^{2,3}, Detre TESCHNER^{2,3}, Fabrice BOURNEL^{4,5}, Jean-Jacques GALLET^{4,5}, Spyridon ZAFEIRATOS¹
¹*Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), CNRS, Université de Strasbourg, Strasbourg, France*
²*Max-Planck-Institut für Chemische Energiekonversion (MPI-CEC), Mülheim a.d. Ruhr, Germany*
³*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
⁴*Laboratoire de Chimie Physique-Matière et Rayonnement, CNRS, Sorbonne Université, Paris, France*
⁵*Synchrotron SOLEIL, Gif-sur-Yvette, France*

15h20 Metal-Organic Framework as a Template to Form Co Nanoparticles in Porous Carbon Matrix for CO₂ Methanation
Nadia GHOLAMPOUR, Damien.P DEBECKER
University Catholique de Louvain, Louvain-la-Neuve, Belgium

15h40 Coupling Plasma and Catalysis: Influence of Metal Oxides Properties for CH₄ and CO₂ Transformation
Nassim BOUCHOUL¹, Elodie FOURRE¹, Houcine TOUATI¹, Jean-Marc CLACENS¹, Isabelle BATONNEAU GENER¹, Alysson DUARTE², Nathalie TANCHOUX², Catherine BATIOU DUPEYRAT¹
¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*
²*Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France*

Coffee Break

16h30 DivCat Prizes

18h30 ICC 2024

Friday, June 3rd

8h30 **Plenary Lecture: Guylène COSTENTIN**

Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France

Hydroxyapatites: Toward a Swiss Army Knife Material for Heterogeneous Catalysis

9h20 **Keynote: Petra DE JONGH**

Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, The Netherlands

Bimetallic Catalysts for Selective Hydrogenation – The Power of Combining Forces

Coffee Break

Oral Communications 9 (OC9): Bifunctional and acid-base catalysis

10h20 **On the Intimacy of Bifunctional Catalysts for the Conversion of Syngas to Light Olefins**

Christophe COUDERCY¹, Valentin L'HOSPITAL², Ruben CHECA¹, Anthony LE VALANT², Pascal FONGARLAND³, Pavel AFANASIEV¹, Stéphane LORIDANT¹

¹*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

³*Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France*

10h40 **Insights on Acid and Metallic Site Proximity in Pt/Gamma-Al₂O₃-Cl Bifunctional Catalysts**

Ana BATISTA, Anne-Sophie GAY, Fabrice DIEHL, Céline CHIZALLET, Pascal RAYBAUD

IFP Energies Nouvelles, Solaize, France

11h00 **Bifunctional Metal/Acid Zeolites with Hierarchical Porosity as Catalyst in Synthesis of Alkyl-Branched Fatty Acid Methyl Esters**

Jonathan SIERRA CANTOR², Olinda GIMELLO¹, Carlos Alberto GUERRERO FAJARDO³, Francesco DI RENZO¹, Corine GÉRARDIN¹, Nathalie TANCHOUX¹

¹*Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France*

²*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

³*Université Nationale de Colombie, Bogota, Colombia*

11h20 Nanometric Metal Oxo/Hydroxo Fluoride Catalysts Prepared by Anion Exchange Method for Dihydroxyacetone Conversion in Aqueous Phase

Roua BEN SALEM, Shashank MISHRA, Nadine ESSAYEM

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

11h40 Magnesium Hydroxide Fluorides: A New Family of Heterogeneous Acid-Base Catalysts for Aldol Condensation

Julie MARSOUIN¹, Stéphane CELERIER¹, Mathieu DUTTINE², Alain DEMOURGUES², Jean Marc CLACENS¹, Frédéric RICHARD¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Institut de Chimie de la Matière Condensée (ICMCB), CNRS, Bordeaux INP, Université de Bordeaux, Pessac, France*

Oral Communications 10 (OC10): Depollution

10h20 Adsorption - Oxidation Process (Ad-Ox) for Bisphenol a Removal from Polluted Water Using Green Activated Carbon and Pd-Doped Transition-Metal Catalysts

Nadia El OUAHEDY^{1,2}, Rachid BRAHMI², Gwendoline LAFAYE¹, Laurence PIRAULT-ROY¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*LCCM, University of El Jadida, Faculty of Sciences, El Jadida, Morocco*

10h40 Direct Valorization of Recycled Precious Metals as Heterogeneous Catalysts for Toluene Total Oxidation

Michaël Martin ROMO Y MORALES^{1,2}, Damien BOURGEOIS¹, Helena KAPER², Jérôme MAYNADIE¹, Daniel MEYER¹, Caroline TARDIVAT²

¹*Laboratoire des Systèmes Hybrides pour la Séparation, Institut de Chimie Séparative de Marcoule (ICSM), CEA, ENSCM, CNRS, University of Montpellier, Marcoule, Bagnols sur Cèze Cedex, France*

²*Laboratoire de Synthèse et Fonctionnalisation des Céramiques (LSFC), Saint-Gobain Research Provence, Cavaillon, France*

11h00 Total Oxidation of Toluene on Cu/Al₂O₃ Catalyst Prepared by Dielectric Barrier Discharge Plasma

Victor DEBOOS^{1,2}, Savita Kaliya PERUMAL VEERAPANDIAN², Jean-Marc GIRAUDON¹, Nathalie DE GEYTER², Rino MORENT², Jean-François LAMONIER¹

¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

²*Ghent University, Ghent, Belgium*

11h20 Cu-Hierarchical-SAPO-34 Catalysts with Enhanced Low-Temperature NO_x Removal and High Hydrothermal Stability

Brenda Roberta SILVEIRA DE ARAUJO¹, Jon Ander ONRUBIA-CALVO², Antonio NIETO-MARQUÉZ³, Pareda-Ayo BEÑAT², Juan Ramón GONZÁLEZ VELASCO², Angel CARAVACA^{1,3}, Sonia GIL¹

¹*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France*

²*Department of Chemical Engineering, Faculty of Science and Technology, University of the Basque Country, Leioa, Spain*

³*Mechanical, Chemical and Industrial Design Engineering Department, ETSIDI, Universidad Politécnica de Madrid, Madrid, Spain*

12h00 Conclusions

PS1-1 Mesoporous Zeolites to Solve Diffusion Limitations for Alkylation of Aromatics into para-Isomers

Lucie DESMURS, Anne GALARNEAU, Claudia CAMMARANO, Vasile HULEA

Institut Charles Gerhardt Montpellier (ICGM), CNRS, ENSCM, Univ. Montpellier, Montpellier, France

PS1-2 Green Synthesis of Heterogenous Catalysts by Solvent-Free Reactive Extrusion

Ryma HADDAD¹, Pierre-Igor DASSIER¹, Clément SANCHEZ^{1,2}, Damien P DEBECKER³, Corinne CHANEAC¹, Cédric BOISSIERE¹

¹*Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), CNRS, Sorbonne Université, Paris, France*

²*Collège de France, Paris, France*

³*Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCLouvain), Louvain-La-Neuve, Belgium*

PS1-3 Direct Functionalization of UiO-66 Metal-Organic Framework as an Effective Way Towards UiO-66-SO₃H - An Active Solid Acid Catalyst for Fructose Dehydration

Bakytzhan YESKENDIR^{1,2}, Priscilla MAGALHAES DE SOUZA¹, Robert WOJCIESZAK¹, Yannick LORGOUILLOUX², Christian COURTOIS², Jean-Philippe DACQUIN¹, Jérémy DHAINAUT¹, Sébastien ROYER¹

¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

²*Laboratoire de Matériaux Céramiques et Procédés Associés (LMCPA), Université Polytechnique Hauts-de-France, Maubeuge, France*

PS1-4 Depolymerization of Hemicelluloses Through Mechanocatalytic Process Using Aquivion, a Perfluorosulfonic Acid Polymer, as Catalyst

Jonathan Fabian SIERRA CANTOR¹, Denilson DA SILVA PEREZ², Gilles LABAT², Karine DE OLIVEIRA VIGIER¹, François JEROME¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Institut Technologique FCBA, Champs-sur-Marne, France*

PS1-5 Catalytic Fast Pyrolysis on H-ZSM-5 Zeolite: Activity and Stability of NNN Pairs of Al Atoms During Anisole Transformation

Nathan PICHOT¹, Anthony DUFOUR², Ludovic PINARD¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Laboratoire Réactions et Génie des Procédés (LRGP), CNRS, Université de Lorraine, Nancy, France*

PS1-6 Effect of Al Content on the Reaction Pathways of m-Cresol Transformation over Pd/Al-SBA-15 Catalysts

Camila ABREU TELES¹, Carmen CIOTONEA², Vinicius GONÇALVES³, Jean-Marc CLACENS¹, Sébastien ROYER⁴, Fábio BELLOT NORONHA⁵, Frédéric RICHARD¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

²*Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), CNRS, Université du Littoral Côte d'Opale, Dunkerque, France*

³*Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*

⁴*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

⁵*National Institute of Technology, Rio de Janeiro, Brazil*

PS1-7 Supported Mixed Valence Molybdenum Oxide Catalysts for the Hydrodeoxygenation of Lignin Derived m-Cresol

Bertha FARAH¹, Carole LAMONIER¹, Christine LANCELOT¹, Frédéric RICHARD²

¹*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

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PS1-8 Controlling Ni Nanoparticles Size within SBA-15 Porosity toward Selective HDO Reaction of m-Cresol

Carmen Ciotonea^{1,2,4}, Camila Abreu Teles², Anthony Le Valant³, Jean-Marc Clacens³, Sébastien Royer², Frédéric Richard³

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⁴Institut Michel-Eugène Chevreul (IMEC), CNRS, INRA, Centrale Lille, Université. Artois, Lille, France

PS1-9 OH-Oligomers by Lignin Catalytic Depolymerization

Lucile OLIVIER, Christophe GEANTET, Dorothee LAURENTI

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

PS1-10 Towards Silica Supported Bimetallic Ni/Rh Catalysts for the Optimization of Phenols Production through Lignin Hydrogenolysis

Rita RAACHINI^{1,2}, Maya BOUTROS², Franck LAUNAY¹

¹Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, Paris, France

²Laboratoire de Chimie Physique des Matériaux (LCPM/PR2N), Lebanese University, Jdeideh, Lebanon

PS1-11 Sequential Fractionation of Pine Wood to Bioproducts in Supercritical Methanol by Using Heterogeneous Catalysts

Awalah KOMENAN, Marion ETERNOT, Nadine ESSAYEM

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), CNRS, Université Claude Bernard Lyon 1, Villeurbanne, France

PS1-12 Black Liquor Valorization Via Reactive Distillation and Heterogeneous Catalysis

Laura REYES, Clémence NIKITINE, Léa VILCOCCQ

Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France

PS1-13 Consecutive Pyrolysis-Catalytic Dry Reforming of Plastics to Produce Synthesis Gas

Muriel CHAGHOURI¹, Aida YOUNIS¹, Jane ESTEPHANE², Cedric GENNEQUIN¹, Samer AOUAD², Edmond ABI AAD¹

¹Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV), CNRS, Université du Littoral Côte d'Opale, Dunkerque, France

²University of Balamand, Kelhat El Koura, Lebanon

PS1-14 Investigation of the Effect of the Commercial ZSM-5 Catalyst and their Modified Forms in the Pyrolysis Reaction of Plastic Waste

Paola ARANGO PONTON, Sophie DUQUESNE, Jean-François LAMONIER

Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France

PS1-15 Novel Bio-Inspired Catalytic Tools for Versatile Applications

David EDOUARD

Université Claude Bernard Lyon1, Villeurbanne, France

PS1-16 Synthesis of Metallic Nanoparticles in Continuous Flow and Catalytic Applications in Hydrosilylation

Dolorès BOURBIAUX, Yousef SWESI, Anna SLADE, Anthony VIVIEN, Laurent VEYRE, Clément CAMP, Chloé THIEULEUX, Régis PHILIPPE, Claude DE BELLEFON

Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, CPE Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France

PS1-17 Sonocatalytic Oxidation of Benzyl Alcohol to Phenol over a Sonochemically Synthesized CuO Catalyst

Teseer BAHRY, Prince Nana AMANIAMPONG

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

PS1-18 Chemical Transformations of Alcohols Using Nanostructured Ceria for the Synthesis of Specialty Chemicals

Claire SQUARZONI¹, Anne PONCHEL¹, Marc PERA-TITUS²

¹*Unité de Catalyse et Chimie du Solide, Université d'Artois, Lens, France*

²*Eco-Efficient Products and Processes Laboratory, Shanghai, China*

PS1-19 Photocatalytic Direct Methane Conversion to Acetic Acid with Water as Oxidant

Chunyang DONG

Université de Lille, Lille, France

PS1-20 Reduction of Alkenes by Hydrazine Produced from Ammonia Under High Frequency Ultrasound

Anaëlle HUMBLLOT, François JEROME

Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

PS1-21 Ru/RScSi Intermetallic Materials for Eco-Efficient Synthesis of Ammonia at Low Pressures

Charlotte CROISE¹, Fabien CAN¹, Khaled ALABD², Sophie TENCE², Xavier COURTOIS¹, Nicolas BION¹

¹*Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France*

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PS1-22 Bio-Ethanol Dry Reforming Over Ni-Co Catalysts for Hydrogen Production

Valeria FEDOROVA², Ksenia PARKHOMENKO¹, Ekaterina SMAL², Marina ARAPOVA², Anne-Cécile ROGER¹, Konstantin VALEEV², Yulia BESPALKO², Vladislav SADYKOV², Mikhail SIMONOV²

¹*Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), CNRS, Université de Strasbourg, Strasbourg, France*

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PS1-23 Preparation and Characterization of a Nickel-Based Catalyst Supported by Silica Promoted by Cerium for the Methane Steam Reforming Reaction

Ali ZAZI^{1,2}, Ouiza CHERIFI²

¹*University Mouloud Mammeri of Tizi Ouzou (UMMTO) Algeria, Tizi Ouzou, Algeria*

²*University of Sciences and Technology Houari Boumediene (USTHB), Bab ezzouar Algiers, Algeria*

PS1-24 Impact of the Sulfiding Agent on the Activation of a CoMoP Hydrotreatment Catalyst Under Industrial Conditions

Julien DUPONT^{1,2}, Pascal BLANCHARD², Christine LANCELOT², Svetan KOLITCHEFF¹, Georges FRÉMY¹, Carole LAMONIER²

¹*ARKEMA, Groupement de Recherche de Lacq (GRL), Lacq, France*

²*Unité de Catalyse et Chimie du solide (UCCS), CNRS, Université de Lille, Villeneuve d'Ascq, France*

PS2-1 Sorption-Enhanced Fischer-Tropsch Synthesis

Ljubisa GAVRILOVIC¹, Saima SULTANA KAZI¹, Antonio Geraldo DE PAULA ANTONIO GERALDO DE PAULA OLIVEIRA¹, Mogahid OSMAN⁴, Arnstein NORHEIM⁴, Arvid LOKEN³, Oscar Luis IVANEZ ENCINAS², Edd Anders BLEKKAN²

¹Institute for Energy Technology (IFE), Kjeller, Norway

²Norwegian University for Science and Technology (NTNU), Trondheim, Norway

³Avinor AS, Gardermoen, Norway

⁴Institute for Energy Technology, Kjeller, Norway

PS2-2 Syngas Production by Various Reforming of Methane Processes

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PS2-3 CH₄ and CO₂ Adsorption Over Ni/Al₂O₃ Catalyst in Dry Reforming of Methane Reaction: A DFT Investigation

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PS2-4 Mixed Oxides Catalysts Derived from Layered Double Hydroxide: Application in Methane Dry Reforming

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PS2-7 The Effect of Fe Presence in NiMgAl Catalysts on the CO₂ Methanation Reaction

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PS2-8 Influence of Nitrogen/Carbon Structure on the Stability of Immobilized Ruthenium Catalysts for CO₂ Hydrogenation to Formate

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PS2-9 Single Catalytic Extrudate Reactor for Kinetic Studies of the Oxidative Coupling of Methane

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PS2-10 Predicting the Stability of Single-Atom Alloy Catalysts Under Hydrogen Reactive Media

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Aline MESNIER, Frederic BORNETTE, Clémence NIKITINE, Marie-Line ZANOTA, Régis PHILIPPE, David EDOUARD, Pascal FONGARLAND

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PS2-12 Multi-Elemental Analysis of Catalysts at ppm-Level and High-Speed Acquisition: Elemental Laser Microscopy

Lina JOLIVET^{1,2}, Loïc SORBIER², Charles-Philippe LIENEMANN², Vincent MOTTO-ROS^{1,3}, Samuel MONCAYO¹, Leonor CATITA², Tiago SOZINHO², Florine GAULIER², Jérémie BARBIER², Florian TRICHARD¹

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PS2-13 Acidity of Naphta Reforming Catalyst: 2,6-di-tert-Butylpyridine, a New Probe Molecule

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PS2-15 A Comparison of Layered Materials Used as Catalysts for Diols Conversion

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PS2-17 Better Understanding the Structural Dynamics of Pt/CeO₂ Catalysts

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PS2-19 Effect of Cobalt Substitution on LaFeO₃ Catalysts for Propene Total Oxidation

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PS2-20 Co-Mn-Al mixed oxides issued from Layered Double Hydroxide precursors for total oxidation of VOCs

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PS2-21 Interest of Co Based Mixed Oxide in Total Catalytic Oxidation of VOCs Mixture

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PS2-22 Elaboration, Characterization and Photocatalytic Properties of Zinc Oxide: Impact of Structural Defects

Nouha MEDIOUNI^{1,2}, Chantal GUILLARD¹, Frederic DAPPOZZE¹, Abdesslem BEN HAJ AMARA², Hafsia BEN RHAÏEM², Lhoussain KHROUZ³, Stephane PAROLA³, Philippe NAMOUR⁴

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PS2-23 Effect of Gas-Treatments of Cu-Al Layered-Double Hydroxides on Catalytic Reduction of NO by CO Under Oxidative and Wet Conditions

Madan Mohan BEHERA^{1,5}, Carmen CIOTONEA^{2,3}, Lilian OLIVET¹, Lucette TIDAHY¹, Sébastien ROYER², Diane THOMAS⁴, Guy DE WEIRELD⁵, Stéphane SIFFERT¹, Christophe POUPIN¹

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PS2-24 Competitive Adsorption of NO_x and Ozone on the Catalyst Surface of Ozone Converters: In-Situ DRIFTS Measurements

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PS2-25 The Unexpected Role of NO_x During Catalytic Ozone Abatement at Low Temperatures

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PS2-26 Glass Furnaces Emissions Measurement: SO₂ Storage Catalyst Optimization for NO_x Electrochemical Sensors Protection

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Plenary Lectures

Catalysis for a Circular Carbon Economy: Valorizing Renewable and Recycled Feedstocks

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Large-scale manufacturing of platform chemicals from fossil carbon feedstocks is mostly achieved in the gas phase using high surface area porous catalytic materials with embedded active sites under continuous flow conditions. A sustainable chemical industry will use non-volatile biomass and waste plastic as non-fossil sources of carbon. The transition will require new solid catalysts capable of continuous operation under liquid phase conditions. Their performance is strongly influenced by partitioning of solvents, reactants, and products between the bulk liquid phase and the surface or pore volume. The relative affinities of the reacting molecules for the solution phase vs. the catalytic surface give rise to strongly non-monotonic activity and selectivity trends. Solvent choice and surface affinity are key tools to control catalytic behavior.

This talk will describe recent work at UC Santa Barbara to study and control these effects at the molecular level, by designing solid catalysts with tailored interfacial properties and by probing the molecular composition of the solid-liquid interface, while simultaneously observing the kinetics of catalytic reactions. For example, addition of an organic cosolvent (GVL) to aqueous sugar solutions results in partitioning of the carbohydrate into hydrophilic pores. Organic solvents can also be used to drive oxygenates to metal surfaces where they undergo sequential reactions with hydrogen before being released back into solution. The formation of a hydrocarbon solvent phase during depolymerization of polyolefins changes the affinity of the catalytically active surface for the reacting polymer phase.

I will discuss examples that lead to upgrading of carbon-based molecules via acid/base-catalyzed isomerization of carbohydrates, metal-catalyzed hydrogenolysis and hydrogenation of oxygenated aromatics, and bifunctional (acid/metal) catalytic hydrogen redistribution in the upcycling of waste polyolefins.

Supported metal nanoparticles catalysts obtained in one-step

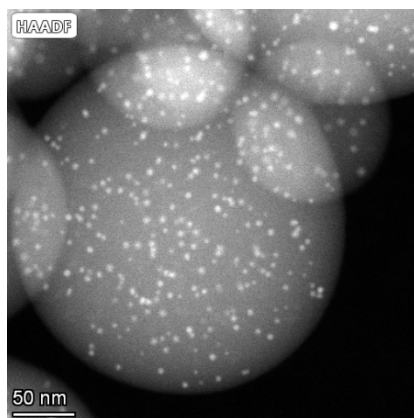
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Dispersing metal nanoparticles onto (porous) oxide carriers is a recurring challenge for catalysis scientists. Conventionally, impregnation, grafting, deposition, and precipitation methods are used – often using complex multi-step procedures – in an attempt to stabilize small particles, to disperse them homogeneously throughout the support, to prevent their sintering during thermal treatment or reaction, to optimize their interaction with the carrier. The task is even harder when considering silica as the support.

Here, we propose a different approach, based on the one-pot synthesis of metal-doped silica microspheres followed by calcination. The preparation leverages on the aerosol assisted sol-gel process.^[1] The method – which earlier proved successful for the preparation of various mesoporous mixed catalysts for many different applications^[2] – is shown to allow trapping metal precursors into a mesostructured silica matrix in a highly dispersed manner. Then, upon calcination, the controlled formation metal nanoparticles can be triggered. Importantly, the method can be coupled with templating strategies (using evaporation-induced self-assembly) to obtain mesoporous catalysts. Also, the direct doping with other oxides is straightforward.

In this contribution, we will demonstrate the versatility of the method with a series of recent examples: Ag- and Cu-based catalysts for the upgrading of ethanol to butadiene or to acetaldehyde, Au-based catalysts for the selective oxidation of glycerol, Cu-based catalysts for the CO₂ to methanol reaction.^[3] We show how the control on metal nanoparticles size, location, embedding in and interactions with the support allows tuning the behavior of the catalyst and reaching higher performance.



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Catalytic Strategies for the Reduction of C-O Bonds and their Utilization in the Conversion of CO₂ and Other Small Molecules

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Supported bimetallic catalysts for sustainable chemistry: Surface redox reaction for tuning the catalytic surface composition

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Since the success of the first generation of bimetallic catalysts for petroleum reforming at the end of the 1960's, numerous studies have been devoted to the design of such systems with the aim of improving the activity, selectivity or stability of the catalysts. The development of a bimetallic catalyst for a given reaction not only needs to choose the appropriate couple M1M2 but also to control as far as possible the distribution of the two metals together and at the support surface. Whereas classical coimpregnation and successive impregnation techniques lead to an unpredictable deposition of the two metals, different methods were developed to obtain bimetallic nanoparticles and favor the metal-metal interactions, as for example methods based on surface organometallic chemistry, chemical vapor deposition, deposition via colloidal route, or codeposition-precipitation. At the University of Poitiers, preparation methods using redox reduction-oxidation reactions were developed 40 years ago for specifically depositing a second metal M2 at the surface of monometallic M1 supported nanoparticles. Various methods are possible to reduce the precursor salt of M2 at the surface of M1 depending on the electrochemical potentials on the species involved: either a direct redox reaction, also named galvanic replacement, or the reduction of an intermediate reducing agent activated at the surface of M1. In this presentation, the fundamental bases of the preparation of bimetallic catalysts by both types of redox reactions will be given along with examples of their application for reactions in liquid or gas phase.

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Hydroxyapatites: toward a Swiss army knife material for heterogeneous catalysis

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Known as the main mineral component of bones and teeth and also abundant as natural phosphate in mines, hydroxyapatite is a calcium phosphate of generic formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ that is extensively used in biomedical applications and for sequestration of radionuclides or heavy metal present in ground and wastewater. The increasing attractiveness of this inexpensive environment-friendly system for heterogeneous catalysis appeared in the 2000s. Beside exhibiting large surface area and various morphologies, hydroxyapatite is stable both in aqueous medium (above 4.5 pH) and up to high temperature ($> 900^\circ\text{C}$). It can thus operate for many classes of liquid or gas phase reactions. The main originality of this system comes from its amazing tunable composition that makes it a swiss army knife for heterogeneous catalysis. First, the control of its non-stoichiometric properties that can be described by the modulation of the bulk Ca/ P molar ratio (i.e. calcium and hydroxide deficiencies, incorporation of hydrogenophosphate and carbonates defects) is used as a key empirical parameter allowing to tune the surface acid-base balance. In addition, substitution ability on both its cationic and anionic sites offers endless opportunities for the design of hydroxyapatite or heteroatom modified hydroxyapatite to be used as active phases or as suitable supports for the deposition of highly dispersed catalytic metallic centers (even as monomeric centers). As a result, hydroxyapatite-based system was investigated in many classes of acid-base or multifunctional reactions of societal interest, with very promising results, and even some important breakthroughs for the ethanol to butanol Guerbet reaction or more recently for the dry reforming of methane. Although most studies still focused so far on the catalytic performance, this presentation will go beyond empirical structure reactivity relationships and will aim at rationalizing the behavior of apatite-based catalysts and at providing comprehensive guidelines to tune their synthesis conditions depending on the target application.

Keynotes

Simplifying and controlling the catalytic upgrading of biomass through functionalization

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The development of various renewable chemicals has been limited by the complexity and efficiency of their production, as well as their lack of competitive properties. Notably, existing lignocellulosic biomass fractionation processes lead to various degrees of condensation of carbohydrates and lignin products including through the formation of random interunit C–C linkages that constrain their use. Here, we exploit the aldehyde stabilization of lignin and carbohydrates to tailor their structure, functionality, and resulting properties, expanding upgrading possibilities. We can notably use one or two bifunctional aldehydes to install controlled quantities of specific functionalities on lignin and xylose and thereby control their physical properties and reactivity. Rational selection of the aldehyde allows us to produce acetal-stabilised lignins that are soluble in either polar or non-polar solvents such as water and toluene. Exploiting these novel solubility properties, we can exploit solvent effects in lignin hydrogenolysis to tune the product distributions of this reaction. Similarly, aldehyde selection can allow us to install reactive functional groups such as carboxylic acids or aldehydes on the lignin backbone for use in subsequent transformation such as phenolation or crosslinking with gelatin. On the other hand, acetal functionalization of xylose could lead to the direct formation of valuable chemicals including polar aprotic solvents and polyester precursors. The direct production of interesting intermediates and useful chemicals by straightforward acid-catalyzed functionalization during biomass fractionation could drastically simplify the production of several biobased chemicals.

Impact of Deep Eutectic Solvents on the Synthesis and Properties of Metal-Organic Frameworks

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Deep Eutectic Solvents (DESs) represent an emerging class of solvents featuring some characteristics of their ionic liquids cousins - low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species - along with unique specificities, such as their limited toxicity and an improved biocompatibility.¹ Their use as media for the ionothermal preparation of Metal-Organic Frameworks (MOFs) has been recently explored, showing that not only DESs represent green and less toxic alternatives to solvents commonly used in the synthesis of these porous crystalline materials, but also that they may play different roles in the MOF construction.²

Aiming at further investigating the potential of DESs for MOF synthesis and their impact on the properties of the materials, we are exploring their use for the preparation of prototypical MOFs as well as of new architectures. In this contribution, our recent efforts in this area will be presented.³

Notably, the reline DES choline chloride/urea (1:2) and its analogue based on e-urea (2-imidazolidinone, ethylene urea) were employed for the preparation of the prototypical MOFs HKUST-1 and Mg-MOF 74. In these crystallization media, the desired materials with good textural properties can be successfully obtained albeit with unusual crystal morphology. Furthermore, it was also demonstrated that, upon heating in reline, HKUST-1 converts to a non-porous chloride-incorporating material, highlighting the role of the DES that allows not only the synthesis of the MOF but also its structural transformation. Furthermore, the unprecedented use of a DES for the ionothermal synthesis of Ca-MOFs allowing the successful preparation of 3-D Ca-MOFs with a series of dicarboxylic acid ligands, demonstrating that DESs can be considered as effective solvents for the synthesis of water-sensitive MOFs.

Through these results and others, the potential and interest of this class of solvents for the synthesis of MOFs and their impact on the properties of the materials will be highlighted.

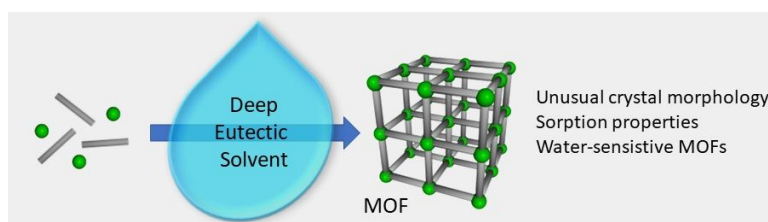


Figure 1. DES for MOF synthesis and their impact on morphology and properties.

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Novel catalysis via insights in dynamic structures and electronics

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As we all know, catalysis is key to solving some of the world's major challenges. It does mean we have been shifting gears and have to move to different feedstocks and products, develop truly sustainable catalysts and processes, recycle, and move towards circularity.

Using different catalyst materials (e.g. non-scarce, non-toxic metal systems), using less energy and looking at different types of reactions (e.g. using different feedstocks), etc... are amongst the challenges for the field. In order to rationally design and develop novel catalyst systems, we have to understand their performance and (catalytic) mechanisms.

In this lecture I will present different examples, from homogeneous and heterogeneous catalysis, and demonstrate that the combination of catalysis and advanced characterisation (operando, time- and/or spatial-resolved) provides insights in the mechanisms and (re)active species present, as such guiding us towards novel or optimised catalyst molecule/material design and processes. Examples will include industrially relevant processes like selective oligomerisation and oxidation, dehydrogenation, and small molecule activation.

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Double function materials for integrated CO₂ capture and conversion towards synthetic natural gas

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The power to gas (PtG) technology produces methane or synthetic natural gas (SNG) through the Sabatier's reaction, $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$, also known as the CO₂ methanation reaction. The PtG concept allows the storage of energy using SNG as energy carrier. First, H₂ is produced by electrolysis using the surplus electricity obtained from renewable resources; then, H₂ is catalytically reacted with pre-concentrated CO₂ to produce methane. Thus, SNG can be fed directly to the existing extensive transport and distribution network. Also the utilization of the as-produced SNG as a fuel represents a carbon neutral cycle.

Recently, the CO₂ hydrogenation in consecutive adsorption and hydrogenation cycles has been proposed for applying to CO₂ diluted streams, without needing previous sequestration and purification steps, which present a better management of the heat generated (high exothermicity). This strategy requires the use of dual function materials (DFM), to operate in alternate cycles of CO₂ capture and methanation. The DFM contains an alkaline or alkaline earth element that acts as CO₂ adsorbent (e.g. Ca, Na components) and a noble metal (e.g. Ni, Ru) that assists the methanation reaction. First, CO₂ is adsorbed in the DFM until saturation; then, when H₂ is injected, a spillover phenomenon occurs that leads the chemisorbed CO₂ to the noble metal where the methanation takes place. Both the CO₂ capture and hydrogenation to CH₄ processes can operate at temperatures ranged 250–400 °C. The synthesis and characterization of several home-made DFMs are presented, including Me_{ads}-Me_{Hyd}/Al₂O₃ [1, 2], and also perovskite-based formulations [3].

The modeling of the CO₂ hydrogenation in consecutive adsorption and hydrogenation cycles can also be a suitable tool to define optimal operation conditions, such as, the duration of adsorption and hydrogenation cycles, temperature or H₂ dose during the hydrogenation. A kinetic model to describe the CO₂ capture and in situ conversion to CH₄ on a 4%Ru10% Na₂CO₃/Al₂O₃ dual function material is described. A dynamic one dimensional isothermal heterogeneous plug flow reactor model with axial dispersion is considered. The model is able to predict the evolution of gas phase CO₂, CH₄ and H₂O together with the fractional coverages of carbonates, hydroxides and bicarbonates along the reactor length to gain a deeper understanding on the mechanism and the dynamics of the CO₂ storage and hydrogenation process.

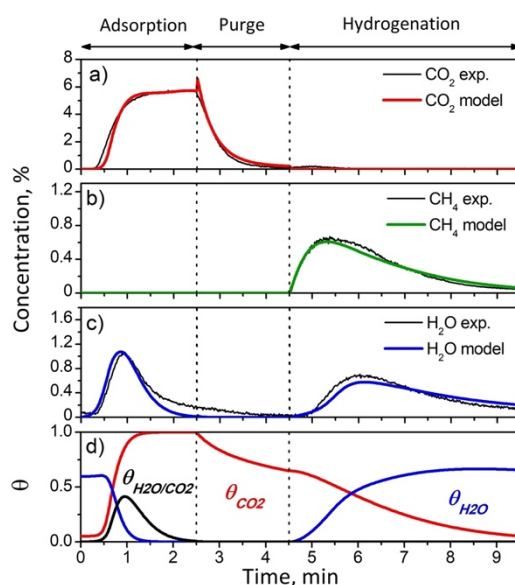


Figure 1: Experimental (black thin lines) and predicted by the model (colored thick lines) gas phase CO₂, CH₄ and H₂O concentration, and covering factor in the last node of the reactor (350 °C, 5.7 % CO₂/5.7 % H₂ feed).

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Theoretical Approaches to Pt-based ORR Catalysts

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The widespread adoption of proton-exchange membrane fuel cell (PEMFC) devices for electrochemical energy conversion is currently limited by the lack of appropriate catalysts. Highly active and durable (under acidic condition) platinum-based catalysts would in fact be indispensable to accelerate the sluggish oxygen reduction reaction (ORR), but their development face serious issues, and has been slow and incremental. In the present talk, I will present recent results of combined experimental/theoretical studies to single out the factors affecting activity and stability of Pt-based systems under ORR conditions. I will discuss how to disentangle the interplay of the various components of the coordination environment of exposed Pt atoms: strain, surface structure, and ligand effects, in determining the catalytic propensity and robustness. I will then introduce corresponding descriptor quantities, and in particular a binary descriptor capturing both strain and alloying phenomena, defined simultaneously on experimental (X-ray absorption spectroscopy) and theoretical observables, and I will show how it correlates with both the calculated oxygen binding energy of the Pt-alloy catalyst surface and the experimentally determined ORR activity, and how it can be used to predict not only the catalytic activity but also the durability of a wide range of Pt-alloy ORR catalysts.

Bimetallic Catalysts for Selective Hydrogenation – The Power of Combining Forces

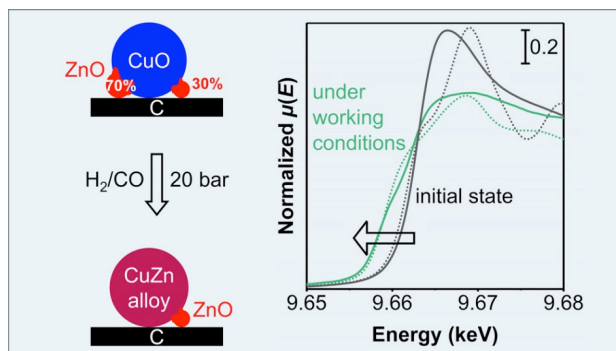
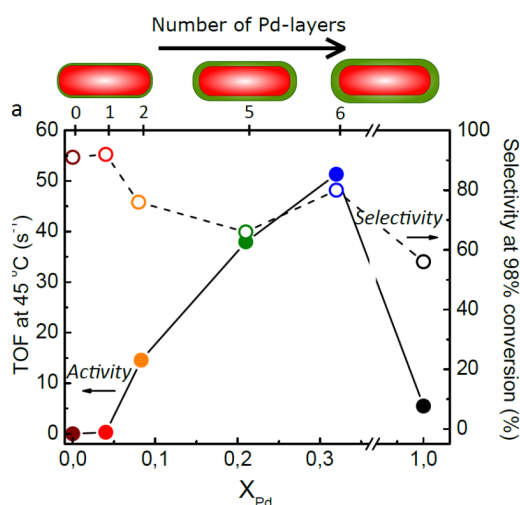
Petra DE JONGH

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Supported catalysts typically contain small metal nanoparticles, or sometimes even single metal atoms or ions, to maximise the metal surface area and hence minimise cost. Increasingly it is appreciated that the structural and electronic properties of the metal surface can be tweaked by adding a second phase that is in contact with, or sometimes mixed with, the metal nanoparticle. Controlling the structural parameters is essential for catalyst performance, and understanding their influence on catalyst functionality requires testing and characterisation of these catalysts under relevant working conditions (i.e. high temperature and pressure).

In my presentation I will highlight how advanced control over catalyst preparation, combined with advanced characterisation techniques, such as in-situ electron microscopy and synchrotron-based X-ray spectroscopy, help us to understand what makes a great catalyst. For this we build on 3D model catalysts; catalyst in which for instance the specific nature of the support or preparation allow fundamental studies, while at the same time being robust enough to be tested under industrially relevant pressure and temperature conditions.

In more detail I will highlight two examples, both involving a synergy between two metals, and between Dutch and French researchers. I will first discuss how synergy between Au and Pd is achieved in carefully tuned bimetallic Au-Pd catalysts for selective hydrogenation of butadiene, while in the second example I will discuss promoted Cu catalysts for the hydrogenation of CO₂ with hydrogen to renewable fuels and chemicals.



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Flash session 1

Mesoporous Zeolites to Solve Diffusion Limitations for Alkylation of Aromatics into para-Isomers

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Catalytic processes enable a large range of industrial reactions by lowering activation energies. Furthermore, current environmental and energetic challenges asks for sustainable processes with optimized resources consumption. Regarding catalysts, high conversion and selectivity for products of interest are an efficient way to maximize atom economy and carbon efficiency. The catalytic alkylation of toluene with methanol leads to p-xylene, a product in high demand for the production of polyethylene terephthalate (PET). Over commercial zeolite catalysts, a mixture of xylene isomers was commonly obtained due to intraparticle diffusion limitation in the microporous catalyst. In order to increase diffusion and therefore the selectivity in p-xylene, the present study aims at developing the use of hierarchical zeolites. Adding mesoporosity to zeolites enhances reactants and products diffusion, increases the accessibility to the active sites, improves catalyst lifetime thanks to the diminution of coke formation and a slower deactivation rate¹⁻⁴. Hierarchical zeolites prepared by “micelle-templating”¹ and presenting a MCM-41-type homogeneous and ordered mesoporosity have shown promising catalytic performances¹⁻⁴. In this study, various hierarchical zeolites (FAU-Y, ZSM-5, MOR, *BEA) were prepared by “micelle-templating”. Their structural and textural properties were fully characterized by XRD, scanning and transmission electronic microscopies, Nitrogen sorption isotherms at 77K and advanced t-plot analysis^{5,6} to precisely calculated their micro- and mesopore volumes. In micelle-templated modified zeolites, it was shown that acidity decreased for a too high level of transformation.⁵ There is a compromise to find between the amount of mesopores generated by this method and the remaining acidity. Acidity was evaluated by NH₃-TPD and FTIR pyridine, and also by a catalytic test reaction. The phenol alkylation with tert-butanol⁷ was chosen to highlight the compromise between the increase of diffusion coming from the additional mesoporosity and the decrease of acidity. We found that adding mesopores in ZSM-5 enhanced drastically the conversion, as native ZSM-5 was not able to catalyse this reaction due to steric hindrance. The best compromise was reached for modified ZSM-5 exhibiting micropore and mesopore volumes of 0.14 and 0.16 mL/g, respectively, leading to the conversion of phenol into ditert-butylphenol as high as 80%. This reaction allowed to select the best catalyst to improve the p-xylene production through toluene alkylation with methanol.

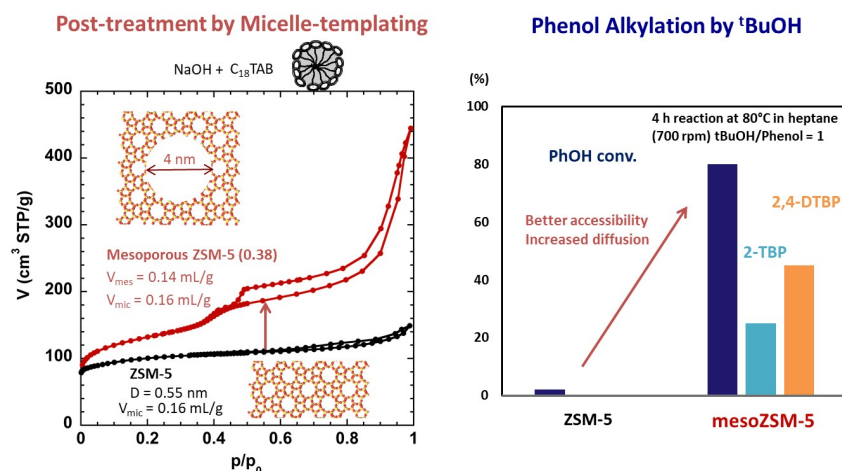


Figure 1: Mesoporous zeolites to solve diffusion limitations for alkylation of aromatics into para-isomers

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Towards Silica Supported Bimetallic Ni/Rh Catalysts for the Optimization of Phenols Production through Lignin Hydrogenolysis

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Bio-sourced phenols can be expected from lignin reductive depolymerization through hydrogenolysis as long as side-reactions such as aromatic ring hydrogenation are minimized. Depolymerization usually involves supported or unsupported noble or transition metal catalysts affording active hydrogen species either from H₂ or H-donors such as alcohols under an inert atmosphere (Ar or N₂). Typically, reported temperatures are ranging from 100 to 350°C but it is possible to make the conditions milder by starting with pre-oxidized lignin. In this contribution, using a model of such lignin, *i.e.* 2-phenoxy-1-phenylethanone (K1_{HH}), studies were carried out in order to optimize phenol production by varying the metal catalyst (Ni or Rh), its loading onto silica (5 or 10 wt.%) and the source of active hydrogen species (H₂ or isopropanol). Impregnation of Aerosil 380 by aqueous nickel(II) nitrate in the presence of ammonia led to Ni-silica-based catalysts with 5 to 10 wt.% of Ni characterized by highly dispersed nanoparticles (Transmission Electron Microscopy) greatly interacting with the support (TPR analyses). Ni-O-Si phyllosilicate phases could be systematically emphasized (X-Ray Diffraction) prior to reduction by H₂ at 500°C. For the sake of comparison, a reference 5 wt.% Rh catalyst was also synthesized. The Ni- and Rh-based materials were tested either at 120°C under H₂ (20 bar) with ethanol or at 180°C with isopropanol under N₂ atmosphere (5 bar) keeping a 100 substrate/metal molar ratio. Conversion and yields were expressed based on carbon atoms. Under H₂, no reaction was observed with Ni-catalysts, nor with Rh ones. With isopropanol at 180°C under 5 bar of N₂, K1_{HH} was transformed. RhNH₃/SiO₂-5% led to the slowest reaction (70% conv.) with a partial conversion of K1_{HH} into the corresponding alcohol (A1_{HH}) with a 10% yield. RhNH₃/SiO₂-5% mainly gave rise to acetophenone and phenol (30% yield each) formed through hydrogenolysis of the C-O bond in K1_{HH}. On the other hand, NiNH₃/SiO₂-5% was more active (100% conv.). With Ni, hydrogenation of the carbonyl group of K1_{HH} leading to A1_{HH} is the favored pathway, followed by C-O hydrogenolysis of the resulting alcohol affording C1_{HH} (32% yield). The latter seems to be at the origin of ethylbenzene and phenol (C-O bond cleavage), but, unfortunately, phenol (max. yield of 26%) was partly hydrogenated into cyclohexanol (8% yield) in these conditions. Better yields of monomers (40% of ethylbenzene, 22% of phenol and 18% of cyclohexanol) and a lower yield in C1_{HH} (20%) could be obtained with NiNH₃/SiO₂-10%. Such results led us to test bimetallic Rh-Ni-silica-based catalysts obtained through the co-impregnation of Aerosil 380. We will show in this contribution that those materials bring a compromise between lignin depolymerization activity and phenol selectivity.

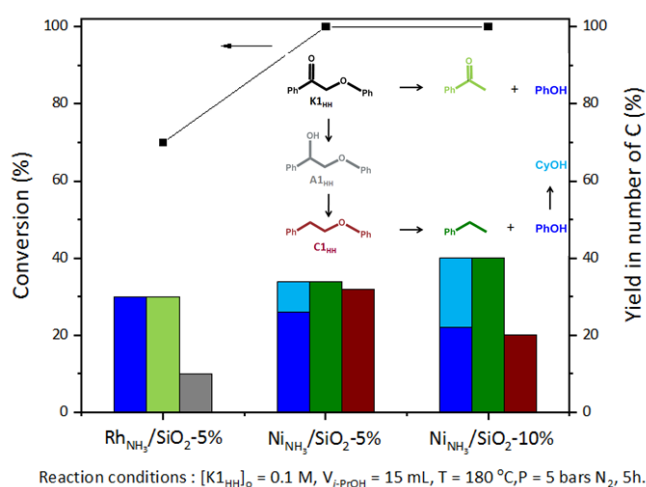


Figure 1: Conversion and products yields (based on carbon) for the hydrogenolysis of K1HH in the presence of isopropanol

Supported Mixed Valence Molybdenum Oxide Catalysts for the Hydrodeoxygenation of Lignin Derived m-Cresol

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Out of the three principal components of lignocellulosic biomass, lignin has proven to be the major aromatic resource of bio-based economy. Processes of lignin depolymerization and conversion to high value chemicals have received increased attention in recent years as possible alternatives to the petrochemical industry. In particular, hydrodeoxygenation (HDO) allows to convert phenolic oxygen compounds of lignin-derived feeds to aromatics. Several catalyst formulations have been tested for HDO, the most active being γ -alumina supported CoMoS and NiMoS that are widely used in hydrotreating processes. However, their superior activities can only be preserved by continuous addition of sulfur to the feed, resulting in the contamination of end products. Sulfur free catalysts were thus considered. Previous reports have especially highlighted molybdenum oxide-based catalysts great selectivity to aromatics by the direct cleaving of the $C_{\text{aromatic}}\text{-O}$ bond (direct deoxygenation (DDO) route), with however lower activity than sulfided ones. Hence, in this work, supported MoO_x catalysts are being developed for the HDO of lignin-derived phenolic m-cresol, the precise aim being the design of catalysts that could challenge the activity of sulfided $\text{Mo}/\text{Al}_2\text{O}_3$.

The effect of the support on the HDO activity was evaluated. 15 wt.% MoO_x were deposited on different materials: commercial Al_2O_3 , ZrO_2 and TiO_2 as well as prepared mesoporous silica COK12, by incipient wetness impregnation of an oxide precursor solution followed by drying and calcination steps. The resulting catalysts were then pretreated in-situ at 340°C and 30 bars under a flow of hydrogen, and tested for the HDO of m-cresol in the same experimental conditions. Aromatics (toluene) formation was favored in all cases (selectivity to DDO $\geq 80\%$), the other products being methyl cyclohexenes. In terms of activity, Mo/Zr followed by Mo/Ti were the most active. It was previously reported that oxophilic zirconia and titania supports most likely stabilize the reduced Mo^{5+} state concomitant with oxygen vacancies that could be the active phase in HDO. H_2 -TPR experiments of the fresh catalysts confirmed that the reducibility of molybdenum strongly varies with the support nature. Reduction of Mo^{6+} species of MoO_3 proceeds in two steps for all four catalysts, the first being that of octahedral Mo^{6+} to Mo^{4+} at a temperature range of $400\text{-}600^\circ\text{C}$ followed by that of Mo^{4+} to $\text{Mo}(0)$ at $T > 700^\circ\text{C}$. The first stage reduction temperatures of the catalysts followed the order $\text{Mo}/\text{Zr} < \text{Mo}/\text{Ti} < \text{Mo}/\text{Al} < \text{Mo}/\text{COK12}$, indicating that Mo^{6+} is more easily reducible when supported on ZrO_2 and TiO_2 than on Al_2O_3 and COK12. This is further demonstrated by the calculated total reduction degrees of MoO_3 which were found to be about 100% for Mo/Zr and Mo/Ti, 72% for Mo/Al and 44% for Mo/COK12. The obtained TPR results indicate that molybdenum oxides supported on oxophilic materials are more favorable to the formation of Mo^{5+} species, supposed to be the active phase in HDO. In order to confirm this hypothesis, EPR and XPS analyses of the activated and tested catalysts will be performed for a detailed study of the reducibility of MoO_3 and its effect on HDO performances.

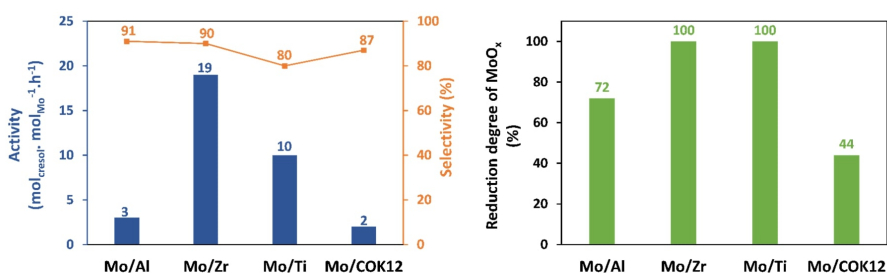


Figure 1: Support effects on activity and selectivity of Molybdenum oxide catalysts in HDO of m-cresol (left) and on reducibility of these oxides (right)

Investigation of the Effect of the Commercial ZSM-5 Catalyst and their Modified Forms in the Pyrolysis Reaction of Plastic Waste

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Introduction: Plastic is an indispensable material in everyday life and therefore in our economy, its use is justified thanks to its physical-chemical qualities and low production costs compared to other types of materials, and to the plastic end-use in the market. Despite its qualities and applications, plastic can have harmful effects on health and the environment. Plastic pollution is a problem that increases with the rising production of plastic, as a consequence of the growing population, and thereby, the demand for this material, mostly in developing countries, and the fact that about 40% of the total production of plastic is intended for single-use plastic. As a consequence of the raise of consciousness of all these issues, the post-consumer waste is transiting from a linear economic model of consumption and traditional dispose treatments to circular economy since 2008, which involves *Reduce, Redesign, Reuse and Recycle*. As a result of this circular economy in Europe, between 2006 and 2018 recycling increased by 100%, the use of plastic waste in energy recovery increased by 77% and landfill decreased by 44%. The European Commission envisages to recycle 100% of plastic by 2025, to decrease the number of single-use plastic bottles by 50% in 2030 and to ban the use of single-use plastic packaging by 2040.

Catalytic pyrolysis of plastics is a promising alternative that allows to give value to these plastic wastes thanks to thermal and chemical cracking in oils of high chemical value. Catalytic pyrolysis is carried out in an inert atmosphere, at a lower temperature than thermal pyrolysis (in the case of mixing polymer and catalyst) and because its closed system, doesn't generate pollutants.

Aim: A key point to obtain a high-value liquid phase derived from the pyrolysis of plastics, is to have an optimal design and geometry of the equipment used in pyrolysis, which will eventually give a full techno-economic view of the project. In addition to pyrolysis reactor geometry and design, other main factors that have an effect on the catalytic pyrolysis process are the temperature, retention time, pressure, type and rate of carrier gas, feedstock composition, quantity and type of catalyst. In this work the effect of catalysts was particularly examined in order to optimize the concentration of aromatic hydrocarbons in the derived oils.

Methods: The performance MFI type zeolite (ZSM-5) and its modifications in the catalytic pyrolysis of polyethylene at 450°C and atmosphere pressure was evaluated. The ZSM-5 commercial catalysts with the ratio of Si/Al, 23, and three doped ZSM-5 were selected. In this manner the effects of catalyst porosity and acidity was more particularly examined.

Results: The liquid yield increases with a major specific surface, but the nature of the acid sites (Lewis/Bronsted acid sites) was determinant in the selectivity to aromatic compounds.

Conclusion: The optimization of the main factors that affect catalytic pyrolysis can lead to the second phase of research on the stability, regeneration and reuse of catalysts to carry out a process with economic and environmental sustainability.

Synthesis of Metallic Nanoparticles in Continuous Flow and Catalytic Applications in Hydrosilylation

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This project aims to develop the synthesis of metallic colloidal suspensions in continuous flow, to reduce metal loading used in industry while keeping their catalytic activity. Continuous flow offers many advantages compared to batch synthesis as a shorter time reaction, a smaller reactional volume and a safety improvement thanks to the small volumes involved. Our first investigations have been carried out on Pt NPs from Pt(dba)₂ precursor (PRE) with n-octylsilane (RED) as stabilizer and reducer with or without the contribution of H₂ as reducer. This synthesis, performed under inert atmosphere, was inspired from a previous work in batch reactor in our laboratory (Thieuleux, C. et al. *New J. Chem.* 38, 5952–5956, 2014). The impact of temperature, reagents flow rate and RED/PRE ratio on Pt NPs synthesis in continuous flow were studied. The Pt(dba)₂ consumption was followed by UV visible analysis by measuring the intensity of the precursor characteristic band at 569 nm. Optimum parameters were found with 1.5 as RED/PRE ratio at 60 °C, with 2 NmL/min of H₂ and 10 min of residence time. Pt NPs with a narrow size distribution centred at 1.4 nm and without aggregates were obtained (Figure 1). As comparison, Pt NPs obtained in batch reactor were synthesised in 16 h with a mean diameter between at 1.1 to 1.6 ± 0.3 nm (Thieuleux, C. et al. *New J. Chem.* 38, 5952–5956, 2014).

The next investigations were carried out regarding the catalytic activity of Pt NPs synthesised in continuous flow on hydrosilylation. Octene hydrosilylation was performed with heptamethyltrisiloxane (MDHM) in toluene, to obtain MDOctM. The first experiments were conducted in batch reactor at 45 °C with 2 equiv. of MDHM/octene, 0.015 mol% of Pt NPs compared to octene. A complete conversion was obtained after 10 min, with a selectivity in MDOctM higher than 95 %, with Pt NPs synthesised by both methods (batch and continuous). Some kinetic follow-ups were performed at temperatures between 15 to 70 °C and show us that an induction phase occurred in this reaction. The next experiments were conducted in continuous flow reactor by studying the residence time, the temperature and the Pt/octene ratio. A complete conversion with a high selectivity in MDOctM was noted with batch Pt NPs with a residence time of 7 min at 45 °C and with 0.15 mol% of Pt. Studies with continuous Pt NPs still to be done.

Additional studies in continuous flow are currently performed on the synthesis of other metallic nanocatalysts (Pd, Co...), their applications in hydrosilylation and C-C coupling reactions and also on the mechanism action of the catalysts.

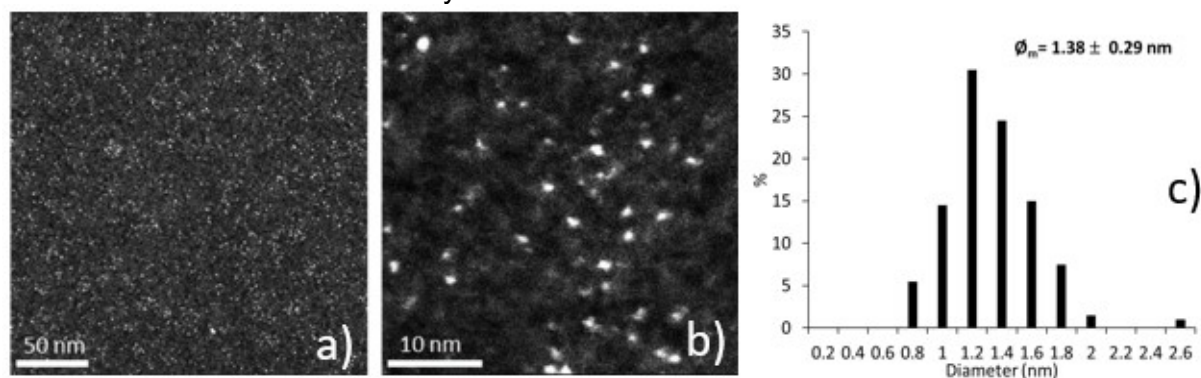


Figure 1: a) b) TEM analysis of Pt NPs synthesised in continuous flow at 60 °C with 10 min as residence time and c) size distribution on 200 particles

Sonocatalytic Oxidation of Benzyl Alcohol to Phenol over a Sonochemically Synthesized CuO Catalyst

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Phenol is an industrially relevant chemical often used as the precursor for the manufacturing of phenolic resin, fibers, aniline, and polysulfone, as well as a precursor for a plethora of pharmaceutical products. Currently, more than 90 % of phenol is produced by the cumene route in which acetone is generated as a recyclable by-product. However, the economics of this route depends critically on the demand for acetone and its selling price. On the other hand, the popular Dow-Phenol Process, which is based on the oxidation of benzoic acid to phenol, requires harsh oxidation conditions such as extreme pressures (14 MPa) and high temperatures (> 300 °C) with yields to Phenol, not more than 30 %. Taking advantage of the extreme local conditions of temperature (~ 5000 K) and pressure (100 atm) generated during ultrasound cavitation bubble implosions, water vapors trapped in these bubbles can be cleaved to H and OH radicals, which are then propelled into the bulk solution or on the surface of solid materials (catalysts) present in the ultrasound reactor, to initiate radical reactions. We previously demonstrated that, when copper oxide catalyst is used in concert with high-frequency ultrasound irradiation for glucose oxidation, a synergistic effect occurred where glucose was selectively oxidized to glucuronic acid (yield ~ 94%), a reaction that is conventionally difficult to obtain over classical catalysis. Inspired by this work, we explored the potential production of phenol using benzyl alcohol as a benzylic substrate, using a high-frequency ultrasound reactor (578 kHz) at mild conditions of temperature (25 °C) and under argon atmosphere. Contrary to literature-reported results (where benzyl alcohol oxidation classically yields benzaldehyde as the major product), we successfully converted benzyl alcohol to phenol with a conversion of (~20 %) and a phenol selectivity of 72 % within 1 h of reaction time (optimization in the process), over sonochemically synthesized CuO catalysts with a myriad of morphologies. These results represent a proof-of-concept for the direct successful production of phenol from benzyl alcohol under mild reaction conditions without the need for any external oxidant like H₂O₂ or O₂.

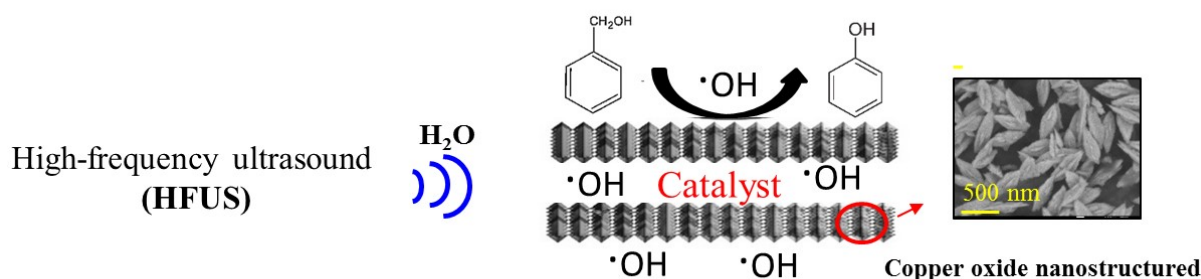


Figure 1: Oxidation of Benzyl Alcohol to Phenol by High-Frequency Ultrasound over Cupric Oxide Catalyst

Chemical Transformations of Alcohols Using Nanostructured Ceria for the Synthesis of Specialty Chemicals

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Alcohol oxidation reactions are commonly used in fine chemistry. The resulting ketones, aldehydes and carboxylic acids find applications in various domains like pharmaceuticals, food industry, polymer synthesis and biomass valorization. The reactions are usually catalyzed by noble metals using harmful oxidants in alkaline conditions. In a current trend towards circular economy, it would be desirable to engineer new eco-efficient processes operating with recyclable metal-free catalysts, green oxidants and without base (to avoid salt generation). In this context, cerium dioxide, ceria (CeO_2), emerges as an abundant and inexpensive catalyst compared to noble metals. This oxide has attracted the attention of the scientific community due to its mixed $\text{Ce}^{3+}/\text{Ce}^{4+}$ valence and its oxygen storage capacity. Used for the three-way catalytic converters, this material is considered as a candidate of choice for metal-free alcohol oxidation. In this study, ceria 5nm octahedra were first employed as a reference catalyst for selective oxidation reactions carried out in liquid phase. The catalytic activity of such nanoparticles was evaluated in the model oxidation reaction of benzyl alcohol with tert-butyl-hydroperoxide ($t\text{BuOOH}$). The key reaction parameters were studied to enhance the activity and tune the selectivity to carboxylic acids, with special emphasis on the solvent.

At optimized conditions, 90% conversion was achieved after 48h reaction with a 86% yield of benzoic acid (carbon balance higher than 99%), when performing the reaction in acetonitrile at 60 °C. With these results, we further extended the scope of the system to a family of aromatic and aliphatic alcohols of industrial interest and unveiled structure-reactivity correlations. In parallel, we studied the influence of the morphology of ceria nanoparticles on the oxidation mechanism for benzyl alcohol. Various nanoparticle morphologies were obtained via hydrothermal synthesis assisted with NO_3^- as inorganic directing agent. During the synthesis, the directing agent was selectively adsorbed on different crystallographic facets, blocking their growth ⁽¹⁾. Octahedra, rods, and cubes were selectively obtained by adjusting the temperature of the synthesis protocol.

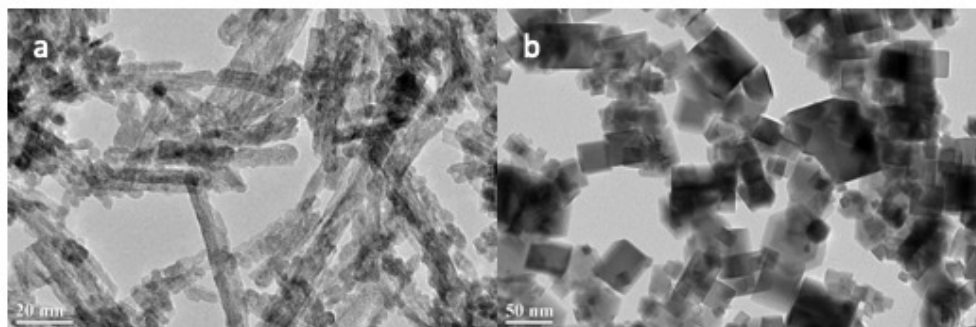


Figure 1: Nano-rods (a) and nano-cubes (b) obtained via hydrothermal synthesis at 100°C and 180°C respectively.

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Flash session 2

Comparative NAP-XPS Study of the Surface Oxidation of Ni-Cermet Electrodes in CO₂ and H₂O Atmospheres

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The oxidation of porous Ni-yttria-stabilized zirconia (YSZ) and Ni-gadolinia-doped ceria (GDC) ceramic-metal (cermet) electrodes in H₂O and CO₂ atmospheres was studied by near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). We show that the oxidation of nickel by the two gases is not similar, as is commonly believed, but it depends on the ceramic type. As shown in figure 1, nickel is vulnerable to oxidation in H₂O but it resists to CO₂ in Ni-GDC, as compared to the Ni-YSZ electrode under identical exposure conditions. Inspired by this observation we conceptualize and fabricate Ni-YSZ electrodes modified by ceria nanoparticles, which show significantly higher resistance to CO₂ oxidation as compared to conventional Ni-YSZ electrodes. The preparation of tailor-made cermet electrodes with identical bulk/mechanical characteristics but very different surface properties offers a promising fabrication strategy for high-performance and durability solid oxide electrolysis cells for CO₂ conversion.

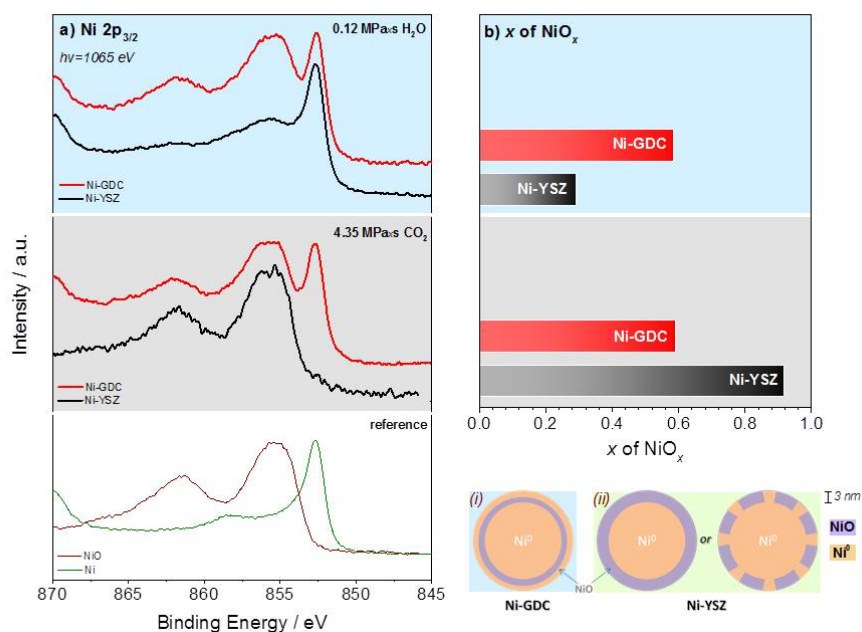


Figure 1: (a) Ni 2p_{3/2} NAP-XPS spectra of the Ni-YSZ and Ni-GDC cermets after H₂O (top) and CO₂ (middle) treatments. (b) The nickel oxidation state x at the outer 1.8 nm of the surface after Ni 2p_{3/2} spectra. Schematic representation of the Ni and NiO arrangement.

The Effect of Fe Presence in NiMgAl Catalysts on the CO₂ Methanation Reaction

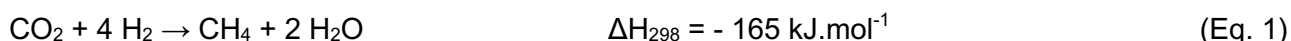
Michel OBEID^{1,2,3}, Christophe POUPIN¹, Samer AOUAD³, Madona LABAKI², Edmond ABI-AAD¹

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One of the major challenges that humankind is facing nowadays is to decrease net-carbon dioxide (CO₂) emissions in the atmosphere to stabilize the greenhouse gas effect. One of the devised strategies is the conversion of the emitted CO₂ into methane that has a very high-energy value, can be injected in the natural gas network, and can be directly used as a fuel in the transportation sector. However, even though the CO₂ methanation reaction (Eq. 1) is thermodynamically possible in a practical range of conditions, it remains kinetically limited.



An efficient catalyst will increase the rate of the methanation reaction at the considered temperature range. Nickel catalysts are widely used for methanation due to their high catalytic activity and low cost. However, the conventional nickel-alumina industrial catalyst suffers from the formation of nickel aluminate species that are difficult to reduce. Since it is the reduced nickel that is active in the methanation reaction, the formation of nickel aluminate species hinders the performance of the catalyst. To tackle this issue, different parameters such as the type of support, metal promoters and the synthesis methods can be modified.

From this perspective, Layered Double Hydroxides (LDHs) materials are chosen. It consists of mixed hydroxides of di- and tri-valent metals, present in the brucite like layers with anions present between the layers to compensate the positive charge. The calcination of LDHs leads to the formation of mixed oxides having interesting features such as high specific surface areas, enhanced porosity, good thermal stability and basic properties, and high metal dispersion.

In this work, magnesium is used to increase the basicity, allowing CO₂ capture, while the presence of aluminum ensures a high specific surface area. Iron partial substitution for aluminum is carried out to improve the reducibility of nickel species. Therefore, MgAl and MgAlFe-based LDHs are synthesized and used in the CO₂ methanation reaction. Nickel active phase (10 wt%) was added to the LDHs, either by wet impregnation, by traditional coprecipitation, or by ultrasound assisted coprecipitation. The dried and calcined catalysts were characterized by various physicochemical techniques such as X-ray diffraction, thermogravimetric analysis, H₂ temperature programmed reduction, and Brunauer–Emmett–Teller method. The prepared oxides were then evaluated in the methanation reaction.

Figure 1 shows that the substitution of Fe for Al improves the CO₂ conversion into CH₄ which is probably due to the decreased nickel-aluminate formation. A full account on the comparison between the different preparation techniques and more insights on the role of iron substitution for aluminum will be presented during the conference.

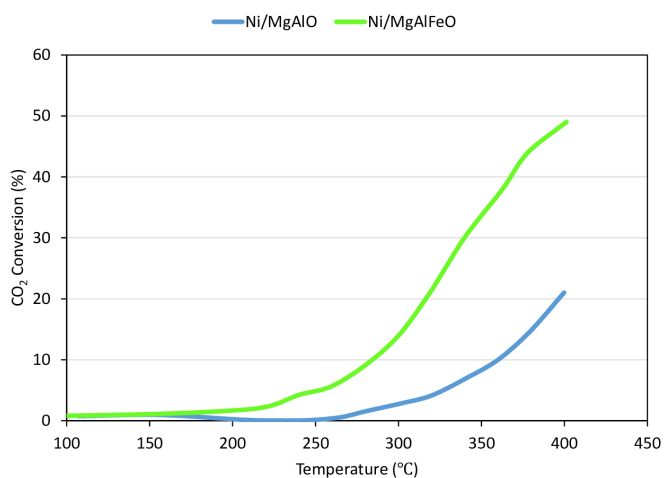


Figure 1 : Figure 1: Catalytic performances in CO₂ methanation over Ni/MgAlO and Ni/MgAlFeO prepared by impregnation

Design of an Innovative Continuous Process for Recycling Catalysts Supported on Magnetic Particles

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The NANOTRAP project proposes to design a new continuous process to obtain a permanent recycling of a catalyst based on metallic nanoparticles supported by magnetic particles. The objective is to operate a "quasi-homogeneous" catalysis chemistry with a catalyst that cannot be separated by usual techniques (filtration), for example to avoid intragranular diffusional limitations observed with classical heterogeneous catalysts. The separation is then based on magnetic deviation approach using magnetic nano/microparticles as can be seen in many studies; but the main difference in our paper is to develop the separation and the recycling of the particles in the process. The challenge is to develop the separation in continuous to allow the magnetic particle to be trapped in a closed loop while the products and reactants can go in and out of the process in presence of a gas and liquid. Final goal would be to achieve a "proof-of-concept" in the presence of a multiphase reaction in a first part with a model reaction and ultimately to apply the concept for catalytic oxidative depolymerization of lignins using Pd-based nanocatalysts.

First, the nano/micro particles are homogenized in a reservoir by agitation. Then, the liquid is co-injected with a gas flow in a continuous tubular reactor with a diameter of 1mm (gas/liquid system) over 2m long. At the output, a separator is set up to reach a 90% recycling rate on the liquid while gas is separated from the rest of the reaction. The goal is not to lose any MNP that could be carried away by gas and liquid flow. For better control of the exit flow, a T-separator was designed with an entrance path, a recycle path and an exit path. Separator's first function is to maintain MNPs in the recycle loop by deflecting their course with magnet. Its second function is to separate the gas from portion of liquid by gravity. The positions of the separator and the magnets inside the process have been optimized by an incremental "trial and error" approach as the first attempts of scaling up were quickly shown to be highly limited.

We tried several positions of the T-cross for microparticles in liquid/solid phase. Thanks to the optimization of the separator, we have succeeded in obtaining losses of MNPs limited to less than 1%wt. We applied a down-flow because the microparticles are sensitive to the gravity. But this down-flow was not appropriate in a liquid/solid/gas phase. In fact, there is a formation of a stagnant gas pocket in the separator which destabilize the flow and therefore the recyclage of MPs. We decided to use nano-sized particles, which are less sensitive to sedimentation, and by applying an up-flow, we were able to minimize particle losses and optimize gas evacuation by avoiding the formation of a gas pocket. We obtain less than 2% of losses of MNPs for 2hours of operating. The proof of concept of magnetic recycling needs to be validated by a model reaction which is the hydrogenation of 4-nitrophenol catalyzed by gold particles supported on MNPs.

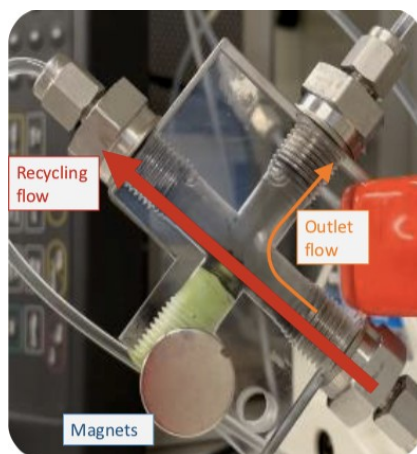


Figure 1: Picture of T-cross separator with gas/liquid/solid. Various path and flow are shown on the picture

A Comparison of Layered Materials Used as Catalysts for Diols Conversion

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The development of new catalysts for biomass conversions induces new demands on the materials as reactions are often carried out in the liquid phase, catalysts should be water tolerant and allow sufficient access of the reagents to the active sites because derivatives from biomass often involve the transformation of large substrates that may require large porosities (saccharides, glycerol, diol ...)¹. Interestingly, some layered materials could meet these criteria and could be tested for these conversions.

Diols can be used as a representative model reactant, and we showed recently that acidic layered materials HNbMoO_6 and HNbWO_6 were efficient catalysts for 2,5-hexanediol cyclodehydration to 2,5-dimethyltetrahydrofuran in liquid phase^{2,3}. Nevertheless, despite their proximity, HNbMoO_6 proved to be far more active than HNbWO_6 and this difference could be related to differences in accessibility to the interlayer sites in liquid phase, namely the intercalation of the reactant or product. The development of suitable layered catalysts necessitates the understanding of such behavior. However, the characterization of heterogeneous catalysts directly in the liquid phase is not that common and operando characterizations are lacking. These conditions require specific characterization methodologies that need to be developed to account for this specific reaction medium.

In this context, the present contribution aims to study the intercalation process in layered materials catalysts during a reaction, notably through the development of a suitable methodology for the characterization by Raman spectroscopy in the liquid phase. The intercalation of liquid probe molecules can be followed by this spectroscopy in addition to XRD and allows to evaluate the accessibility to the acidic sites. Besides, Raman spectroscopy was also used for the operando characterization of the solids during the reaction and their evolution. In order to compare the relative influences of the chemical composition and the accessibility to the active sites, niobate layered materials were compared with their tantalate equivalents HTaMoO_6 and HTaWO_6 . Tantalates appear less active than the niobates while molybdates appear more active than the tungstates. Nevertheless, these chemical changes are also accompanied by changes of the interlayer spacing affecting at the same time the intercalation of the diol. Reactivity with 2,5-hexanediol was thus compared with that of other diols and the relative position of the alcohol groups influences both reactivity and intercalation. Therefore, while layered materials can be very efficient catalysts for the transformation of polyoxygenates, our results point out the importance of the ability to accommodate the reactant in their interlayer and its large influence on their reactivity.

1. Weingarten, R.; Tompsett, G. A.; Conner Jr, W. C.; Huber, G. W. *Journal of Catalysis* 2011, 279, 174–182.
2. Fayad, G.; Boullay, P.; Clet, G. *Journal of Colloid and Interface Science* 2020, 570,41–51.
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Supported Carbides for Bifunctional Hydrogenolysis of Wood into Glycols

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For a more sustainable production of chemicals, the use renewable resources is essential. We present here the formation of ethylene glycol (EG) and propylene glycol (PG) for lignocellulose. They can be obtained by catalytic hydrogenolysis of cellulose or hemicellulose, polysaccharide components of wood. The transformation requires successive steps, involving different catalytic sites: hydrolysis of polysaccharides and carbon-carbon cleavages (retro-aldol) by acid catalysis, then hydrogenations by metal catalysis (see Figure).

Literature indicates that supported $M-W_xC$ catalysts ($x = 1-2$; $M = Ni, Ru, \text{etc.}$) have the required characteristics. Lewis acidity is provided by the tungsten carbide phase and the hydrogenating power by the supported metal, while the Bronsted acidity is provided by water in the reaction conditions. Therefore, they are good candidates for the target catalytic transformation.

We present here our studies on the influence of the preparation method on the surface species of $Ni-W_xC/AC$ materials (see Figure), and on their application to wood transformation into EG and PG. Results indicate that the transformation selectivity depends on several factors involved in the catalyst preparation, and on wood reactant composition.

For example, the co-impregnation method leads to several metal species at the surface while the successive impregnation gives a main phase, moreover without loss of carbon support. Hence, the various materials present different catalytic behavior that influence the wood transformation. Overall, molar yields up to 60% of EG and 30% of PG could be obtained at 250 °C in reaction times less than 1 hour with 5%Ni-30% W_xC/AC catalysts.

Insights on catalyst preparation, characterization and application conditions with possible structure-reactivity relationships will be given during this presentation.

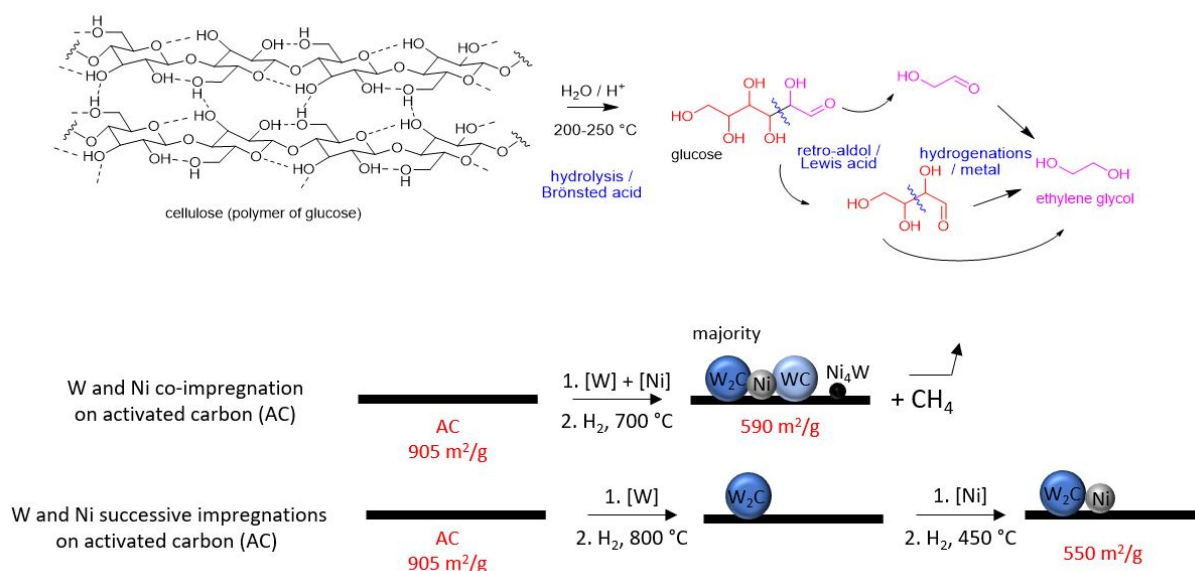


Figure 1: Hydrogenolysis of cellulose to ethylene glycol and a representation of the two different catalyst impregnation methods.

In-Situ FTIR to Unravel the Bifunctional Nature of Aromatics Hydrogenation Synergy on Zeolite/Metal Catalysts

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Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), CNRS, Université de Poitiers, Poitiers, France

Acid sites, in particular Brønsted sites, are often reported to enhance the catalytic performance of metal catalysts, like platinum, in hydrogenation. The significant boost in catalytic performance suggests a bifunctional mechanism takes place under such conditions. Therefore, aiming to unravel the mechanism behind the synergy effect in hydrogenation reaction observed on bifunctional Brønsted/metal catalysts, the hydrogenation of pyridine adsorbed on *BEA (HBEA) and gamma-Al₂O₃ (Al₂O₃ - A) promoted by platinum at low pressure, i.e., P= 150 mbar. The hydrogenation reaction was followed by FTIR aiming to identify the different phenomena linked to pyridine coordinated on Lewis (PyL) and protonated on Brønsted sites (PyH⁺), the formation of the reaction products, and modifications on the catalyst.

Three series of catalysts with different levels of proximity to the active sites, an important parameter for bifunctional reactions, were used: PtHBEA < PtA+HBEA < PtA|HBEA » PtAl₂O₃ ». The experimental results indicate a link between the hydrogenation activity and the proximity between Brønsted sites. Indeed, the formation of piperidine on PtAl₂O₃ and PtA|HBEA was almost null and comparable with HBEA. At the same time, complete pyridine conversion on PtHBEA catalyst was attained at low hydrogen pressure, i.e., P(H₂) = 45 mbar. Furthermore, an intermediate case on PtA+HBEA catalysts was observed with the hydrogenation performance proportional to PtAl₂O₃ concentration in the mixture. Hence, the results indicate the catalytic hydrogenation also follows a bifunctional mechanism when Brønsted and metal sites are present in the catalyst. The dependance of proximity between acid and metal sites of the synergy effect observed in pyridine hydrogenation on zeolite/metal catalysts displayed a behaviour similar to that observed for bifunctional reactions. Indeed, the requirement for fast surface diffusion of H_{SP}, a reaction intermediate, into the acid sites vicinity, where the unsaturated molecules are adsorbed, was found to be important the boost in hydrogenating activity observed in metal/zeolite bifunctional catalysts (Scheme 1).

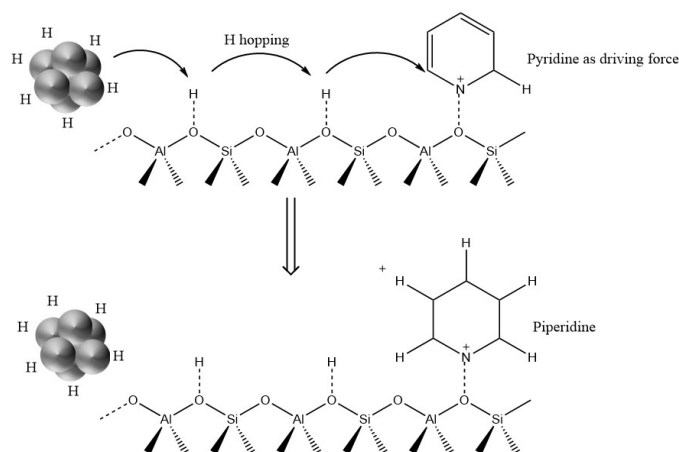


Figure 1: Hydrogen hopping on bifunctional catalyst

Interest of Co Based Mixed Oxide in Total Catalytic Oxidation of VOCs Mixture

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Volatile organic compounds (VOCs) are among the most common air pollutants emitted by the chemical and petrochemical industries. They are one of the main sources of photochemical reactions in the atmosphere, leading to various environmental risks for which severe restrictions, such as the European Parliament and Council Directive 2001/81/EC, have been established to regulate their emissions. As a result, the development of effective techniques to eradicate them is critical.

One of the most effective technologies for the elimination of VOCs is catalytic oxidation since it operates at much lower temperatures than conventional thermal treatment, resulting in energy savings. In addition, its high overall selectivity avoids the formation of by-products due to incomplete VOCs combustion, unlike other techniques such as thermal incineration. However, choosing the right catalyst for this type of treatment is a challenge. Mixed metal oxide catalysts are frequently used, apart from supported noble metals, as catalysts for the total oxidation of VOCs. An interesting way to obtain mixed oxide catalysts is the heat treatment of materials prepared by the "Layered double hydroxide" (LDHs) route under specific conditions. Indeed, after thermal treatment, mixed oxides are formed which have unique properties such as specific surface, porosity, thermal stability and good dispersion of metal oxides.

Among the metal oxides, manganese or cobalt oxides are the most interesting owing to their ability to reach variable oxidation states. Therefore, the synthesis of catalysts based on mixed oxides comprising these two elements seems to be very suitable for redox reactions and thereafter for VOCs oxidation.

In this work, a series of $Mn_xCo_{6-x}Al_2$ spinel oxides with x varying between 0 and 6 and keeping a molar ratio of $(Mn+Co)/Al$ equal 3, are synthesized via the LDH route by co-precipitation at constant pH. These materials were then characterized by different techniques such as X-Ray Diffraction (XRD), Thermal Analysis (TDA/TGA), Temperature Programmed Reduction by hydrogen (H_2 -TPR)...

Because industrial use requires the shaping of catalytic materials, one of these mixed oxides was deposited on an alumina support in the form of pellets or foam using a simple dip-coating technique from slurry containing the powdered oxides and other additives to achieve their dispersion. This presentation will elucidate the catalytic activities of the synthesized materials towards the oxidation of a VOC which is ethanol taken as model molecule as well as the physicochemical properties of our materials.

Elaboration, Characterization and Photocatalytic Properties of Zinc Oxide: Impact of Structural Defects

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A simple synthetic approach, either from direct precipitation of $\text{Zn}(\text{CH}_3\text{COO})_2$ or via a thermal conversion approach from $\text{Zn}(\text{OH})_2$ or ZnO_2 , have been employed to elaborate ZnO-based photocatalysts. The effect of calcination temperature on structural and photocatalytic properties have been investigated in all the cases. X-Ray Diffraction (XRD), UV-Vis, BET, X-ray photoelectron spectroscopy (XPS), Raman, and Electron Paramagnetic Resonance (EPR) have been used to correlate the impact of the surface area, the introduction of oxygen and/or zinc vacancies, and the charge carrier dynamics, with their photocatalytic properties for the model degradation of formic acid (FA) and phenol (PH) under UV-irradiation.

The main objective is to provide a new approach to the impact of structural defects on ZnO semiconductors determined by using Raman and EPR techniques and by coupling with the important role of the surface area considered as one of the most relevant characteristics in photocatalysis in terms of performance. Our results show that the fewer defects, the more photoactive the catalyst is.

This result highlight the importance of considering the role of structural defects on photocatalytic properties and show that both kinds of defects decreased the photocatalytic activity of ZnO at similar surface area, and favor the recombination rate of electron/hole contrary to the conclusions generally assumed in the literature. Overall, surface area and structural defects are complementary to each other, directly dependent on the choice of the precursor, and needs to be considered in a strategy towards efficient ZnO photocatalyst.

**Oral Communications 1 (OC1):
Porous Materials**

Template Removal Processes of Mesophase MCM-41: Revealing the Effect of Gas Atmosphere on Detemplation Mechanism at High Sample Loads

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Understanding of the template removal from as-synthesized mesoporous materials are of great interest because the detemplation procedure might impact on the structural properties of the solid and hence their performance in adsorption or catalysis. Among the different pathways for detemplation, direct calcination of the material is the method of choice due to its easy scalability. However, increase in local temperatures at high mass loadings and structure deterioration of the resulting solid demand an in-depth insight. Moreover, investigations of detemplation have been limited mainly to TG-DTA/MS data completed by NMR, XRD, TPD and FTIR characterizations. Indeed, these studies are constrained to low material loadings.

In this communication, a specifically designed experimental rig is employed to in-situ follow the heat transfer phenomena during calcination of the as-synthesized MCM-41, when scaling-up the sample loads by a factor of thousand, in comparison to the open literature.

Elimination of hexadecyltrimethylammonium template occluded in the mesoporous material is carried under air and inert gas flows, leading to identical structural properties of the resulting solids vis-à-vis the surface area measured by N₂ physisorption, XRD patterns and no remaining traces of organics after treatment.

Figure a. presents a bar chart simulating the calcination bed under the different process conditions performed. Thermal profiles are represented by maximal thermal differences (ΔT_{max}) between the temperatures recorded during the calcination and a blank test (carried out employing the same operating conditions) at different heights of the sample bed. Hence, without solid, no temperature gradients are observed. Under inert conditions, compared to the TG/DTA results (small-scale), calcination of high sample amounts display similar endothermic behaviors, relatively uniform along the bed (ΔT_{max} from -5 °C to -25 °C). On the other hand, in presence of oxygen, heat released from the organic surfactant combustion is transported in the direction of the flow which increases the thermal local conditions (ΔT_{max} up to 130 °C). This sudden increase in the local temperatures also results in earlier formation thermal cracking products (starting from 300 °C).

Concerning the detemplation mechanism, Hofmann degradation is the main removal process, irrespective of the operating conditions. A secondary mechanism, hydrolysis, is proposed based on the presence of hexadecyldimethylamine (DMAC16). Compared to Hoffman main product, hexadecene, DMAC16 is more prone to crack and be oxidized. Under both environments, alkylation and hydrogen transfer products are detected. Interestingly, due to the elevated thermal local conditions in presence of oxygen, cyclization products are identified.

Overall, independent of the environment, complete elimination of the template is achieved and detemplation mechanism mainly depends on the thermal conditions inside the material. Hence, calcination under anaerobic environments, preventing thermal runways issues, can be considered as an attractive alternative.

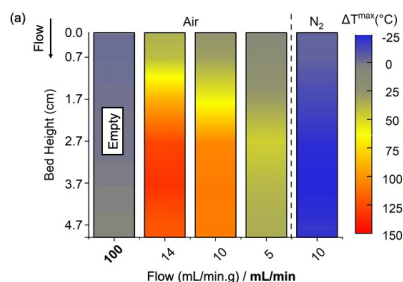


Figure 1: Figure 1.a. Maximal temperature gradients (T_{max}) recorded during MCM-41 calcination under air and N₂ atmosphere along the sample bed

Investigation of Diffusion Properties of Zeolite-Based Catalysts by Inversion Methods: Principle and First Applications

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The diffusion of reactants and products plays an important role in zeolite catalyzed reactions, where microporosity – while conferring exceptional catalytic properties – also imposes high diffusion limitations.¹ Diffusion properties are, however, rarely assessed in complex systems such as hierarchical or composite zeolite-based materials. In particular, classical macroscopic measurements of diffusion only provide diffusion parameters averaged over the whole material despite parallel diffusion domains. Further, they do not give information on the location of diffusing species (external surface/mesopores/micropores). Here, we report the development and application of a new method of investigation of mass transport in zeolite-based materials aiming to overcome the limitations of classical approaches. It consists in hyphenating gravimetric analysis and infrared spectroscopy. The former allows assessing the diffusion from the gas phase to all the porosity, while IR allows for selective assessment of the diffusion to the zeolite active sites located in the micropores.² Further, these data are processed by an original methodology implemented in SpectroChemPy³ allowing to recover the distribution of diffusion domains by inversion of the integral equations describing the uptake curves or the evolution of the infrared spectra.

The general methodology was validated by evaluating the mass transport properties of isooctane in model bimodal systems consisting in mechanical mixture of H-MFI and H-FAU zeolites. As illustrated in Figure 1, the combination of gravimetric analysis and in situ IR makes possible to monitor and distinguish the diffusion within each component of the mechanical mixture. The inversion of the gravimetric uptake curve (a) leads to a distribution showing three diffusion domains (b). The inversion of the evolution of IR spectra (c) leads to a two-dimensional map (d) which also shows three species. Examination of their frequencies allows assigning the fastest domain to the H-FAU component and the two slow domains to the H-MFI component. Finally, the quantification and position of the corresponding peaks of the TG distribution (b) were consistent with the composition of the mechanical mixture and the diffusion rates measured in individual components, respectively. After validation, this methodology was applied to assess the impact of steaming on H-MFI zeolites in powder form or in form of extruded bodies. The results show that the relative values of diffusion rates as measured by gravimetry and IR spectroscopy are indicative of the quality of connectivity between meso and microporous networks.

In conclusion, the present methodology has the potential to provide unique insights into the assessment of diffusion properties of complex zeolite-based catalysts.

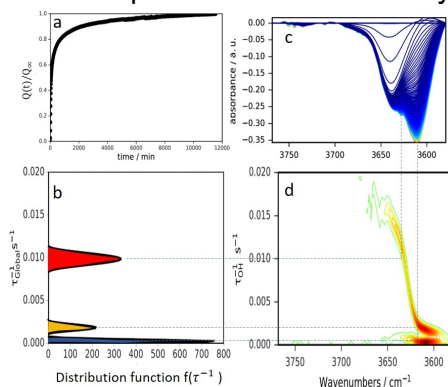


Figure 1: Comparison of distribution functions in the mechanical mixture obtained from inversion of the IR (in the right) and of the gravimetric analysis (in the left)

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2. Peng, P. et al, ACS Catal. (2020) doi:10.1021/acscatal.0c01021.
3. SpectroChemPy v0.2.18. <https://www.spectrochempy.fr>.

Multi-Scale Modeling as a Tool for the Prediction of Catalytic Performances: The Case of n-Heptane Hydroconversion in a Large Pore Zeolite

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The optimization of predictive kinetic models for catalytic processes is a challenge, in particular for hydroconversion of alkanes on acid-limited bifunctional catalysts, owing to the size of the reaction network, and because of the difficulty in obtaining independent data such as thermokinetic constants for the various reactions involved at the zeolite (alkene adsorption, protonation, isomerization, cracking). Thanks to a combination of data obtained from static and molecular dynamics calculations based on density functional theory (DFT) implemented in VASP code, and a multi-scale single event microkinetic modelling (home-made code), a predictive model for n-heptane hydroconversion in large pore zeolites has been obtained. This model was validated by high-throughput kinetic experiments (HTE) (Avantium unit, 270 operating conditions sampled, Fig. a) performed with a well-balanced 1%wt Pt/Beta catalyst (obtained by Pt(NH₃)₄Cl₂ incipient wetness impregnation).

HTE experiments allow the acquisition of a large set of kinetic data, supporting an apparent mechanism between linear, mono-branched, dibranched and tribranched heptenes, followed by cracking of mono and dibranched isomers. DFT calculations (Fig. b) show that secondary cations are less stable than tertiary cations and adsorbed alkenes.[1] This impacts type B isomerization reactions barriers, depending on the type of carbenium ion. Cracking reactions barriers are also strongly affected by the nature of cation that cracks, and that of the cracking products.[2] The agreement between simulated and experimental kinetic data (Fig. c) shows the reliability of the multi-scale kinetic approach, avoiding the simultaneous fit of dozens of thermokinetic parameters. In fact, only 5 parameters (for 45 reactions) had to be adjusted to improve the correspondence with experiment. First, the number of active acid sites was strongly decreased (by a factor of more than 3) to reproduce the observed conversion levels, suggesting that only a fraction of acid sites measured by XRF/NMR or probed by pyridine catalyzes the reaction at temperature higher than 220°C. Second, cracking barriers were increased by about 15 kJ/mol, indicating a possible deficiency of the level of theory employed (here PBE+D2). Isomerization barriers evaluated by DFT calculations were kept unaltered. The analysis of the simulated coverage demonstrated that, at the relevant experimental conditions, a very small fraction of acid sites is involved in the alkene adsorption and the subsequent reactions. When these reactions occur, tertiary carbenium ion intermediates appear at significantly higher concentration than the other species.

Altogether, this approach is promising for the prediction of catalytic performance. In addition to providing a molecular basis for assumptions made in kinetic modelling, it allows for elimination of a large part of empiricism employed in the usual fitting approach. The model obtained herein is supposed to be transferable to a majority of large pore zeolites in the bifunctional hydroisomerization of n-heptane, and should serve as a basis for the prediction of the behavior of longer chain alkanes, of relevance for the catalytic transformation of conventional hydrocarbon sources and of renewables.

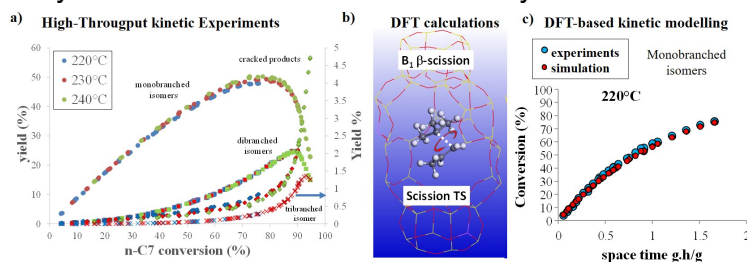


Figure 1: Kinetic-DFT-HTE

1. J. Rey et al., J. Catal., 373, 361, 2019, ACS Catalysis, 9, 9813, 2019.
2. J. Rey et al., Angew. Chem., Int. Ed., 59, 18938, 2020.

Synthesis of a New Polyacid-Functionalized Mesoporous Material and Evaluation of Its Performance in Heterogenous Catalysis

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Polymer-functionalized mesoporous silica materials combine the textural properties of mesoporous materials and the chemical properties of polymers. These two features make them excellent candidates for applications in catalysis, adsorption, for environmental remediation and as drug delivery systems. However, the synthesis of efficient hybrid materials is difficult to obtain due to the functionalization step that requires both a high density of polymers and its homogeneous distribution within the pores¹. Our research intends to synthesize and study the catalytic properties of polymer-functionalized mesoporous silica materials prepared by an innovative and versatile process based on polyion complex (PIC) micelles, which overcome the issues of density and homogeneity of functionalization^{2,3}.

A system of two hydrophilic polymers is used for the PIC micelle formation through electrostatic interaction, one is a double-hydrophilic block copolymer (DHBC) named poly(ethylene oxide) polyacrylate – poly(styrene sulfonate) (PAPEO-b-PSS) and the second is an oppositely charged polyamine (oligochitosan). A sol-gel process allows the PAPEO chains to be anchored in the silica. The polyamines are removed from the structure by pH change, thus revealing the porosity and the acidic functions. Analyses confirmed that no polyamines remain in the material after synthesis and that it has a function density of about 0.6 mmol of acid group per gram of material. The functions are homogeneously distributed, as evidenced by the highly ordered 2D hexagonal structure and the narrow 10nm pores size distribution of the material. These materials have been tested as acid catalysts in the esterification of fatty acids by methanol. This reaction was chosen because it seems to be a good starting point to study the catalytic activity of the material, corroborated by the number of publications on this reaction for other sulfonic acid functionalized silicas. In our work the reaction presents a conversion around 20%-30% for the esterification of palmitic acid by methanol and 20% for caprylic acid. The results confirmed that the material can be used as a catalyst, but further analysis is needed to fully understand the catalytic behavior of the materials.

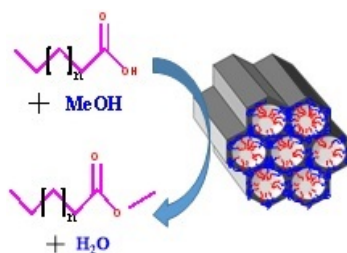


Figure 1: Illustration of the catalytic experience

Reference layout:

1. N. Baccile et al. *Angew. Chem. Int. Ed.*, 2008, 47, 8433.
2. D. Houssein et al. *Microporous and Mesoporous Mater.*, 2017, 239, 244.
3. E. Molina et al. *Beilstein J. Nanotechnol.*, 2019, 10, 144-156.

3D Printing as Innovative Strategy to Enhance Catalytic Performance in the Methane Dehydroaromatization Process

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Introduction

Non-oxidative Methane Dehydroaromatization (MDA: $6 \text{ CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9 \text{ H}_2$) on bifunctional catalyst (Mo/HZSM-5) is a key technology to decarbonize natural gas to high-value chemicals and clean energy vectors. However, low catalytic stability remains a major challenge to be overcome. In fact, the MDA process has not been implemented other than under lab-scale conditions at a technology readiness level (TRL) of 4. To make the process industrially viable and reach TRL 5, new ways of shaping the catalyst and sorbent materials are a key step in ensuring the optimization of the reactor geometry, heat and mass transfer properties, mixing behavior, and pressure drop [2]. The currently available shaping technologies can roughly be divided into two categories: dense randomly packed beds and cellular structures. This study proposes a third type of shaping technology a 3D printing technology that is in its infancy but holds promise as a key strategy to locally tune porosity as well as control the geometrically regular flow patterns and hence tune the pressure drop and heat and mass transfer limitations across the reactor. In this study, we build on these early efforts to present an innovative process for improving catalyst performance, which relies on achieving shaped catalytic systems through advanced 3D printing technology.

Materials and Methods

Three sets of samples were prepared. The first one formed of 3wt. %Mo/HZSM-5; employed as reference material. This reference material is further bound with a 20wt. % of resin and 3D-printed. This crude catalyst is thereafter crushed (Z3D-P) or used as cylindrical shaped monolith (Z3D-M). Z3D-P and Z3D-P' are crushed bound materials which come from two batches with different binder nature. The catalytic tests were carried out in a continuous flow fixed bed reactor at 700 °C under atmospheric pressure. A gas mixture (15/85) (v/v) N_2/CH_4 was introduced into the reactor with a WHSV of 1 h^{-1} (TRL 4)

Principal results

Deep characterization technics (XRD analysis, N_2 -physisorption, Ir-chemisorption of pyridine at 150°C,...) confirmed cautiously adjusting the synthesis conditions (i.e. binder nature, calcination temperature) are crucial to keep the initial textural properties of the reference nano-sized catalyst. Once the synthesis of manufactured material had been optimized, these catalysts afforded surprisingly higher aromatics production per gram of zeolite. However, the use of shaped catalyst displayed no significant effect on the overall yield (Figure 2) as a similar cumulative yield was obtained. This demonstrates that 3D-shaping does not impact chemical production at this scale (TRL 4). The nano-sized zeolite bearing materials showed robustness operating under harsh conditions at TRL 4, i.e. at high temperatures and low contact times. It was proven that the initial textural properties of the catalyst could be preserved while enhancing the catalytic performance. The required steps to scaling up this process to TRL 5 and the catalytic tests carried out in this scale will be presented too.

Conclusion

The use of manufactured catalysts should allow for a higher aromatics production in MDA process. The 3D catalyst shaping holds great potential towards the industrial scale-up of this challenging reaction.

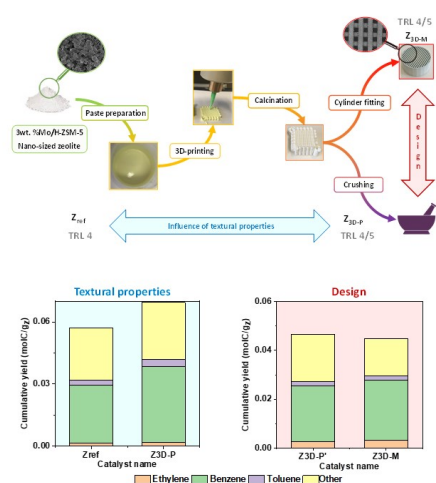


Figure 1: Catalyst preparation and cumulative yields obtained after 10 hours of reaction per gram of zeolite

**Oral Communications 2 (OC2):
Sugars and Cellulose**

Green and Scalable Synthesis of UiO-66-SO₃H Metal-Organic Framework and its Catalytic Activity in Dehydration of Fructose

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Metal-Organic Frameworks (MOFs) are hybrid crystalline microporous solids. Their hybrid nature comprising both inorganic metal sites (ions, clusters) and organic ligands allows for unique 1-, 2- or 3D structures. With almost 10 000 discovered structures within the past 30 years, MOFs have taken leading positions in materials science with numerous applications in gas storage, sensing, energy storage, catalysis, water purification and others. UiO-66 (Universitetet i Oslo) is one of the most famous MOFs nowadays. Built of Zr-oxoclusters and terephthalate linkers, UiO-66 exhibits a continuous 3D structure with pronounced textural properties such as surface areas surpassing 1000 m² g⁻¹ and cages with diameters of 7.5 and 12 Å. Moreover, free metal sites on the Zr-oxoclusters provide Lewis acid sites which together with the MOF's chemical and thermal stabilities enable applications in various media and elevated temperatures (< 450 °C). Besides, by employing functionalized linkers (sulfo-, aminoterephthalates etc.) it is possible to insert functional groups into the UiO-66 framework to eventually form UiO-66-X (where X is -SO₃H, -COOH, -NH₂ or others). This opens up the possibility to apply functionalized UiO-66-X in a wide variety of chemical processes requiring either Brønsted acid or base sites.

Nevertheless, one of the challenges concerning MOFs production and application on industrial scale is upscaling and shaping. Indeed, oftentimes MOFs synthesis implies using hazardous and toxic solvents (such as DMF: N,N-dimethylformamide) which hinders their further implementation on large industrial scale production and application. Therefore, this work is an attempt to overcome these issues and provide an example of a green, scalable synthesis of a UiO-66 based MOF with its further application in the conversion of a biomass derived molecule. The strategy of this work is built around UiO-66-SO₃H and includes several steps (Fig. 1): 1) small scale synthesis in H₂O; 2) synthesis upscaling in a 3 L reactor; 3) MOF shaping into extrudates; 4) application in catalytic dehydration of fructose into 5-hydroxymethylfurfural (5-HMF). The latter is intended to probe its newly formed Brønsted acid sites provided by -SO₃H groups. Once the reaction conditions were optimized, UiO-66-SO₃H showed superior 70 % fructose conversion and 40 % 5-HMF yield under mild conditions (60 °C) and low fructose-to-catalyst weight ratio (11:1). The identical test over the classical UiO-66 and blank (no catalyst) test demonstrated no fructose conversion which allows to confirm the positive effect of -SO₃H groups as well as to eliminate the solvent effect (dimethylsulfoxide, DMSO). The presented work further includes the upscaling and shaping applied on UiO-66-SO₃H powder to highlight the effect of extrusion on the structural, textural and catalytic properties of the parent MOF.

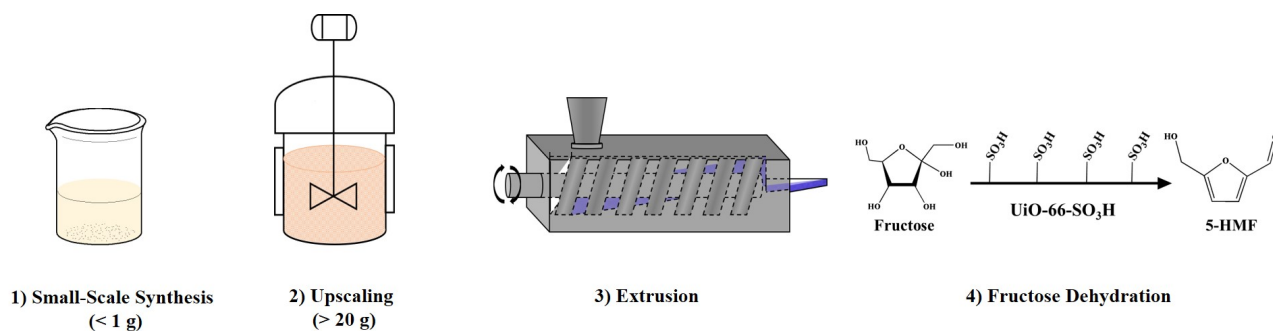


Figure 1: Fig.1 Schematic representation of the steps performed in this work

Glucose Transformation into Levulinic Acid by Hydrothermal Process Assisted by Photocatalysis in Absence of Added Brønsted Acids Catalysts

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Biomass has attracted considerable attention as an abundant carbon source and a promising alternative for fossil resources. The valorization of its simplest molecule (glucose) has been studied by mean of different processes such as hydrothermal process and photocatalytic process. Hydrothermal process (high energy consuming: high temperature and pressure) transforms glucose into a variety of value-products such as lactic acid, 5-hydroxymethylfurfural, levulinic acid but with carbon losses due to uncontrolled humins formation ... While photocatalytic process (low energy consuming: low temperature and pressure) is mainly used to mineralize glucose or to produce hydrogen from glucose. Herein, we studied glucose transformation in aqueous solutions by hydrothermal process assisted by photocatalysis (UV irradiation) in the presence of a commercial TiO₂ anatase catalyst (UV100) with the objective of combining the advantages of the two processes: decreasing energy expenditure without carbon loss in uncontrolled humins' formation.

Under inert atmosphere (15 bar of Ar) and at 120 °C, glucose was almost completely converted with almost the same time course by hydrothermal process assisted or not by photocatalysis. However, while gluconic acid was the major product formed by hydrothermal process, levulinic acid became the major product formed by hydrothermal process assisted by photocatalysis. In fact, at glucose conversion of 90 %, levulinic acid selectivity was around 5 and 55 C% without and with UV irradiation, respectively. While gluconic acid selectivity was 28 and 5 C% without and with UV irradiation, respectively.

When temperature was increased to 150 °C, levulinic acid selectivity reached 70 C% at glucose conversion of 90 % with hydrothermal process assisted by photocatalysis. Beside the formation of levulinic acid and importantly in absence of noble metal, H₂ and ethylene formation was enhanced (180 and 94 μmol at 150 °C instead of 32 and 0.28 μmol at 120 °C, respectively). Note that ethylene was not produced and H₂ was formed in negligible amount (< 0.25 μmol) by hydrothermal process (at 120 or 150 °C) and photocatalysis (ambient T)).

Levulinic acid is industrially formed from saccharides using strong Brønsted acids catalysts like H₂SO₄. The levulinic acid formation, by coupling hydrothermal and photocatalytic processes in the presence of UV100 (anatase TiO₂) whose original surface is free of any Brønsted acid sites could be explained by the generation of Brønsted acidity under UV irradiation at 120 and 150 °C.

Our research shows the interest of this innovative process, associating an activation of a metal free catalyst under moderate pressure and temperature and UV irradiation for the elaboration of energy (H₂, C₂H₄) and platform molecules such as levulinic acid in absence of strong mineral acids.

Development of an Innovative and Compartmented Fixed-Bed Reactor for Hemicelluloses Valorization into Sugar Alcohol

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Lignocellulosic biomass is the major renewable carbon source at the human time scale, an interesting candidate for fossil resources substitution. Even if it can represent almost 40% of the lignocellulose structure, hemicelluloses remain under-exploited nowadays. One pathway to valorize hemicelluloses is the synthesis of polyols, value-added products mainly applied on food and pharmaceutical industries. These carbohydrates can be obtained by ex-hemicellulosic sugar hydrogenation. Hemicellulose hydrolysis is susceptible to the formation of by-products (acetic acid, furfural, 5-HMF, for example) because of the fast degradation of xylose in acid media. It is therefore important to execute a rapid separation after the hydrolysis to avoid the side reactions and to increase polyols yield at the end of the hydrogenation step. For this reason, this project aims coupling the three steps in one compartmented reactor.

Each synthesis step was tested separately:

1. 50 g/L of xylan from corncob (CarboSynth) aqueous solution was introduced in a reactor containing a fixed-bed of 2 g TiO₂-WO_x, prepared by wet impregnation, to study xylan hydrolysis. Several temperatures and liquid flows were tested to study the effect of these parameters on the reaction.
2. A mixture of xylan and xylose was used to study the membrane separation of both compounds. The 50 g/L of xylan and 25 g/L of xylose (Sigma-Aldrich) solution was continuously separated by tangential filtration on a ceramic TiO₂ membrane.
3. Solutions of 0.33 mol/L of arabinose, galactose, xylose, mannose, and glucose were hydrogenated in the continuous trickle-bed reactor. In continuous mode, the solutions were introduced in through a fixed-bed reactor containing 1 g of Ru/TiO₂, prepared from incipient wetness impregnation.

The three steps of polyols production were studied separately. First, the temperature effect was tested for the hemicellulose hydrolysis. Figure 1 shows the hydrolysis products yield and xylan conversion as a function of the contact time for 140°C and 180°C. It is noticeable that the increase of the temperature favors the xylan conversion (a maximum of 100% at 180°C against 40% at 140°C). Besides that, the higher is the contact time between the reagents and the catalyst, the lower is the xylose selectivity. Three main by-products were identified: furfural, HMF, and acetic acid. Furfural selectivity is the most favored by temperature increasing for both temperatures, represented by the increase of the orange curves of Figure 1.

Then, ceramic membrane separation presented almost 30% of xylan mass retention, while xylose mass retention is up to 10%. It is probably due to the different polymerization degrees of the studied xylan, smaller molecules might be able to pass through membrane pores.

Finally, in order to come closer to hemicelluloses hydrolysate, different sugars hydrogenation were tested. The C5 sugar (xylose) presented faster conversion when compared with C6 sugars (galactose, glucose, and mannose). This effect suggests that the hydrogenation rate depends on sugars structure. As far as we know, it is the first time this behavior is described in the literature. Individual models are being developed to provide enough information to establish the innovative reactor model, which will also be tested experimentally.

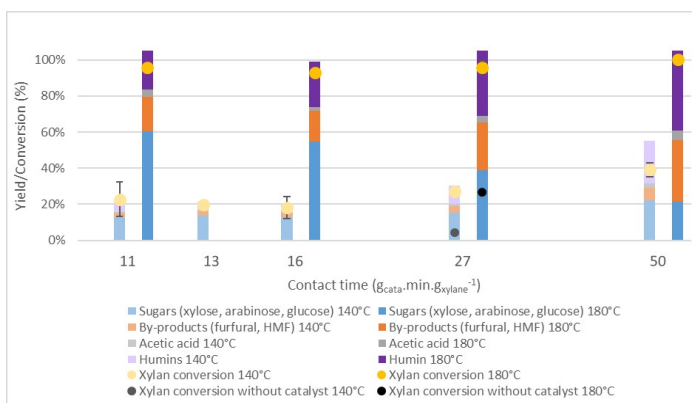


Figure 1: Temperature effect on hydrolysis products yield and xylan conversion

Recyclable Ru/Alumina for the Catalytic Water-Mediated Hydrogenation of Glucose to Sorbitol: Process Optimization Study and Mechanistic Insights by *in Operando* Spectroscopy

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Hydrogenation reaction is a crucial step in upgrading biomass-derived feedstocks to renewable fuels and high-value added chemicals. This work focuses on the understanding of glucose hydrogenation to sorbitol in aqueous phase in the presence of a Ru/Alumina catalyst commercially available. We were pleased to see the great performance of this catalyst and particularly its outstanding stability in water without further modification of the support. The glucose (10 wt. %) was selectively converted to sorbitol with a yield around 97 % under optimized conditions (100°C, 30 bar of hydrogen, 150 min of reaction) in the presence of 5 wt. % of Ru/Alumina. This catalyst was highly stable up to 10th cycles and without thermal reactivation under gaseous hydrogen between cycles. The reasons for its high stability in water will be presented based on catalyst characterizations. Additionally, to go deeply inside the understanding of the high performance of the catalyst Ru/Alumina compared to Pt/Alumina and Pd/Alumina, that were both inactive in the hydrogenation of glucose to sorbitol, *in operando* IR/Raman spectroscopy was performed. The main goal was to investigate the H/D exchange reaction of deuterated water with hydrogen. For conducting these experiments, a singular experimental set-up which combined both ATR-IR and Raman spectroscopy in a single high-pressure cell allow us to follow *in operando* the formation of HOD, HD and D₂ species related to the catalytic conversion of deuterated water and hydrogen by Ru, Pt and Pd supported on Alumina. After 24 h at 25°C under 30 bar of hydrogen, the Pt/Alumina exhibits the most effective exchange of deuterated water and hydrogen with around 30 % of conversion, followed closely by the Ru/Alumina whereas less than 10 % of deuterated water and hydrogen were converted by Pd/Alumina. These results show that for all the catalytic systems investigated, the water directly participates in the hydrogenation mechanism and act as a co-catalyst, in particular for both Ru/Alumina and Pt/Alumina. To fully understand the catalytic activity of Ru/Alumina catalyst, complementary experiments are underway to propose a plausible mechanism in the water-mediated catalytic hydrogenation of glucose.

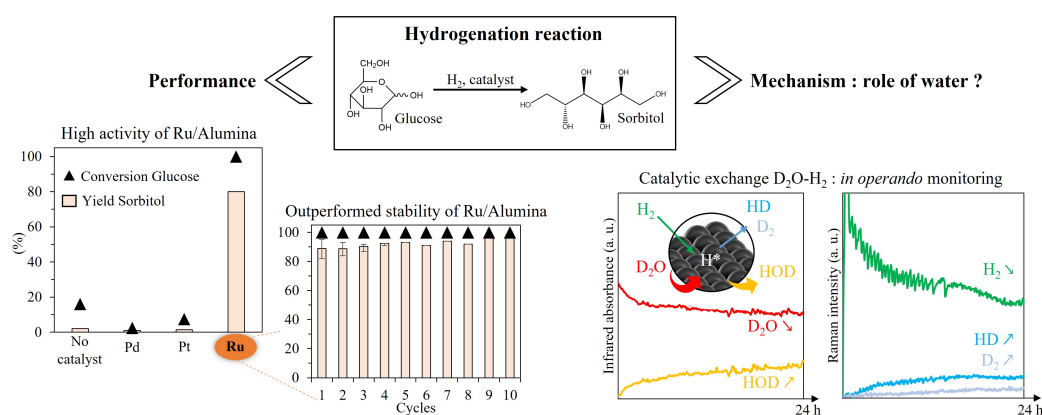


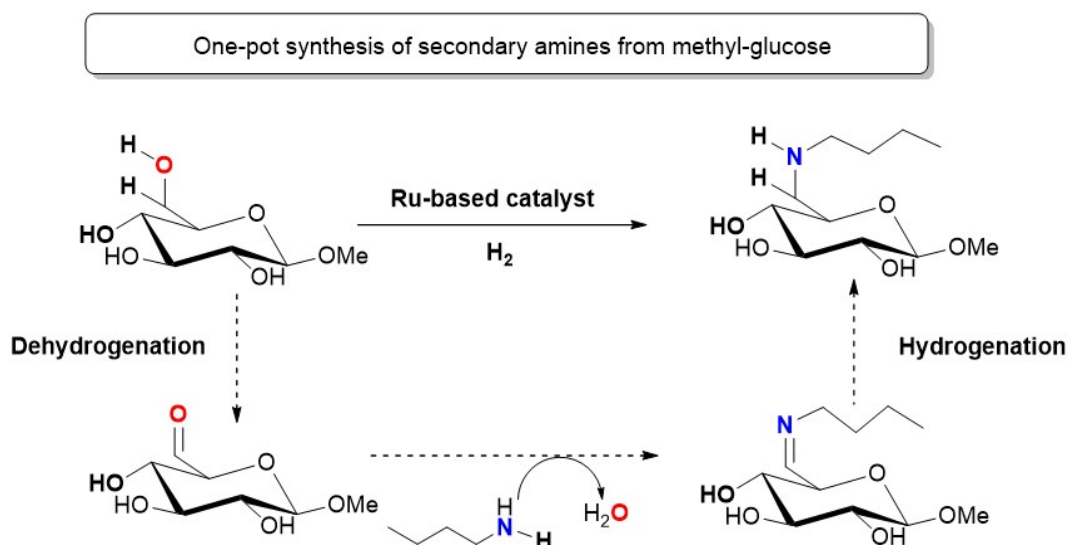
Figure 1: Water-mediated catalytic hydrogenation of glucose to sorbitol performed by Ru/Alumina

Selective Amination of Sugars in the Presence of a Recyclable Ru-Based Catalyst

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Due to the high decrease of fossil resources, biomass appears to be a very useful source of renewable carbon. Sugars that can be obtained from lignocellulose are a very efficient renewable and low cost platform molecules. In this context, they can be used to prepare surfactants for detergents, lubricants, polymers, agrochemical and pharmaceutical industries. Hence, the hydrophilic head of surfactant is generally composed of a poly-hydroxylated molecule while hydrophobic part can be fatty acids or alkyl amines. Although 96% of surfactants come from petrochemical industry, there is an increase demand for the production of bio-based surfactants. Consequently, the synthesis of these bio-based surfactants for example from sugars is the focus of a lot of research works. In this study, the amination of methyl-glucose in the presence of alkyl amine was investigated. This reaction occurs first through the dehydrogenation of a hydroxyl group of sugars follows by a reductive amination of the aldehyde produced (Figure 1). The main aim of this work was to selectively aminate the hydroxyl group of the C6 carbon atom of the sugars in the presence of a heterogeneous catalyst. This is a challenging reaction due to the reactivity of all the hydroxyl groups contained in sugars leading to a mixture of several amines. Herein, the control of the selectivity was performed thanks to the use of a Ru-based catalyst under H_2 atmosphere. The amination occurs on the C6 carbon atom of methyl-glucose and secondary and tertiary amines were produced depending on the conditions uses. Moreover, the catalyst was recyclable up to 10th cycles.



**Oral Communications 3 (OC3):
Atom Economy in synthetic chemistry**

Immobilization of Metal Complexes in Hydrophobic Zeolites for Ethylene Dimerization

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The development of catalytic processes in the aqueous phase is an important issue in the context of sustainable development. Indeed, unlike organic solvents, water has a low environmental impact, lower production costs, limits the risks of explosion and toxic inhalation. Classically, transition metal based molecular complexes are used as catalysts in some industrial processes because of their high selectivity towards linear alpha olefins (C4, C8 and C10) which are the main products of interest. However, their stability in presence of water is an obstacle to their uses as they can hydrolyse and lose their activity. In this context, we report here the design of hydrophobic porous support materials protecting a water sensitive molecular catalyst active towards the ethylene dimerization.

To this end, we have synthesized a series of microporous zeolite with different topologies (ITH, MFI, BEA and FAU) and we have adapted the synthesis conditions (high silica on alumina ratio and low synthesis gel pH) to obtain almost defect free zeolites. For some of these as synthesized zeolites, we have applied post-treatments to create mesoporous cavities to facilitate the hosting the molecular complexes. We have then immobilized a Ni-based molecular complex catalyst in the zeolites' cavities by using a "ship in the bottle" methods. The different catalysts have been tested in batch mode for the dimerization of ethylene and the activity and selectivity have been evaluated.

By studying the adsorption of water in zeolites assisted with IR and solid state ^{29}Si NMR measurements, we find that adsorption switches from non-wetting to wetting as the hydroxyl surface density reaches a critical value. Then, we show the presence of organic ligands inside the nickel exchanged hydrophobic zeolites by different techniques such as IR or TGA analysis. We propose that the catalytic activity increases after complexation and with the creation of mesoporosity and macroporosity inside the microporous structure.

We believe that the development of an encapsulation concept inside hydrophobic systems that addresses all types of catalysts, with a particular focus on water sensitive transition metal catalysts can be applied advantageously in a wide range of catalytic reactions.

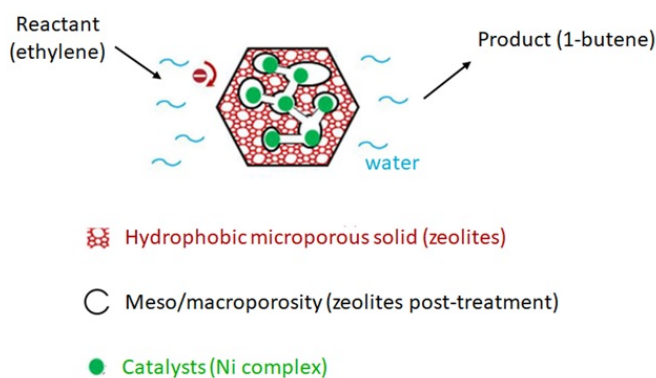


Figure 1: Illustration of the project concept. Hydrophobic support materials containing water sensitive Ni catalysts

Acknowledgment: We thank the French National Research Agency (ANR), CATCALL (ANR-19-CE07-0025)

Developing a Highly Active Catalytic System Based on Metal Nanoparticles for Alkene Hydrosilylation

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Alkene hydrosilylation is considered as a key reaction for the preparation of silicones and functional silanes. Currently, unsustainable platinum based complexes are still preferred in the industry. To replace platinum, major efforts were directed towards the development of non-noble metal complexes as alternatives. In this field, a major step forward was made by Chirik and co-workers with the development of an iron-based complex bearing a pyridinediimine (PDI) ligand. Additionally, very recently, other base-metal complexes containing pincer-type ligands also were reported. In this context, we will show here the development of original base metal NPs (Ni, Fe, Co) as alternatives to Pt and earth abundant metal complexes. These NPs are prepared from commercially available starting complexes and silanes as stabilizing surface ligands at low temperature. While the Ni particles were found poorly active, the Co NPs were found extremely active at low temperature with a set of terminal alkenes and non-activated tertiary silanes.

The protocol used to synthesize the Co NPs is simple and quite different from those classically used in the literature which require the use of surfactants (amines, carboxylic acids etc.), stabilizing agents (polymer, phosphine, olefin etc.) and/or high temperature boiling solvents (dichlorobenzene, diphenyl ether for instance). Indeed, the Co NPs catalysts were prepared from commercially available $\text{Co}_2(\text{CO})_8$ in toluene in the presence of *n*-octylsilane (7.5 mol% compared to Co-atom) as stabilizer under 4 bars of H_2 at different temperatures from 140 °C to 60 °C. The obtained solutions of Co NPs were first tested as catalysts in 1-octene hydrosilylation with MD^HM (1,1,1,3,5,5,5-heptamethyltrisiloxane) at 30 °C with a catalyst loading of 0.2 mol%. The best results were obtained with the Co NPS prepared at 60°C with a 1-octene conversion >97% and selectivity of 95% toward the anti-Markovnikov hydrosilylated product within 3.5 h. Based on these results, we decide to perform alkene scope tests (10 substrates). While most of the reactions led to the expected anti-Markovnikov products in excellent yields, three substrates (styrene, tert-butylethylene and allyl acetate) were however found problematic. We thus decided to carry out the same reactions under UV irradiation (>250 nm). UV irradiation was found highly beneficial, allowing a drastic increase of product yields for the three substrates. Taking advantage of such results, we decided to study the possibility to transform otherwise inactive internal alkenes into anti-Markovnikov hydrosilylation products through a tandem isomerization-hydrosilylation reaction. The catalyst was able to isomerize of the internal C=C bond of 2-trans-octene and methylcyclohexene, giving rise to the corresponding terminal hydrosilylated products under UV-irradiation. In light of the possibility to utilize otherwise inert internal alkenes for the exclusive chemoselective synthesis of anti-Markovnikov products, unsaturated fatty ester derivatives containing two types of functionalities were tested and could be selectively hydrosilylated. Note that this reaction was never reported as such using directly unprotected fatty esters and a non-noble metal catalyst and that the starting $\text{Co}_2(\text{CO})_8$ used in the exact same conditions was completely inactive.

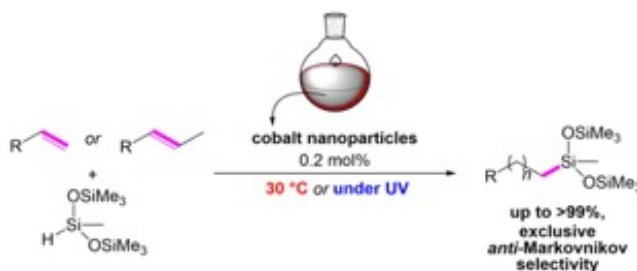


Figure 1: Figure. Hydrosilylation of alkenes with MDHM using Co NPs catalysts.

Tuning the Cobalt:Nickel Ratio of Nickel-Cobalt Nanoparticles for Phosphine-Modulated Catalytic Silane Activation

Anthony ROPP, Sophie CARENCO

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Designing catalysts for the activation of small molecules under mild conditions is a challenge. Such a breakthrough was enabled by Frustrated Lewis Pairs (FLP) for H₂ heterolytic cleavage at room temperature. FLP are composed of bulky strong Lewis acid and base, typically tertiary boranes and phosphines, whose adduct formation is prevented by their steric hindrance. Recently, a similar interaction was proposed by our group between NiCo nanoparticle surface and phosphines for the activation of phenylsilane during the hydrosilylation of benzaldehyde.

The present work aims at providing a deeper understanding of the active site proposed for this semi-heterogeneous FLP. Instead of varying the molecular Lewis base, we focused on the nanoparticle surface design by tuning the Co:Ni ratio. Thus, we synthesized core@shell Ni@Co_x according to a two-step colloidal synthesis and we varied the quantity of cobalt introduced during the second step to obtain nanoparticles with various Co:Ni ratio of 0, 0.1, 0.2, 1, respectively corresponding to a sub-monolayer, a monolayer, and an excess of Co. We characterized the nanoparticles by X-Ray powder Diffraction and Transmission Electron Microscopy. Similar size distributions were obtained (10-12 nm). Further characterizations with Energy Dispersive Spectroscopy on a Scanning Electron Microscopy (SEM-EDS), X-Ray Fluorometer (XRF) and surface-sensitive X-Ray Photoelectron Spectroscopy (XPS) confirmed the Co:Ni ratio of the samples. Additionally, XPS confirmed that the surface state was similar for the three samples, in terms of metal oxidation state and phosphide doping.

The similar size and surface state of the various samples allowed us to compare their catalytic activity, in combination with two phosphines, for silane activation. Our previous study showed an optimal catalytic activity for a limited range of Tolman cone angles (130°-150°). Therefore, we selected triphenylphosphine (145°) and tri-*n*-butylphosphine (132°). Phenylsilane conversion, monitored by ¹H NMR, decreased strongly with decreasing Co:Ni. This suggested that the cobalt sites were the sole active sites on the surface alloy.

The presented results provided a deeper understanding of the catalytic active site at the interface between the surface of a core-shell Ni@Co nanoparticle and molecular phosphines, whose catalytic activity was related to the number of Co sites. DFT computations may help to grasp first the interaction of bulky phosphines on a NiCo surface and then with a Si-H bond. Moreover, further work is undergoing to understand the influence of phosphide surface species in cobalt-containing nanoparticles.

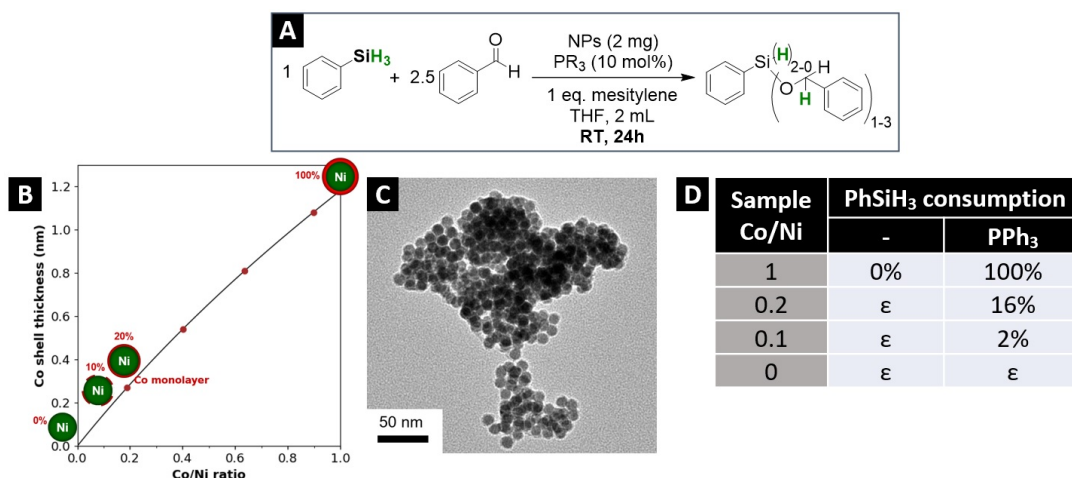


Figure 1: Influence of the Co/Ni ratio on the catalytic activation of phenylsilane by Ni@Co nanoparticles

Rhodium Catalysed Asymmetric Hydroaminomethylation of α -Substituted Acrylates and Acrylamides

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Amines constitute powerful building blocks in the synthesis of biological active molecules and agrochemicals, therefore the efficient and selective synthesis of chiral amines using easily available and abundant precursors is a long-standing goal of chemical research.¹ In this context, rhodium catalyzed hydroaminomethylation is an attractive reaction, since it allows the direct synthesis of amines starting from readily available alkenes in a high atom economy process.²

Among the different amine containing molecules, γ -aminobutyric acids (GABA) and derivatives have attracted considerable attention since they play an important role in reducing neuronal excitability and this scaffold is present in several natural products.³ For this reason, the rhodium catalyzed asymmetric hydroaminomethylation of acrylates and acrylamides is a promising strategy for the direct synthesis of GABA derivatives.³

In this work, we report the synthesis of chiral γ -aminobutyric esters and amides via rhodium catalyzed asymmetric hydroaminomethylation of α -substituted acrylates and acrylamides in the presence of different amines.⁴ In the case of acrylates, the control of the regioselectivity allow the production of γ -aminobutyric ester or β -amino esters depending on the ligand and conditions applied. In the case of acrylamides, the asymmetric hydroformylation of these substrates is also reported and the synthetic potential of the asymmetric hydroaminomethylation is demonstrated by the single-step synthesis of the brain imaging molecule RWAY.

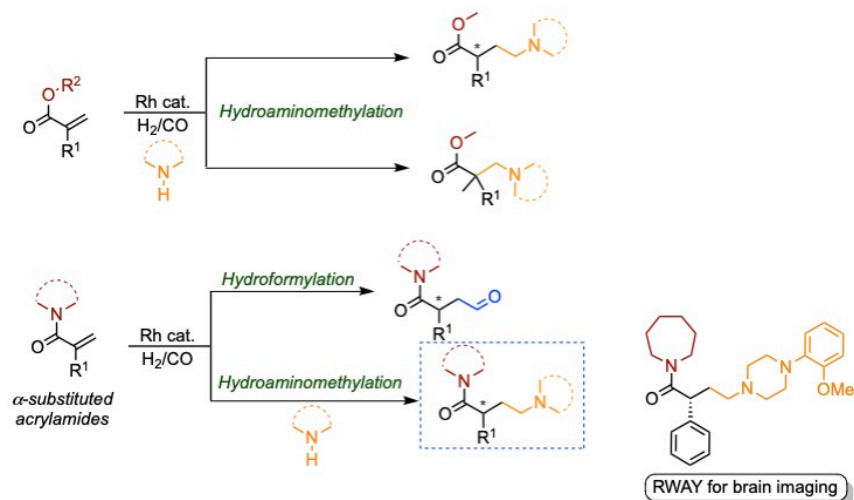


Figure 1: Rhodium catalysed asymmetric hydroaminomethylation of α -substituted acrylates and acrylamides

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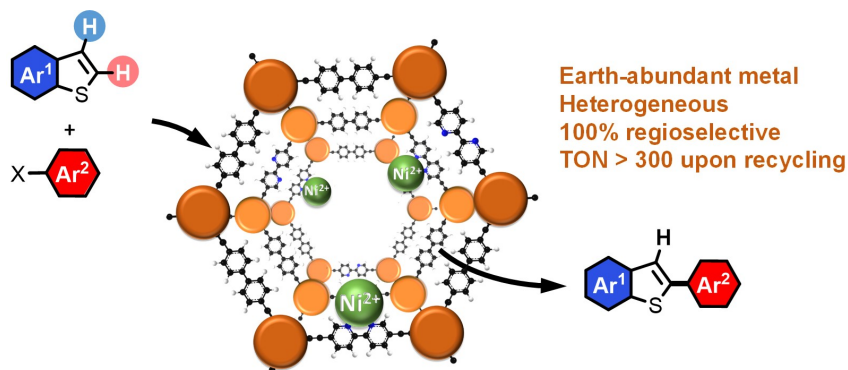
Heterogenized Molecular Ni-Catalyst for the Sustainable Direct C-H Arylation of Heteroarenes

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The use of earth-abundant metals for the direct C-H activation through a heterogeneous protocol would allow reaching appealing sustainability for the synthesis and derivatization of fine chemicals since this approach would enable at the same time (i) the use of accessible resources, (ii) a beneficial atom- and step-economy of non-activated substrates, and (iii) the ability to reuse the catalyst and to easily separate it from products. To change the paradigm of molecular catalytic processes for fine chemical synthesis, we introduced recently the concept of solid porous macroligand for heterogenized molecular catalysis. Having molecularly-defined active sites, porous macroligands have been found to drive the activity and the selectivity of heterogenized catalytic processes on a similar way as molecular ligands but with the advantage of the structuration in a three-dimensional framework and the confinement within a porous nanospace. Here we show the heterogenization of an earth-abundant molecular nickel complex within the structure of a bipyridine-based porous organic polymer, namely BpyMP-1, used as a porous macroligand for the C-H arylation of heteroarenes. In the case of benzothiophene, an important building block for APIs, the optimized heterogeneous catalytic system has been reused for at least seven times with a total TON of ca. 300 and a productivity of 12 grams of 2-phenylbenzothiophene per gram of catalyst without significant Ni leaching.

The applicability of this novel heterogeneous system was further demonstrated by successfully arylating other heterocycles like thiophenes, selenophene and indole. Taking into account their robustness and their potential processability, the porous organic polymers used as macroligands for molecular catalysts further pave the way to molecularly defined and robust heterogeneous systems for a more sustainable synthesis of fine chemicals.



Hydrogen Peroxide Decomposition over Titanium-Siloxpoms

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In a precedent work, $\text{THA}_3[\text{SbW}_9\text{O}_{33}(\text{tBuSiO})_3\text{TiOiPr}]$ was used for allylic alcohol epoxidation using hydrogen peroxide as an oxidant. This titanium complex has been found to be a relevant structural and functional model for the microporous and crystalline titanium-silicalite TS-1, a well-known heterogeneous catalyst active in the propene to propylene oxide conversion. At an industrial scale, one undesired side reaction is the hydrogen peroxide decomposition, thus consuming the oxidant in unproductive way. While a number of works have been devoted to the study of the oxidation mechanisms of organic substrates on these Ti(IV)-based systems, detailed understanding of the H_2O_2 decomposition mechanism and of the nature of the intermediates involved in is still required. Our studies deal with the H_2O_2 decomposition over two different systems: $\text{THA}_3[\text{SbW}_9\text{O}_{33}(\text{tBuSiO})_3\text{TiOiPr}]$ and $\text{THA}_3[\text{SbW}_9\text{O}_{33}(\text{nPrSiO})_3\text{TiOiPr}]$ complexes (Ti-SiloxPOMs). Both complexes differ from the access to the active centres: in the former one the bulky substituents (tBu groups) hinder access of a substrate to the titanium centre, whereas in the latter one the presence of less bulky substituents (n-propyl groups) makes the access easier. Hydrogen peroxide decomposition rates appeared to depend of the size of these substituents and allow some Electron Paramagnetic Resonance (EPR) *in situ* analysis. Only one EPR signal was observed (see Figure) regardless of the complex used and seems to correspond to a titanium-superoxide, $[\text{Ti}]-\text{O}_2^\cdot$, as reported in literature.

In this oral communication, our results on kinetic studies of hydrogen peroxide decomposition and on the reactive intermediates involved will be presented and the possible pathways leading to this decomposition will be discussed.

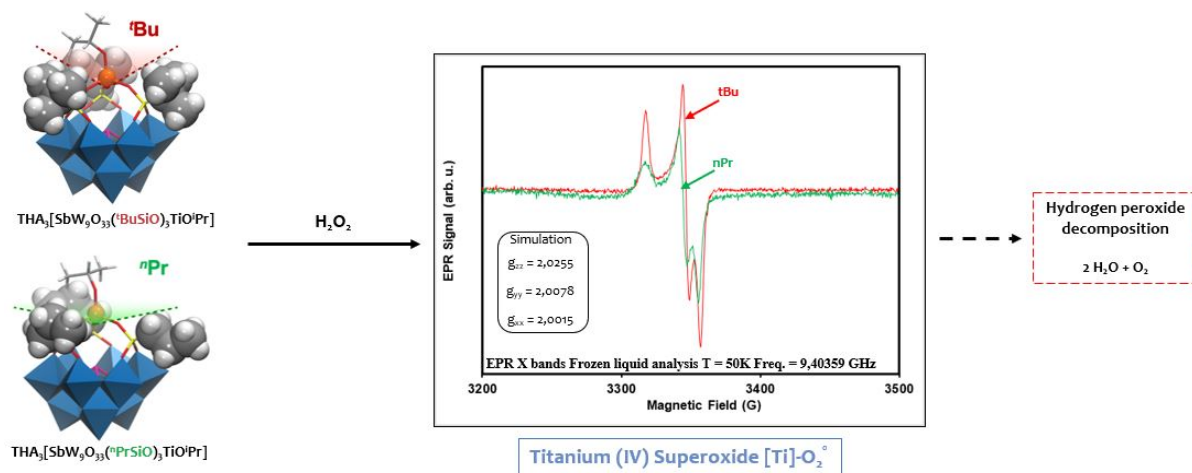


Figure 1: H_2O_2 decomposition over Ti-SiloxPOMs

TEMPO Immobilized on Ru-BEA Catalyzed Oxidation of alcohols under Mild and Base-Free Conditions

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The oxidation of alcohols to aldehydes and ketones is one of the most important reactions in modern chemistry due to the broad application of these compounds for the synthesis of plasticizers, polyols, carboxylic acids etc. Traditional methods require stoichiometric amounts of oxidants such as chromium dioxide, manganese dioxide, iodine etc. which are expensive and toxic. Therefore, molecular oxygen and hydrogen peroxide have been proposed as greener oxidants for the oxidation of alcohols in the past decades over metal-based catalysts. However, oxidation of mono- and polyols containing additional N-, O- or S- functional groups is hard to perform with the selective generation of carbonyl compounds due to over-oxidation of these compounds to acids, esters etc. The most common industrial methods require organic radicals such as TEMPO (2,2',6,6'-tetramethylpiperidine N-oxyl) for selective conversion of alcohols to carbonyl compounds with the generation of TEMPO-H, which can be regenerated back to TEMPO by oxygen over Ru and Cu based metal complexes. The high cost and difficulties related to the separation of complexes prompted us to develop heterogeneous catalysts by deposition of TEMPO over Ru-BEA prepared by ion exchange. The TEMPO-Ru-BEA composite material provides selective oxidation of alcohols to aldehydes or ketones under mild and base-free conditions. Thus, oxidation of 1-octanol over Ru-BEA at 100 °C and atmospheric pressure results in a decrease of the selectivity to octanal from 70 % at the beginning of the reaction to less than 40 % at a full conversion of octanol due to overoxidation of aldehyde to acid. At the same time, the presence of TEMPO over Ru provides oxidation of octanol to aldehyde with selectivity close to 100 %. The substrate scope analysis also demonstrates selective oxidation of other aliphatic and activated mono and polyalcohols over TEMPO-Ru-BEA composite. The catalyst can be recycled without leaching and loss of activity for many cycles. Physico-chemical characterization by different methods (TEM, XPS, EPR and FTIR) confirm the high stability of TEMPO coordinated over Ru species in zeolite BEA. The analysis of the mechanism of the reaction indicates activation of alcohols by TEMPO with subsequent regeneration of TEMPO-H by oxygen over Ru (Scheme 1). In comparison with existing heterogeneous catalysts based on supported metal nanoparticles, the newly developed materials show an oxidation efficiency matching that of homogeneous metal-TEMPO and with the major advantage of its easy catalyst-product separation.

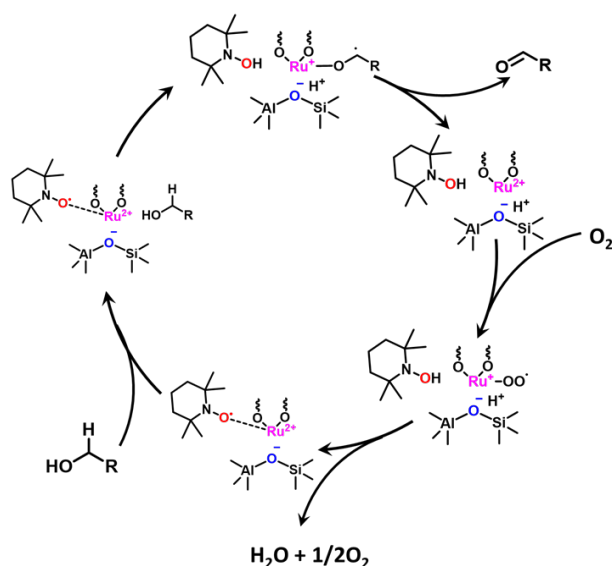


Figure 1: Scheme 1. Possible Mechanism of Selective Oxidation of alcohols with the TEMPO-Ru-BEA Catalyst

CuO/Cu(OH)₂ Supported on ZIF-8 as Nanocomposite Catalyst for Aerobic Alcohol Oxidation under Mild Reaction Conditions Using TEMPO as Co-Catalyst

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Cu-(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) has been extensively studied as a classical catalyst system for the oxidation of alcohols. This catalytic system has the advantages of being active under mild conditions and providing high selectivity. However, expensive and complex copper complexes are usually required. Alternatively, cheaper and more robust heterogeneous catalysts based on copper oxides/hydroxides nanophases were shown to be promising to catalyze alcohol oxidation. But, to our knowledge, they were still very scarcely reported and none of them were associated with Metal-Organic Framework (MOF) yet.

Herein, we report for the first time a CuO/Cu(OH)₂ nanocomposite supported on the Zeolitic imidazolate frameworks ZIF-8, a stable and highly porous zinc-imidazolate MOF, as a heterogeneous catalyst for the aerobic oxidation of alcohols in the presence of TEMPO and 4-Dimethylaminopyridine (DMAP). The catalyst was prepared by a simple impregnation of Cu(NO₃)₂ in the pores of ZIF-8 following by a reduction step with NaBH₄. A CuO composite with nanowire morphology is generated during the oxidation reaction (Figure 1a). These nanowires are believed to be at the origin of the activity as the performances of the recycled catalysts are maintained after the nanowires formation. The CuO/Cu(OH)₂ catalyst exhibited good activities and selectivity to aldehyde. The yield of benzaldehyde converted from benzyl alcohol can reach up to 29.4% at 6 hours as well as a complete conversion after 24 hours and without any benzoic acid obtained (Figure 1b). The catalyst could be recycled 7 times without any loss of activity. As a comparison, the Cu(NO₃)₂ impregnation on ZIF-8 also results in a catalyst for which the Cu active sites are significantly leached out during the oxidation reaction. The formation of the CuO/Cu(OH)₂ nanowires are therefore a prerequisite to the catalyst stability. The catalyst was characterized by XRD, N₂ adsorption, XPS, and TEM.

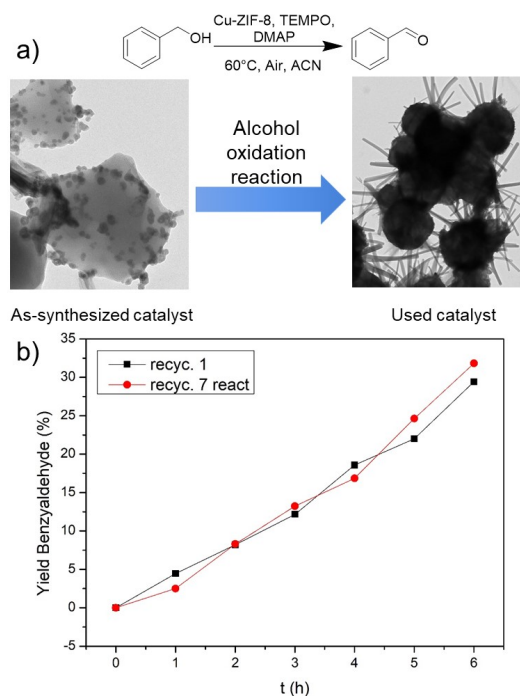


Figure 1: a) TEM images of the catalyst before and after the first oxidation cycle and b) Benzaldehyde conversion as a function of time for the first and the seventh oxidation cycles

Combined Photo- and Thermally Activated Catalytic Process for Direct and Highly Selective CH₄ Oxidation to Formic Acid at Ambient Conditions

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Background

Most of the state-of-the-art methane chemical conversion technologies require high temperatures and result in huge energy consumption and insufficient selectivity to the target products. Photocatalysis, converting solar energy into chemical energy, provides a promising route for methane conversion at room temperature. Direct and selective transformation of methane to formic acid demonstrates a more attractive and valuable route for photocatalytic methane conversion, however, has been rarely reported so far.

Method

Formic acid production from methane occurred in combined photo- and thermal catalytic process over Cs salt of phosphotungstic H₃PW₁₂O₄₀ acid supported by TiO₂ combined with Ru/Al₂O₃, in which the two processes were separated by a sand filter in reactor. Methane photocatalytic oxidation was performed over CsPW-TiO₂ in water using oxygen molecules as oxidant at room temperature. Meanwhile, commercial Ru/Al₂O₃ was employed to oxidize photocatalysis-derived oxygenates to formic acid in the bottom of reactor.

To inhibit the heteropolyacid leaching, Cesium (Cs) was used to substitute the H atoms around the kegging structure of phosphotungstic acid (HPW). Consequently, HPW was stabilized and precipitated as insoluble CsPW salt. Then, CsPW salt was mechanically mixed with TiO₂ as the photocatalyst.

Results

Methane conversion was driven by photocatalysis as no product was observed without light (Figure). No distinct promotion of methane conversion could be observed by neither HPW nor CsPW. Instead, TiO₂ favored predominant formaldehyde production. In dual components, a boosted methane conversion was observed when CsPW was combined with TiO₂. Interestingly, formic acid started emerging as one of the main oxidation products on CsPW-TiO₂ only when HPW was stabilized by Cs. Instead, no HCOOH was observed neither on HPW/TiO₂ nor Cs₂O/TiO₂. The CsPW showed superior stability in four methane oxidation cycles. Furthermore, no HCOOH was observed in the absence of air. The CsPW co-catalyst showed superior HCOOH productivity than the other Cs stabilized heteropolyacids. In synergistic hybrid process involving both photo- and thermal heterogeneous catalysts, a HCOOH production of 5000 $\mu\text{mol/g}$ with more than 80% selectivity was achieved, and HCOOH was detected as the only liquid product in water (Insert picture).

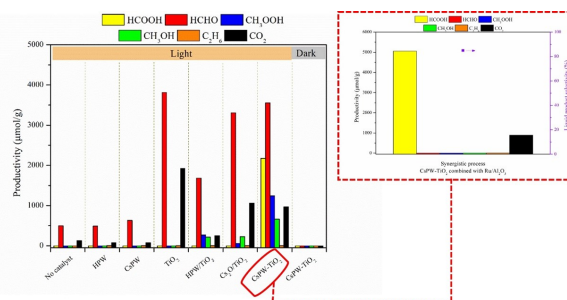


Figure 1: Photocatalytic CH₄ oxidation performance over catalysts and HCOOH production in synergistic process

Conclusion

In this work, we propose a direct process for highly selective conversion of methane to formic acid based on the synergy of photocatalysis and thermal heterogeneous catalysis. We observed high rates of methane conversion to oxygenates over heteropolyacid-titania composite photocatalysts. Cesium played a key role in stabilizing HPW for methane oxidation in heterogeneous reactions, the enhanced charge separation and transfer between CsPW and TiO₂ benefited boosted oxygenates production. Oxygen molecules instead of water mainly contributed to methane oxidation. The formic acid was produced on CsPW via consecutive methane oxidation with intermediate formation of formaldehyde. In the direct combined process of methane oxidation to formic acid, Ru/Al₂O₃ selectively oxidized oxygenates produced by photocatalysis to HCOOH which was observed as the only liquid product of methane conversion.

**Oral Communications 4 (OC4):
Production of H₂ and H₂ Vectors**

Predictive Catalysis by DFT: Generation of H₂ and Fixation CO₂, N₂O

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What can we do from computational chemistry for sustainability? In the line of machine learning, apply predictive catalysis to the maximum. Thus, on a small scale, the research group tries not only to find the reaction mechanism, and once the rate determining step (rds) is discerned, to look for alternatives to the existing catalysts to reach milder conditions.[1]

Even more markedly, the fixation of CO₂ or N₂O, or the generation of H₂ as fuel can be improved processes through DFT. First, the hydrogenation of nitrous oxide by pincer ruthenium complexes supposes a promising way to functionalize a hazardous gas and reduce the greenhouse effect, generating dinitrogen and water. There, the particular PCsp²P pincer ligand directly assists in the formation of a characterized epoxide complex, affording the N₂ release if N₂O is used as a reactant. Second, the generation of H₂ by means of alcohols is another goal. And related to this, to upgrade mechanisms that involve the formation of H₂ instead of the hydrogenation of a sacrificial molecule, the so-called acceptorless dehydrogenative coupling (ADC) reaction, became fundamental. In this new procedure that significantly reduces waste (stoichiometric reactions), the formation of H₂ is combined with the generation of aldimines, acrylonitriles...[2]

On the other hand, the simple modification of current catalysts, by others of less toxic, or lower cost, using more abundant metals, is already a great improvement. And here DFT calculations can do the initial screening, i.e. predictive catalysis, before the synthetic efforts, but already with a candidate or selection of them chosen through the calculations. Take for instance, cyclopentadienone iron dicarbonyl complexes were applied in the alkylation of ketones with various aliphatic and aromatic ketones and alcohols via the borrowing hydrogen strategy in mild reaction conditions. DFT calculations and experimental works highlighted the role of the transition metal Lewis pairs and the base. These iron complexes demonstrated a broad applicability in mild conditions and extended the scope of substrates.[3]

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Electrodeposited Metal Oxide Thin Films and their Application in Alkaline Water Oxidation

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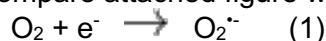
Introduction

The ongoing energy transition results in an increased need for storage, due to the intermittent nature of solar and wind energy. Both batteries and chemical storage (such as H₂) have received a lot of interest. Additionally, green hydrogen can provide an alternative in CO₂ intensive industry processes (e.g. Haber-Bosch process) and serve as a green fuel in steel, cement, aviation and shipping industry. Both alkaline water (AWE) and proton exchange membrane (PEM) electrolyzers are already commercially applied hydrogen production technologies. To further decrease the cost of green H₂ however, the efficiency of these electrolyzers must be increased while their CAPEX must be lowered. An advantage of AWE is its long-term stability and its use of cheap Ni based electrodes. AWE however results in relatively low current densities compared to PEM (~0.2- 0.6 Acm⁻² versus 1.5- 2 Acm⁻²). One solution to decrease the overall cell voltage in AWE is the reduction of the oxygen evolution reaction (OER) overpotential. To avoid the application of scarce and expensive electrocatalysts such as RuO₂, IrO₂ (for PEM) and improve on the SoA NiOOH (for AWE) our research focusses on the development of cheap, stable and highly active thin film oxide OER catalysts.

Preparation and OER Catalyst testing

First row transition metal electrodes are commonly applied as an inexpensive alternative for application in alkaline water electrolysis. In this study, metal oxide thin films NiO_x, FeO_x, CoO_x, MnO_x and alloy combinations thereof were prepared.

To do this, a self-limiting electrodeposition method was utilized, mediated by the in-situ formation of superoxide radicals (O₂^{•-}) in an aprotic electrolyte. This in turn precipitates metal ions M^{x+} present in the solution onto the electrode surface, passivating it in the process to prevent further deposition of metal oxides on the metal surface (compare attached figure with M^{x+}: Mn²⁺):



This process allows the preparation of metal oxide coatings which thickness can be controlled due to the self-limiting nature of the electrodeposition process. This allows the functionalization of porous or nanostructured materials (such as Ni foams, meshes) with a simple electrodeposition step without loss of functionalization by blocking pores of the electrode support. In addition, a thin film coated onto a conductive material reduces ohmic losses within the catalyst layer, minimizing the inherent disadvantage of metal oxides due to their poor conductivity. The prepared catalysts were characterized in steady state galvanostatic experiments to assess their activity towards the OER, exhibiting favorable activity compared to polished Ni electrodes. In addition, the coatings were characterized to study the effect of different metal compositions on the activity and the surface area of the electrode. This allows an assessment of their applicability as a coating in porous, high active surface area electrodes for long-term testing under industrially relevant conditions.

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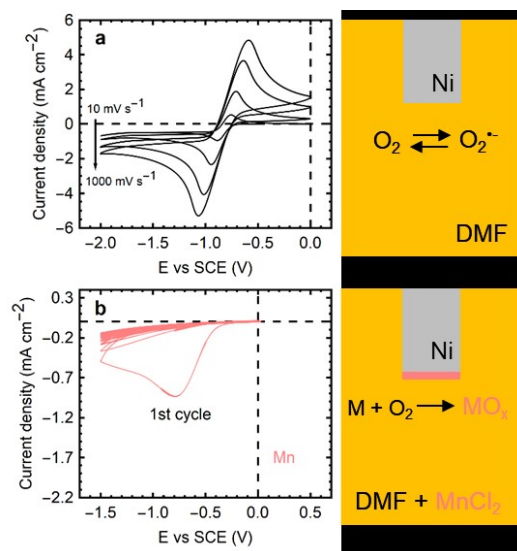


Figure 1: Electrodeposited metal oxide thin films

Photocatalysis vs Photovoltaics: Why not Make it a Symbiosis?

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The development of new technologies to make renewable energy available and affordable is crucial to face global warming. Photocatalysis is a promising method to convert solar energy into solar fuels such as hydrogen (Figure 1.a). The main challenge is to find a photocatalyst able to use efficiently the entire solar spectrum, which is still at the research stage. But even in that case, this technology would be in direct competition with photovoltaics. An alternative approach is to take assets of both these methods, by coupling them using a fast-growing technology, LEDs (Figure 1.b). This innovative concept has however to be cleverly engineered to maximize the solar to hydrogen yields, and make it competitive with conventional heliophotocatalytic processes.

H2TEX project aims at developing a LED-photoreactor for carbohydrate reforming, using UVTEX[®] photocatalytic textiles from BrochierTechnologies to maximize the contact between light, catalyst and reagents. The present study quantifies the effect of several operating factor that can be tuned to maximize the process efficiency, and evaluate their impact on the final hydrogen price considering feedstock expenditures, OPEX and CAPEX evolutions.

Experiments have been performed in a semi-batch reactor containing 220 mL of a solution glycerol/water, with various volume ratio from 1 to 50%vol. The reactor temperature was varied between 10 and 45°C using thermostated water recirculating in a double wall. UVTEX[®] textiles were coated with a Pt photodeposited TiO₂ catalyst. A LEDENGINE UVA LED operating between 100 and 900mA was used as a light source.

Technico-economic analysis has been carried out using the H2A tool v3.2018, considering a daily H₂ production of 50 000kg. As already reported, the effect of glycerol concentration on H₂ production rate follows a Langmuir-Hinshelwood profile. Therefore, the increase of concentration decreases significantly the H₂ cost by increasing the efficiency of the process. The effect of temperature is also in line with literature since it can

be described using an Arrhenius law with activation energies comprised between 7 and 21 kJ/mol depending on experimental conditions. Assuming that heat is recovered from LED cooling, the energy consumption is globally reduced when increasing temperature and so is the cost. The most interesting result concerns the light intensity effect: its increase induces an increase of the H₂ production rate, but not in a perfectly linear manner. The increase starts to slow down at high intensities, which traduces lower electric to hydrogen yields. This is first linked to the LED efficiency, that diminishes slightly at high current intensities (Shokley behavior), but mostly because electrons/holes recombinations accelerate at high intensities. Yet, despite an increase of the electricity consumption, higher current do not significantly impact the hydrogen production cost: CAPEX is also reduced in the same time due higher rate of amortization.

To conclude, photocatalytic reforming efficiency can be significantly reduced by optimizing catalytic parameters such as temperature, light intensity or reagents concentration. Yet, the optimum of cost is not necessary the optimum of efficiency: an optimum between H₂ production rate and efficiency should determined to minimize the overall hydrogen production cost.

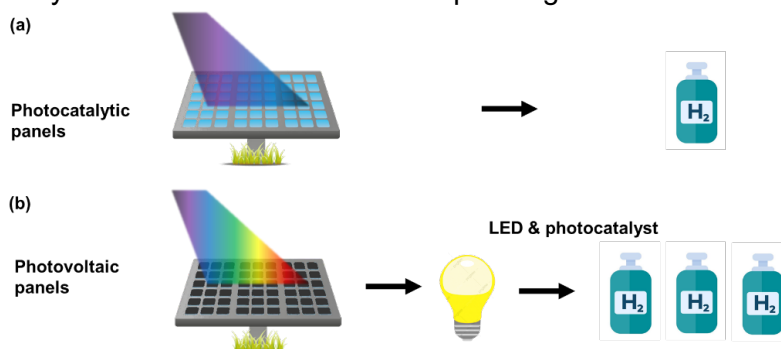


Figure 1: Conventional heliophotocatalysis (a) against photovoltaic-coupled photocatalysis (b) for solar fuels production

Hydrogen Storage by Innovative Liquid Organic Hydrogen Carriers (LOHCs)

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Many recent global efforts focus on reducing fossil fuel consumption and develop renewable energies as a compensation. Their main characteristic is their intermittence. The challenge is therefore to find a dense and secure method of storage. In this context, a possible approach is to transform the electricity into chemicals through the intermediary of H₂. However, the efficient storage of this chemical energy remains an issue. There are different technologies for storing hydrogen and among them LOHCs exhibit large and stable hydrogen storage capacity. The general principle of storage in LOHC pairs is a hydrogenation reaction to store hydrogen by chemically bonding hydrogen atoms within a stable liquid and a dehydrogenation reaction to release it.

In this work, a unique catalytic system for hydrogenation of γ -butyrolactone (GBL) into 1,4-butanediol (BDO) and the reverse dehydrogenation for regeneration of GBL and release of hydrogen has been studied for stationary hydrogen storage using the same catalyst and a single reactor. This LOHC pair shows several advantages. For instance, its dehydrogenation enthalpy of 41 kJ/mol_{H₂} is low compared to other existing LOHCs (DBT/pHDBT: 71 kJ/mol_{H₂}). Moreover, the reactions can be carried out in the presence of available and inexpensive catalysts based on copper and the organic carriers can be produced from biomass.

In order to develop a successful GBL/BDO LOHC process design, thermodynamic and kinetic studies of the system must be performed. In the literature, reliable kinetic and thermodynamic data are not available. The goal of this work is thus to establish a reliable kinetic model for the hydrogenation of GBL and dehydrogenation of BDO.

Various catalytic tests were carried out in the presence of CuO-ZnO-MgO-Al₂O₃ commercial catalyst in a semi-batch reactor in the 185 to 230 °C temperature range with a constant pressure of 50 and 3 bar for hydrogenation and dehydrogenation respectively. During the reaction, the liquid phase is regularly sampled and analyzed by GC and GC-MS. Based on analytical results, mechanisms of side-reactions are proposed. This mechanism consists in the formation of by-products 4-HHB (4-hydroxybutyl 4-hydroxybutanoate) from the transesterification of GBL by BDO in both reactions, and dibutylene glycol from two molecules of BDO in dehydrogenation, considering that all reactions are balanced.

Based on experimental and analytical results, a kinetic model was proposed and tested for hydrogenation and dehydrogenation reactions. The experimental concentration profiles were modeled on Matlab software by using the numerical integration ode23s to solve the differential equation system. Estimation of kinetic parameters for both reactions allowed to predict well the experimental data obtained until thermodynamic equilibrium and able to fit an Arrhenius law. Furthermore, models are valid at short and long reaction times, and the estimation results displays acceptable uncertainties for all tested temperatures.

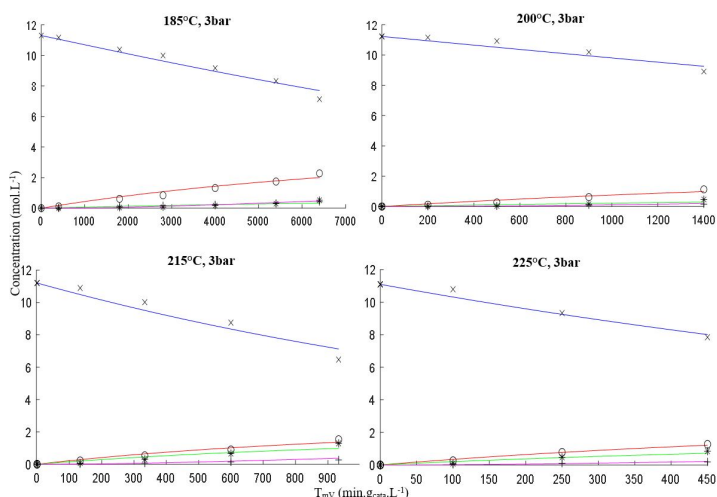


Figure 1: Comparison of the experimental and fitted data for dehydrogenation. BDO (experimental: x; model: blue line), GBL (experimental: o; model: red line), by products dibutylene glycol (experimental: *; model: green line), 4-HHB (experimental: +; model: purple line)

Tuning the Structural Dynamics of Pt/CeO₂ Catalysts for Accelerating the Water Gas Shift Reaction

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Context and purpose

Pt/CeO₂ is a promising catalyst for the low temperature water gas shift reaction (WGS). Moreover, it is “dynamic” since Pt can be dispersed during an oxidative treatment at moderate temperature leading to single atoms catalysts (SACs) while a reducing treatment triggers 3D particles formation. Starting from SACs, suitable redox treatments were previously shown to tailor nanoclusters more active for the low-temperature CO oxidation in the presence of water.

In this work, the influence of different redox treatments on the WGS activity of Pt/CeO₂ catalysts has been investigated depending on the Pt surface density as well as the doping by alkali cations. Relationships between physicochemical and catalytic properties have been established based on several complementary characterization methods including in situ/operando techniques.

Material and methods

Pt/CeO₂ catalysts with different loadings were prepared by wet impregnation using Pt(NH₃)₄(NO₃)₂ as precursor and high surface area CeO₂ as support, followed by calcination in air at 500 °C. A wet impregnation by alkali nitrates was further achieved on selected calcined samples for doping. The catalysts were characterized before, during and after the reaction by various techniques, including ICP-OES, XRF, BET, XRD, STEM-HAADF, H₂ and CO-TPR, CO-DRIFTS, and operando Raman and DRIFTS. The catalytic performances were measured using a fixed-bed reactor flowing a H₂O/CO/Ar:32/8/60 mixture at atmospheric pressure and 235 °C.

Main results

The Pt/CeO₂ catalysts were shown to be predominantly SACs after calcination. Catalytic data

revealed a quick ceria reduction under the reaction feed, while STEM images showed the formation of 3D Pt nanoparticles (NPs) of ca 1.5 nm after only a few minutes on stream. Interestingly, an optimal H₂ productivity was observed after a few minutes likely due to intermediate active sites transiently formed. An optimal H₂ productivity was also observed for a Pt coverage of 0.12 at/nm² (figure 1A), revealing two different behaviors for high and low loadings. They are attributed to a balance between the Pt dispersion and the reducibility of ceria (figure 1B).

Furthermore, different pretreatments were applied to tune the Pt NPs size. A reductive treatment at 500 °C improves the catalytic performances at low Pt loadings by strongly improving the surface ceria reducibility (figures 1B and C), while it decreases the catalytic activity at high loadings by Pt sintering. Various oxidative treatments were also performed to redisperse Pt particles after 1 h on stream. For low loadings, the initial activity is recovered after an oxidative treatment at 230 °C, while this catalyst is strongly activated after an oxidative treatment at 500 °C (figure 1A).

Alkali dopants increase the activity of the Pt/CeO₂ catalysts with high Pt loadings, presumably by stabilizing ultradispersed Pt species and modifying the ceria reducibility. However, they strongly poison the catalysts at low Pt loadings.

Major conclusions

Both structural dynamics and ceria redox properties of Pt/CeO₂ control its catalytic activity in WGS. These two parameters strongly depend on the Pt surface density and the presence of alkali dopants, allowing the use of redox treatments as a key strategy to (re-)activate the catalyst.

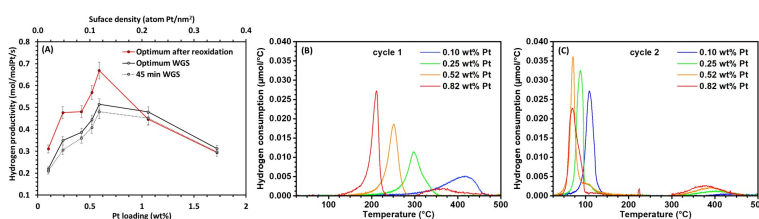


Figure 1: Hydrogen productivity of Pt/CeO₂ vs Pt loading; H₂-TPR curves for different Pt loadings (B) cycle 1: after oxidation at 500 °C for 1 h and (C) cycle 2: after cycle 1 and reoxidation at 500 °C for 1 h

Supported (Co)MoS₂ Catalysts for Production of H₂ through Water Gas Shift Reaction: Active Sites-Mechanism-Stability

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In the way towards non carboneous energy, dihydrogen appears as an optimal energy vector. One option for its green production (green H₂) is to use biomass, a carbon-neutral and naturally abundant sustainable energy resource. The treatment of biomass either thermic or biologic leads to formation of syngas (CO, H₂). The water gas shift (WGS) reaction, which transforms CO and H₂O in CO₂ and H₂, has then attracted renewed interest as the key process of maximum hydrogen production from the biomass-derived syngas. However, conventional metal oxide catalysts for WGS reaction are easily deactivated by sulfur-containing impurities, which are generally present between 100 to 200 ppmv in syngas issued from biomass feedstocks. Establishing an energy-efficient and economical WGS catalytic process requires the development of high-performance and stable catalysts capable of adapting to the diversified qualities biomass feedstocks, especially for the issue of sulfur poisoning. Sulfides are considered good candidates for the sulfur-tolerant WGS catalysts.

Up to now, most of the studies were focused on the activity and stability of the catalysts playing with the composition of the catalysts, but only a few works aim to rationalize the obtained results. In this work, applying the adsorption of CO followed by IR spectroscopy methodology on MoS₂ catalysts prepared with different morphology, it is shown for the first time that the two different edges exposed by MoS₂ slabs, M-edge and S-edge sites, present different behavior towards the reactant CO and H₂O. In particular, it appears that the M-edge sites are sensitive to H₂O through S/O exchange while the S-edge sites are reactive with CO which is transformed in COS. Following the WGS reaction in classical reactor and/or in operando IR cell, it appears that these two edge sites have also different activities and stabilities with time on stream. The M-edge sites partially deactivate during WGS reaction. On these M-edge sites, the formate mechanism preferentially occurs. On the S-edge sites, the WGS goes through a redox pathway involving COS as intermediate. This is the first time that such a modified redox pathway is identified. Thus, to enhance both the activity and stability of sulfide sites for WGS two ways are considered (i) to favor the growth of S-edge sites playing with the preparation method and the support nature (ii) to promote the edges by Co especially to modify the reactivity of M-edge. Following the reaction in operando mode it is shown that the introduction of Co allows to increase the total activity in WGS mainly through the redox pathway. The promotion also favors the stability of the catalysts making the S/O exchange reversible. The work paves the way for tailoring the sulfide catalyst composition and morphology towards improved activity and stability in production of H₂ through WGS reaction.

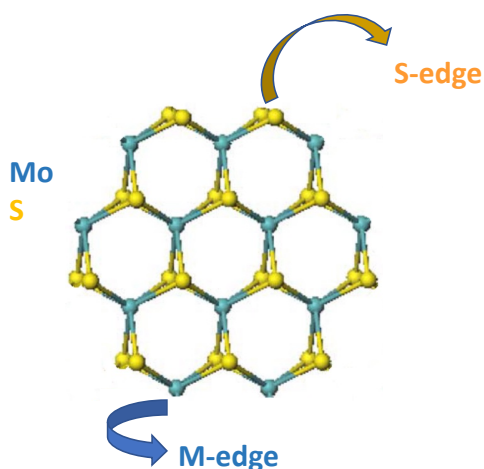


Figure 1: Activity and stability of M-edge and S-edge sites in supported MoS₂ catalysts

The Origin of High Activity of Cu Single Atoms on CeO₂-TiO₂ During CO Oxidation and PROX Reactions: An Operando Spectroscopic Study

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CO oxidation and preferential CO Oxidation (PROX) over heterogeneous catalysis are very important reactions not only from a fundamental point of view but also for its technical applications in different fields.[1] On the other hand, single-atom catalysts (SACs) have attracted great interest due to their unique performance and drastic cost reduction. In this work, we have developed highly active and stable Cu-single atom catalysts (SAC) supported on CeO₂-TiO₂ (40:60) prepared by sol-gel method for CO oxidation and PROX reactions at low temperature. In situ and operando techniques such electron paramagnetic resonance (EPR), FTIR spectroscopy in diffuse reflectance mode (DRIFTS), and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) combined with other characterization methods were applied to gain a deeper insight about the nature of the active sites and to derive reliable structure-activity relationships. We found that incremental increase of Cu loading between 0.06 and 0.9 wt.% caused in a significant diminishing of the Cu-mass normalized CO₂ formation rate due to the formation of less active CuO_x clusters (Figure 1).[2] The catalysts displayed high stability with negligible agglomeration of Cu single sites during 1000 min time on stream. Spectroscopic operando results showed that the active sites are shuttling between -Cu²⁺-O-Ce⁴⁺- and -Cu⁺-O-Ce³⁺ and the interaction between CeO₂ and single Cu ions on the surface of highly dispersed ceria particles enhances the Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ redox activity and creates oxygen vacancy sites needed for molecular oxygen activation and hence oxidation of CO to CO₂. The high activity of Cu/CeO₂-TiO₂ catalysts can be boosted more than one order of magnitude via precise controlling Ce/Ti molar ratio. This work provides deep insights into the rational design of high active and stable supported Cu-SACs for practical applications.

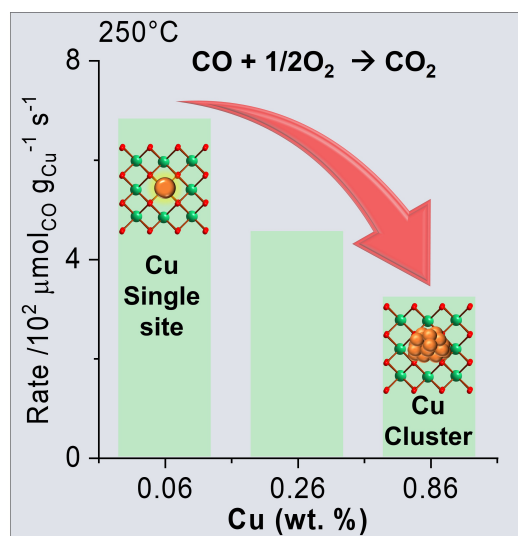


Figure 1: CO oxidation rate to CO₂ vs Cu loading over Cu/CeO₂-TiO₂ catalysts.

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Ammonia Decomposition in Electric Field over CeO₂-based Catalysts

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Green ammonia, produced using hydrogen from the electrolysis of water, is thought to make a considerable impact on the transition towards zero-carbon society. Nowadays, it is regarded not only as a fertilizer, but also as a source of fuel transportation and the chemical energy storage. From the decomposition of ammonia, hydrogen can be produced on-site, significantly reducing the cost and safety issues associated with the generation and storage of hydrogen. As one of the alternatives to the thermal ammonia cracking that requires harsh conditions (850-950°C), the use of electrified technologies such as non-thermal plasma is considered as a possible strategy. In contrast to thermal catalysis, in non-thermal plasma, the process of ammonia decomposition is not at thermodynamic equilibrium, therefore being decomposed to N₂ and H₂, the ammonia synthesis rate will be reduced. Numerous studies have been published up to date showing the possibility of plasma-catalysis ammonia decomposition over perovskites and metal supported catalysts on silica and alumina. Despite the considerable conversion by non-thermal plasma, this process is limited by low energy efficiencies. One of the ways to improve the energy consumption is the application of the electric field (or dark current), which require less energy than plasma, and proceed in milder conditions, in which classical catalytic activity would be negligible as reported by the group of Sekine and co-workers. This concept was introduced to the electric field-induced ammonia synthesis. The activity of different metals was tested over CeO₂, Ce_{0.5}Zr_{0.5}O₂, SrZrO₃ and substituted SrZrO₃ by Ba, Ca, Y and Al. It has been shown that the application of the electric field depends on the gas atmosphere, type of catalyst, temperature, etc. In this framework, the activity of CeO₂-based materials has been investigated in gas phase ammonia decomposition using the electric field. The reaction was carried out at ambient temperature and pressure using the reactor schematically shown on the figure. The role of ammonia concentration in the feed, residence time, presence of the metal nanoparticles and the effect of the diluting gas (argon, helium), and input current are discussed. The energy efficiency of the process in different conditions was evaluated as well.

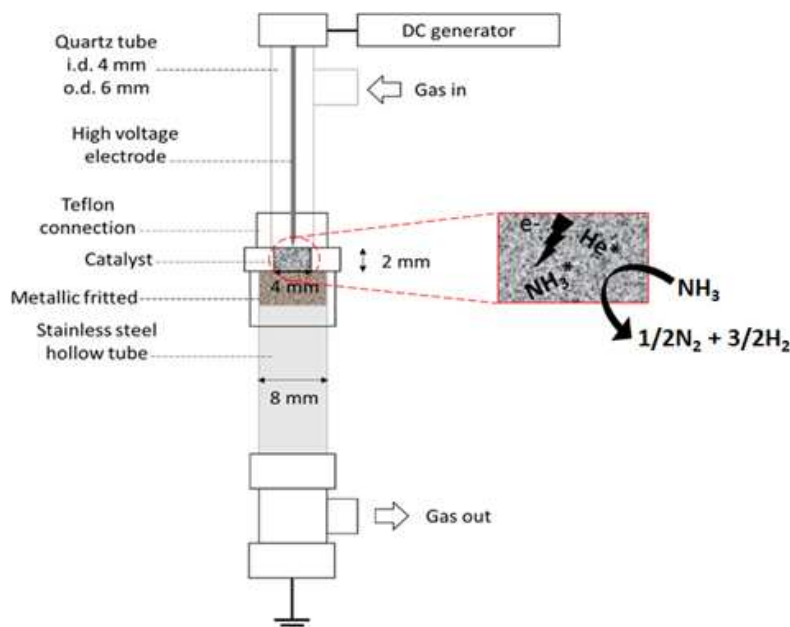


Figure 1: Scheme of the reactor

**Oral Communications 5 (OC5):
CO₂ Valorization**

Activating CO₂ on Amphoteric Catalysts: A Molecular Insight on Monoclinic Zirconia

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CO₂ activation is a scientific challenge which, once met, would open the route to new processes based on CO₂ as a C1 lowly toxic building block. In this field, amphoteric catalysts, as monoclinic zirconium oxide (m-ZrO₂), have recently aroused great interest, as support and/or active phase. In this project, we focus on understanding the heterogeneous catalysis of the nucleophilic addition (A_N) of alcohols on CO₂. In the literature, the reaction intermediates were evidenced on m-ZrO₂ with IR spectroscopy but the catalytic mechanism is still unclear. To the best of our knowledge, no structure-activity relationship has been published yet, even for the simplest reaction, the dimethylcarbonate (DMC) synthesis from CO₂ and methanol. The FTIR analysis of the active species presently relies on empirical assignments that could be improved and precised to give new information. We propose here to explore this pathway by building a consistent description of the active species and their phase diagram in the experimental conditions. The idea is to model the adsorption CO₂ and methanol adsorption with DFT methods and to re-analyze FTIR *in-situ* experiments in light of those new results.

We methodically modeled the adsorption of CO₂ and methanol and their vibrational frequencies upon m-ZrO₂ model surfaces through DFT periodic calculations (VASP code, PBE-D3 functional). All the facets experimentally observed on m-ZrO₂ were considered: (001), (011), (111) and (-111). Geometry optimizations and vibrational analysis were performed for bare and partially hydroxylated surfaces, for a coverage rate up to saturation, thus implying more than 300 adsorbates structures. Considering the CO₂ adsorption on bare zirconia surfaces, our DFT calculations have demonstrated that four types of structures are stable (Figure), whatever the surface, whatever the coverage rate. Those structures are different from the previous experimental assignment and the calculated adsorption energies (from -181 to -5 kJ.mol⁻¹) are consistent with those measured experimentally for this material or calculated on other oxides. Considering the methanol adsorption, we obtained the mono-, di- or tricoordinated methoxy species that were classically described and used in the empirical assignments but the analysis of the frequencies shows that other factors contribute to the spectral shifts of the IR bands.

The thermodynamic stability of the CO₂ and methanol adsorbed phases has been calculated as a function of temperature and pressure for the partially hydroxylated surfaces.

We characterized a m-ZrO₂ sample of high specific area (70 m².g⁻¹) with FTIR *in-situ* spectroscopy to reveal the adsorbed species formed with CO₂ and/or methanol at low pressure. With the methodic description of the CO₂ and methanol adsorption from DFT modeling, we interpreted the evolution of the FTIR spectra in experimental conditions and assign them to extract more information on the nature of the surface sites and on the role of each exposed facet.

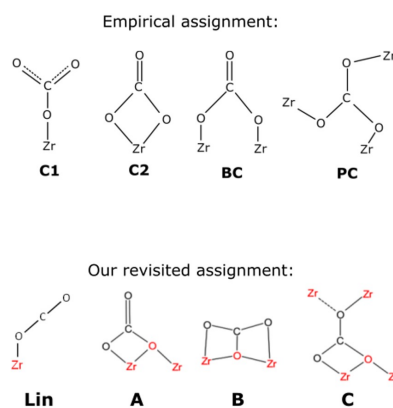


Figure 1: Surface carbonate structures (A, B and C) and linear CO₂ structure (Lin) according to empirical and revisited assignments

Pyrrole-Containing Zinc Complexes as Robust Catalysts for the Valorization of CO₂ into Cyclic Carbonates

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The reaction of CO₂ and epoxides to form organic carbonates requires Lewis base catalysts, such as tetrabutylammonium halides (TBAX). Their activity and selectivity towards cyclic carbonates can be strongly reinforced with Lewis acids, as for example, Salen or porphyrin metallic complexes. We developed a series of nitrogen Schiff base (N-SB) compounds¹ that forms a family of ligands that combines properties of both, Salen flexibility and porphyrins nitrogen coordination sphere. Herein, we present the synthesis and characterization of pyrrole containing Nitrogen-Schiff Base (N-SB) ligands. XRay analysis showed monomeric or dimeric helical structures, according with the coordination mode of the zinc centre that can be tetra or pentacoordinated. Combined to TBAX, the zinc N-SB complexes proved to be efficient and selective co-catalysts for the valorisation of CO₂ into cyclic carbonates. The optimization of the reaction parameters was carried out with styrene oxide, and solvent free reactions allowed very high yields (up to 97%) using very small catalyst/co-catalyst amounts (less than 0.2mol%)². Moreover, the robustness of these zinc complexes allowed various catalytic runs four days long, without any purification, just adding new loadings of styrene oxide. The reaction scope was also enlarged to other epoxides.

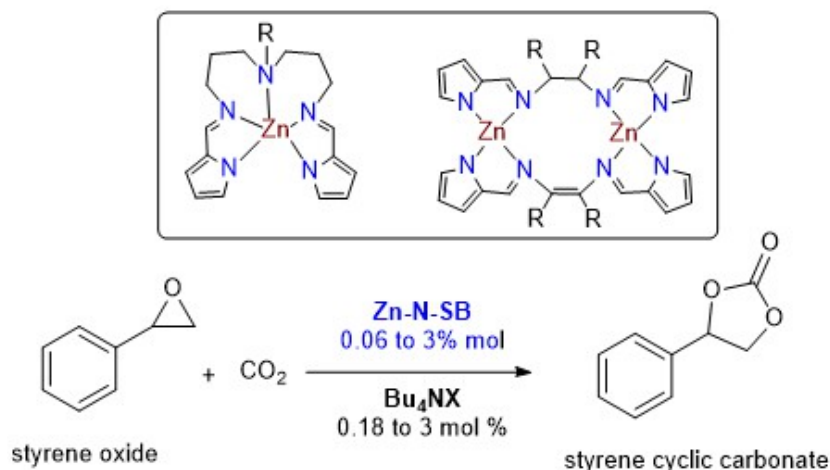


Figure 1: Zinc pyrrol complexes for the CO₂ cycloaddition into epoxides

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2. M. Alonso, L. Merzoud, W. Lamine, A. Tuel, H. Chermette, L. Christ, *J.CO₂ U.*, 44 (2021)101380

CO₂ Conversion by Low-Temperature Fischer-Tropsch

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To fulfil climate objectives, the production of synthetic e-fuels using CO₂ as a raw material appears as part of the solution. In particular, Power-to-Liquid (PtL) concept is combining CO₂ with hydrogen supplied from water electrolysis, powered by renewable sources, is currently gaining interest as it allows the production of sustainable fossil-free liquid fuels. The proposed process discussed here is an upgrading of the well-known Fischer-Tropsch synthesis. The concept deals with two cascade reactions in one pot with first the conversion of CO₂ into CO via the Reverse Water Gas Shift (RWGS) reaction, which is then followed by the Fischer-Tropsch Synthesis (FTS). Instead of using a Fe-based catalyst, which can carry out both reactions, we have chosen the strategy to decouple the two functions (RWGS and FT) on two different catalysts within the same reactor. The FTS shall shift the equilibrium of the RWGS reaction (which alone would be limited to 15-20% of conversion at 250°C) by converting the CO into hydrocarbons. This strategy shall enable optimization of the catalyst pair and thus lower the temperature of reaction thanks to the equilibrium shift to gain selectivity in the liquid fraction. The challenge lies in maximizing the activity of the RWGS catalyst, but also in the ability of the FT catalyst to be highly selective. Methane production is the main concern as the energetic barrier of CH₄ formation is generally lower than that of the RWGS reaction, so the goal will be to minimize methane selectivity. Here we report the study of different combinations of copper-based RWGS catalysts with different cobalt-based FTS catalysts. We investigated their behaviours under mild process conditions by the use of high-throughput experimentation. Our results show that at 250°C and 20 bars, Cobalt catalysts mainly act as methanation catalysts. Indeed, CH₄ selectivity never drops under 80 % despite the addition of various promoters (Nb, K, Pt, Cu) on the catalyst and its coupling with active RWGS catalysts. However, we show that the activity of the RWGS catalyst has an impact and can lead to the longer hydrocarbons chains selectivities (C₂+) of about 10%.

We studied the influence of the reduction temperature on the activity and selectivity of the tandem catalyst system. Similar selectivity and conversion were obtained, at reduction temperatures between 250-400°C. This leads to the question of the active phase of the cobalt catalysts, which is currently investigated by magnetic measurements and DRIFTS.

Thus, in coupling it with a more selective FT catalyst better results are expected. This was achieved using a cobalt/iron FTS catalyst. The CH₄ selectivity dropped to 62 % at 265°C, 20 bars and a GHSV of 2500ml/h/gcat. We propose that the conditions used for the cobalt catalysts could have generated this methanation because these catalysts are known to have their best performance around 210°C in classical FTS whereas the iron catalysts are more flexible but are also known to have an RWGS activity.

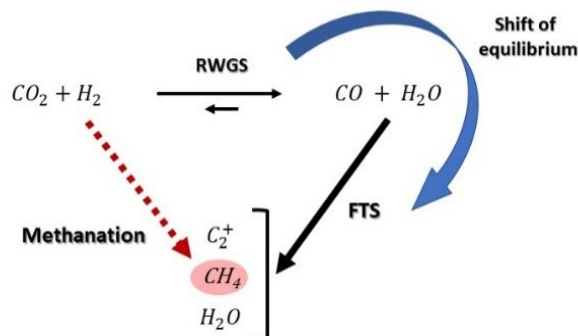


Figure 1: Schematic diagram of the chosen strategy and its main potential drawback

Study of the CO₂ Conversion into Methanol: Catalytic Process Innovation and Optimization

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Nowadays, the reduction of anthropogenic CO₂ emissions is crucial to remedy the global climate change. Beside its sequestration (CCS – Carbon Capture sequestration), the valorisation of CO₂ could be envisaged. It can be used as a raw material for carbon-based products, including fuels, chemicals, and building materials (CCU – Carbon Capture and Utilization).

To this extent, the catalytic hydrogenation of CO₂ into methanol has been confirmed as one of the most promising CO₂ conversion pathways. A wide variety of heterogeneous catalysts has been evaluated in the CO₂ hydrogenation to methanol but copper-based catalysts showed the highest activity toward the named reaction with a low price. Catalytic performance can be evaluated by numerous kinetic models that have been proposed in literature. The most performant are the Langmuir-Hinshelwood-Hougen-Watson (LHHW) models. The model of Graaf was selected from the literature. In this model, three reactions are considered: (i) CO₂ hydrogenation, (ii) Reverse Water Gas Shift and (iii) CO hydrogenation, all reactions are assumed to be based on a dual-site LHHW mechanism.

As a direct consequence of the industrial interest regarding alternative production of methanol, the present work focuses on providing an original integrated process from CO₂ capture to its conversion into methanol. Simulations of an industrial unit have been carried out using Aspen Plus software.

The aim is to optimize the operating parameters as well as the configuration of the conversion unit to maximize the production of methanol but also to improve the reuse of the heat released (thanks to the global exothermicity of the reactions): firstly within the process itself (e.g., providing energy to the reboiler of the rectification column for water-methanol separation) and secondly the possibility to fulfil the energy requirements in the capture unit (i.e., regeneration of the CO₂ capture solvent). A commercial catalyst (Cu/ZnO/Al₂O₃) has been selected for this study. Kinetics were described using the Graaf's model.

In a first configuration, only an isothermal reactor has been used, operating at 250°C and 65 bar. To improve the recovery of heat released, a second reactor configuration has been studied. It consists of considering a first adiabatic reactor allowing to enter at lower temperature than 250°C, the energy released by the reactions leads to preheat the flue entering a second isothermal operating at 250°C. For both configurations, an overall CO₂ conversion of 99.6% is achieved with a flow recycling rate of 98.5% and Gas Hourly Space Velocity (GHSV) of 10000h⁻¹. The methanol productivity obtained is 0.5 kg of methanol per 1 kg of catalyst per hour with a mass purity of up to 99.6%. The second configuration (using two reactors) presents the best interest for an optimized heat recovery. A complete energetic integration and techno-economic study have been investigated.

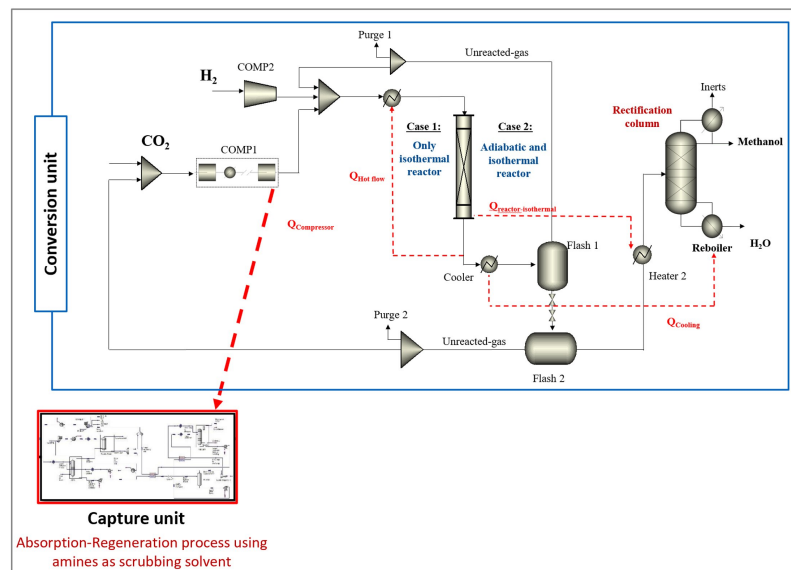


Figure 1: Figure 1 Flowsheet of CO₂ conversion unit with heat integration

Investigation of Molybdenum and Rhenium Ultradispersed Over Titania as Catalysts for Carbon Dioxide Hydrogenation

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In the context of global warming and related carbon capture & utilization strategies, the thermocatalytic hydrogenation of CO₂ is one possible route toward the production of “green” fuels and platform chemicals [1]. As far as methanol production is concerned, besides the industrial Cu/ZnO/Al₂O₃ syngas-to-methanol catalyst, some other materials have been proposed to increase the methanol yields and the catalyst stability, but they mostly involve rare or strategic elements such as Au, Pd, In, Ga, Zn, and Ce.

In this work, we have assessed the potential of early transition metals (V, Cr, Mn, Nb, Mo, Ta, W, Re) supported on various commercial or homemade titanias in the gas-phase CO₂+H₂ reaction in a high-pressure flow fixed bed reactor (275 °C, 18 bar H₂, 6 bar CO₂, WHSV 7.5 L/g/h). The catalysts, prepared by wet impregnation-calcination, consisted of metal single atoms and/or clusters anchored on the support, as visualized by STEM (Fig.). The reference titania materials were commercial anatase (Tronox DT51D, 85 m²/g) and anatase-rutile mixture (80:20%, Evonik P25, 61 m²/g). The metal screening led to the selection of low-loading Mo and Re-based catalysts as the most active ones.

The catalytic performance of Mo/TiO₂, which was previously regarded as inactive for CO₂ hydrogenation to methanol [2,3], is highly sensitive to the Mo loading (0.1-10 wt%) and the titania type (phase composition, surface area, nanoparticle morphology). In particular, molybdenum supported at intermediate loading (3 wt%) on rutile titania nanorods exhibits unexpected efficiency in terms of total activity, methanol yield, and methanol selectivity (Fig.). Catalyst characterization by various techniques including NAP-XPS and *operando* XAS, suggests that the most active sites consist of atomically-dispersed and partially oxidized Mo species in intimate interaction with titania [4].

Like Mo/TiO₂, the Re/TiO₂ system containing a similarly low proportion of supported metal atoms is stable and catalyzes mostly CO, methane and methanol production from CO₂ and H₂. However, it is more active than its molybdenum counterpart. Moreover, Re/TiO₂ favors the formation of higher alkanes and alcohols, and the products distribution is even more dependent on the metal loading and the titania type than for Mo/TiO₂. From Re/RNR to Re/P25, the main reaction route switches from competitive reverse water-gas shift and CO₂ methanolation, to CO₂ methanation (Fig.). Complementary CO hydrogenation tests, CO₂ TPD, H₂-D₂ exchange and *operando* DRIFTS experiments provide additional insights into the mechanistic similarities and differences between those catalysts.

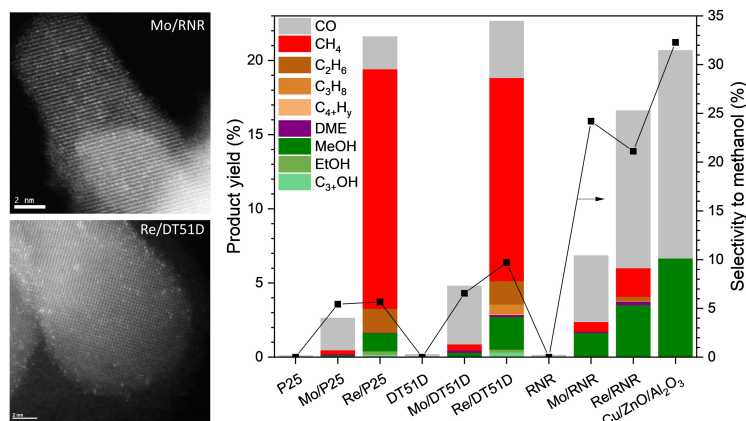


Figure 1: STEM-HAADF images (left) and CO₂ hydrogenation performances (right) of 3.0 wt% Mo/TiO₂ and 5.8 wt% Re/TiO₂ catalysts

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**Oral Communications 6 (OC6):
Hydro(de)sulfurization**

Mo loading and Alkali Ion Optimizations of Zirconia Supported Catalysts for the Direct Synthesis of Methanethiol

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Methanethiol is a platform molecule commonly used in the synthesis of organosulfur compounds such as the amino acid methionine. The industrial way to produce methanethiol corresponds to methanol thiolation with H₂S on sulfided alkali tungstate supported catalysts. Using methanol implies its large-scale production from syngas. To reduce the environmental impact, alternatives are under study to avoid the use of methanol, such as the direct synthesis of CH₃SH from a mixture of H₂S, CO and H₂. Recently, a K-Mo catalyst supported on t-ZrO₂ has been patented for the direct synthesis of methanethiol. The present study thus focuses on tetragonal zirconia supported systems, considering the influence of the Mo content and of the alkali ion (Na⁺, K⁺, Cs⁺) on the catalytic performance in the direct synthesis of methanethiol. Catalysts were prepared by incipient wetness impregnation method using t-ZrO₂ pellets as support. The molar ratio alkali/Mo was fixed at 2 for each catalyst, by using solutions of K₂MoO₄, Na₂MoO₄ or Cs₂MoO₄. The resultant solids were matured under a steamy atmosphere for 2.5h, dried overnight at 100°C and calcined at 480°C (2°C.min⁻¹) in flowing air for 4h. The catalyst oxidic precursors were then charged in a fixed bed reactor supplied by the feed gases (CO, H₂, H₂S and N₂). The preliminary activation procedure consisted in a sulfidation step under 20 vol% H₂S/H₂ at atmospheric pressure with an increasing temperature until a final stage at 350°C for 1h. Performances were estimated for 3 mL of catalyst at 320°C under 10 bar of a CO/H₂/H₂S mixture with a molar ratio equal to 1/2/1 and a gas hourly space velocity of 1333 h⁻¹.

Catalytic activities of potassium molybdate based solids are presented in **Figure 1 (a)**. The maximum productivity (292 g_{MeSH}.h⁻¹.L_{cat}⁻¹) is observed for the catalyst loaded at 8 wt.%. This sample corresponds to the limit of good dispersion of the K₂MoO₄ phase at the support surface in the oxidic precursor, as evidenced by XRD and Raman spectroscopy. Hence, a loading of 8 wt.% was selected to prepare supported catalysts replacing potassium whether by sodium or cesium. While the catalyst prepared with potassium consists in an average MoS₂ particles size of 4.8 nm and an average stacking degree of 1.8, Na⁺ and Cs⁺ containing samples

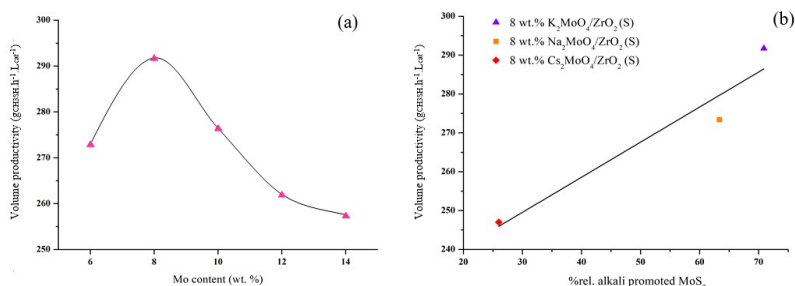


Figure 1: (a) Volume productivity of methanethiol of the activated catalysts with different wt. % Mo, (b) Volume productivity correlated to the relative percentage of alkali promoted molybdenum disulfide detected by XPS

present larger MoS₂ particles with higher stacking degrees. The sample with cesium was particularly distinctive in terms of MoS₂ particle morphology, showing slabs longer than 80 nm and stacking degree reaching more than 20 layers. XPS analysis were performed to identify and quantify the various MoS₂ phases. As illustrated in **Figure 1 (b)**, the volume productivity appeared to be directly correlated to the relative % of alkali promoted 1T-MoS₂ phase, detected by XPS after activation of the samples with different alkali atoms.

These results confirm the relationship between catalytic performance and quantity of this alkali promoted phase in the activated solids. Although this phase may not be stable under reaction conditions, its initial amount after activation is clearly decisive to obtain an active catalyst for the direct synthesis of methanethiol.

Influence of the Synthesis Steps of a CoMoP/Gamma-Al₂O₃ Catalyst onto the Multiscale Mo Organization in the Active Phase by ASAXS Technique

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Due to very high standards to reduce sulfur contents in fuels, the design of more active hydrotreating catalysts remains a major challenge for both research and industry. Traditionally, those catalysts are composed of cobalt-promoted MoS₂ slabs supported on mesoporous alumina. A way to increase the catalysts' activity is to impregnate them with higher amounts of metals but this may lead to a loss of intrinsic activity.

These catalysts present a multiscale organization. At the slab level (around a few nanometers), the active phase is characterized by its length and its degree of stacking. These information make it possible to determine the dispersion of the active phase, which is one of the key parameters driving the intrinsic activity of a catalyst. However, this parameter only considers the active phase at the slab scale, while at a larger scale (around dozens of nanometers), these slabs can form aggregates. The origin of such aggregates and their influence on catalytic activity need to be elucidated. A series of CoMoP/γ-Al₂O₃ catalysts (from 18 to 30 %wt MoO₃) have been prepared by incipient wetness impregnation of active phase precursors on the γ-Al₂O₃ support. Parameters of ageing (with/without), drying (temperatures, times, ramps, gas, flow, freeze-dried) and additivation (with/without) steps have been drastically varied. Catalytic activity has been evaluated by toluene hydrogenation, after an in situ sulfidation.

Anomalous Small Angle X-Ray Scattering (ASAXS) measurements of those oxide and sulfided catalysts have been performed close to the Mo K-edge absorption, on BM02 beamline of synchrotron ESRF (Grenoble). ASAXS technique is the only one able to describe the multi-scale Mo organization (stacking, aggregation, dispersion) inside the porosity of the support and allows to collect information as: (i) the slabs length and their stacking, (ii) aggregates size, (iii) amount of Mo aggregated. ASAXS results complete a multi-technique approach (TEM, XPS, N₂-physisorption, etc.).

Syntheses conditions of each step appear to have a strong influence on the active phase organization. For instance, the ageing step mostly decreases the slabs and aggregates sizes whereas the drying temperature ramp seems to preferentially affect the amount of aggregated slabs. Indeed, a fast temperature ramp increases the slabs aggregation. Finally, the triethyleneglycol post-additivation impacts all the properties as it leads to smaller slab length, less aggregated into smaller aggregates.

The presence of such aggregates has a negative impact on the intrinsic activity, probably due to a loss of accessibility of the active sites. At first sight, the MoO₃ content engaged in the aggregated active phase seems to be the leading parameter as shown in the attached figure. Indeed, the higher it is, the lowest is the intrinsic activity. Also, the aggregates size seems to play a role. It confirms that aggregation has a harmful influence onto the catalytic activity. Control of aggregation at the mesoscopic scale appears to be a key lever, often overlooked, for improving HDS activity.

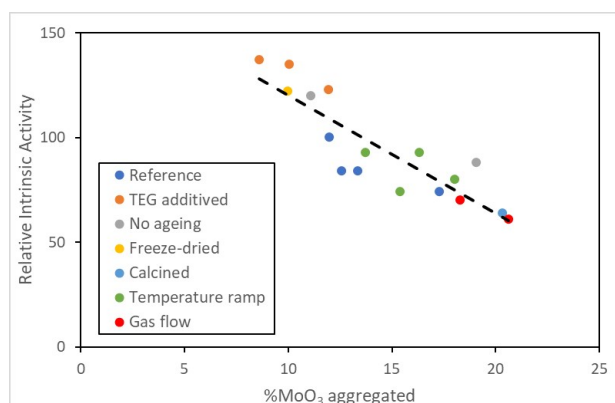


Figure 1: Influence of the MoO₃ amount involved in the aggregated active phase onto the intrinsic activity as a function of various preparation parameters

Innovative Chemical Imaging Speciation Methodology for Studying the Impact of the Impregnation and Drying of Supported CoMoP/Al₂O₃ Hydrotreating Catalysts by Quick-XAS and Raman Spectroscopies

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The controlled dispersion of phosphorus-based molybdenum heteropolyanions (P-HPAs) on alumina support is highly demanded for the preparation of hydrotreating catalysts with a high activity¹. The heterogeneous distribution of P-HPA and polymolybdate species on alumina extrudates has been recently documented by Raman and NMR imaging techniques², however their quantification and sometimes identification remain a major challenge. In this work, the location and quantification of those molybdenum-based oxide species deposited on ≈ 1.6 mm thick quadrilobe-shaped alumina extrudates by impregnation of various solutions of metallic precursors and phosphorus is reported using Full Field (FF) XAS imaging operated at the Quick-XAS ROCK beamline. The in situ time-resolved diffusion of the oxidic species within the alumina support porosity upon impregnation and phase transformation upon subsequent drying at 120°C are also studied using two dedicated cells.

The FF XAS imaging methodology consists in the recording of space-energy resolved 3D Mo K edge XAS hypercubes using a pixelated ORCA Flash 4.0 V3 CMOS camera³. The data processing includes a normalization step leading to the 2D Mo distribution map (Fig. 1a) with a spatial resolution of 1.625 μm per pixel camera, followed by a binning by 30x30 pixels (Fig. 1b) for improving the S/N ratio of the XAS spectrum, mandatory for the further extraction of the EXAFS signal. Finally, linear combination fitting (LCF) of the so-obtained binned EXAFS spectra, using a library of spectra of bulk references⁴ provides for the first time a quantification of Mo-based species dispersed on the support (Fig. 1c), given in relative fraction of spectrum and with a spatial resolution herein of 49.5 μm . This information is complemented with Raman hyperspectral imaging of the same extrudates, which results in qualitative mapping of the location of the P-HPAs (16.2 x 16.2 μm) (Fig. 1d).

The recording of FF imaging hypercubes is repeated, with a time frame of 5.5 s/cube, along the 3-hours impregnation and subsequent 2h-drying. The hundreds of spectra so-obtained provide valuable spatial and time-resolved information on the dynamic uptake behavior of the solution and the hidden complex physico-chemical phenomena, such as Mo diffusion, adsorption and equilibria. Moreover, the use of a cylinder-shaped support will enable the development of a model of the impregnation and drying steps that will contribute to an even greater understanding of the dynamics of the system. Overall, this methodology enables to establish a relationship between speciation of the oxide phase and solution parameters, including P/Mo and Co/Mo molar ratios, and addition with citric acid and TEG, constituting an important tool for improving the synthesis of the catalysts.

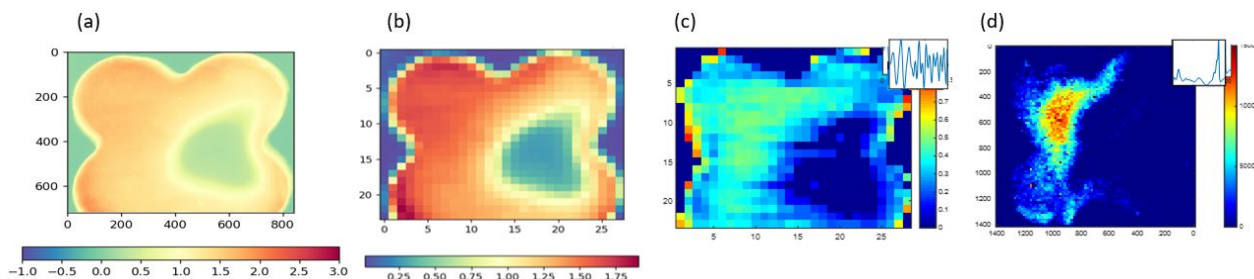


Figure 1: (a) Absorption map after normalization and (b) after binning of a dried CoMoP/Al₂O₃ 8 wt.% MoO₃, Co/Mo 0.4, P/Mo 0.56, (c) LCF analysis as a mapping of the relative fraction of lacunar Keggin's HPA, (d) Raman hyperspectral imaging of the same HPA

High Specific HDS Activity of Ultradispersed Mo Species: Influence of Metal-Support Interaction

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Molybdenum disulfide is a widely used catalyst for hydrodesulfurization (HDS) of petroleum fractions. The current view attributes HDS catalytic activity to the edges of nanoscopic MoS₂ slabs. However, some experimental results indicate that the description of these systems should be improved, namely with the help of recently emerged concept of ultradispersed catalysts. Along with MoS₂ slabs, small subnanometric species are present in the systems which can act as catalytic sites for HDS.

In this work we studied HDS catalytic performance and active species of ultradispersed catalysts with 1 wt.% Mo, prepared on different supports: TiO₂, SiO₂ (KIT-6), Al₂O₃ and activated carbon. It might be expected that Mo species on oxides will bond strongly with surface oxygen and tend to remain single-atomic, whereas Mo species bond weakly with carbon surface and form larger clusters.

Conventional characterization techniques (TEM, Raman, XRD, UV-vis DRS) confirmed that no MoS₂ nanoparticles were present in the samples. On the HAADF STEM images small Mo clusters along with single atoms were observed (Fig. 1a). The species formed during sulfidation and HDS reaction were monitored by means of operando XAS at the ROCK beamline of SOLEIL synchrotron. The differences of sulfidation behavior trends between the samples have been compared.

All catalysts demonstrated high specific activity in HDS of thiophene (Fig. 1b). The differences in HDS rates and in selectivity were explained by the variations of Mo species formed depending on the used support. For the first time it was shown that ultradispersed sulfided Mo species supported both on oxides and carbon are active in HDS. Depending on the nature of utilized support, the strength of metal-support interaction could be varied, impacting the nature of species are formed on the surface.

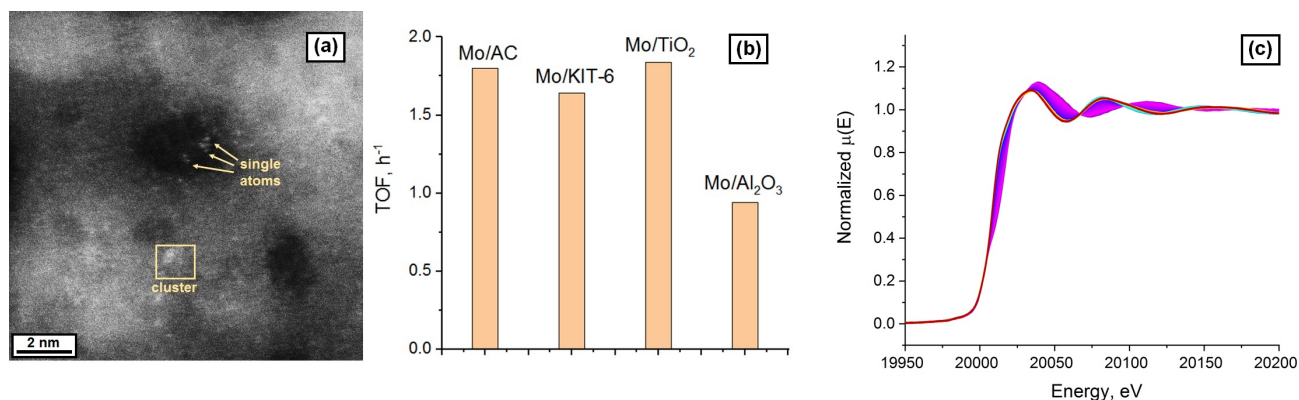


Figure 1: Figure 1 (a) HAADF STEM image of sulfided 1%Mo/TiO₂, (b) Specific HDS activities (?) XANES spectra for 1%Mo/TiO₂ monitored during in-situ sulfidation.

Evaluation of Catalysts in the Gas Phase Oxidative Desulfurization Reaction of a Model Scrap Tires Rubber Oil

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In recent decades, the scrap tires rubber (STR) pyrolysis has been gaining interest as a good alternative for the treatment, management and valorization of these wastes, since it decreases pollution and produces great industrial value products such as oil, syngas or char. Research have shown that oil obtained from pyrolysis of STR has a calorific value between 42-44 MJ/kg, which is similar to standard fuels as gasoline or diesel. However, one of the great limitations of the use of STR oil is the presence of high sulfur content. Several desulfurization technologies have been developed, with oxidative desulfurization (ODS) being one of the most promising. Gas phase ODS has better technical feasibility at the industrial level compared to a liquid phase ODS, however, it has not been studied for oil from pyrolysis of STR.

This study aims to evaluate two types of catalysts for the gas phase desulfurization of STR oils in order to improve these oils for use as fuel. For this purpose, two model STR oils represented by dibenzothiophene in toluene and benzothiazole in toluene (sulfur content of 0.08 wt%) were prepared. The tests were carried out in a pilot pyrolysis unit as shown in the Figure 1. The dibenzothiophene and benzothiazole molecules were chosen as one of the most used model molecules in the ODS studies and the main sulfur compound in the STR oil, respectively. The model STR oil is injected in the vapor phase into the reactor. Nitrogen is used as the carrier gas at a volumetric flow of 155 Nml/min, which is necessary for the optimal production of oils in the reactor. The reactor consists of two zones, the first one guarantees that the model STR oil is kept in the vapor phase and the second one has a dry air injection to carry out the ODS reaction. The oil obtained is recovered in two cooling traps and characterized to determine the conversion of sulfur compounds. For the ODS reaction, the vanadophosphomolybdic heteropolyacid (HPMoV) supported in the commercial silica CARIACT Q-10 and CuO/ZnO/Al₂O₃ composite with a Cu/Zn/Al atomic ratio of 3.06:1:2.84 were used. Heteropolyacids were selected given their multifunctionality and their demonstrated activity in oxidation of sulfur compounds in liquid phase. Oxide catalysts with Cu-Zn-Al composition were selected because they are among the most used in the gas phase ODS with high sulfur removal percentages. Moreover, the ODS reaction were carried out at 300°C and a constant pressure of a 1.5 barg, a O₂/S ratio of 80 and a WHSV of 6 h⁻¹.

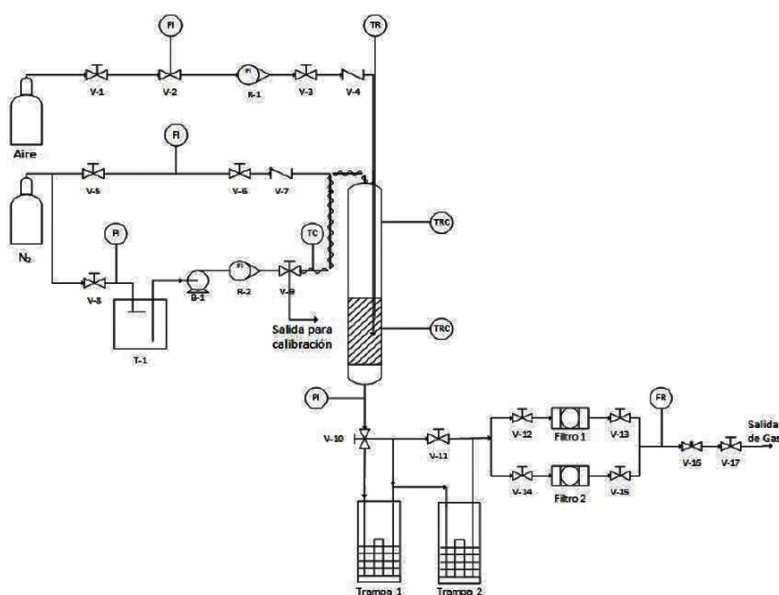


Figure 1: Pilot unit scheme for model STR oil ODS

**Oral Communications 7 (OC7):
Metals, Carbides**

First Atomic Scale Evidence of Hydrogen-Inducing Size Dependent Structural Transition in Gold Nanoparticles: Toward a Realistic Picture of Reactive Surface

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It is generally accepted that the catalytic performance of gold nanocatalysts is critically related to particle size. Smaller is the nanoparticle (NP), larger the proportion of under coordinated sites at edges and corners assuring high reactivity toward interacting molecules. Today, we realize that this paradigmatic picture of static surface and perfect crystal forms with complete outer layers is oversimplified and cannot provide accurate understanding of the catalytic properties of the working active sites. The recent progress in imaging and modeling materials under working conditions provides unprecedented opportunities to follow the evolution of catalyst material and to understand the catalytic processes occurring over the surface at the atomic/molecular levels. In this talk, I will present our recent work combining aberration-corrected environmental transmission electron microscopy (ETEM) and ab initio molecular dynamics (AIMD) to examine at the atomic scale the structural dynamics of Au NPs exposed to H₂ at atmospheric pressure at various temperatures. In situ atomic scale observations under hydrogen reveal that while Au NPs larger than 4 nm are indeed nearly rigid face-centered cubic (fcc) structures, smaller ones exhibit drastic morphological transformations and continuous structure symmetry changes. AIMD simulations at finite temperatures evidence the atomic origin of the observed shape changes and reveal the role of highly mobile gold atoms inducing symmetry transitions. In addition, an unprecedented stable surface molecular structure of hydrogenated gold decorating a highly distorted core is identified (Figure 1). This work (recently published in *Small* 2021, 2104571) provides new atomic scale insights into gold nanostructures during hydrogenation reactions and suggests the necessity of investigating structure-activity relationship through a more realistic picture.

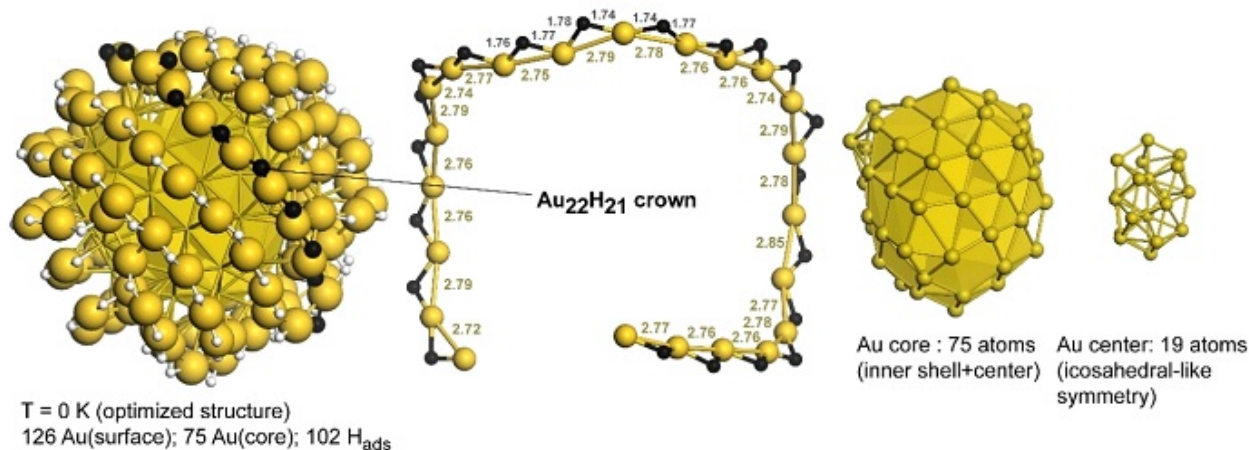


Figure 1: From the left to the right: DFT optimized AIMD configuration (after 60 ps) of hydrogenated gold NP; The formed H-Au-H-Au surface crown line (values are in Angstrom); the distorted structure of the core and the icosahedral-like Au structure of the center.

Networks of $\text{Au}_x\text{Pd}_{1-x}$ Model Catalysts Obtained by the Di-Block Copolymer Inverse Micelle Method: Insights on Nanoparticle Formation and Network Stability at High Temperature Under Gas Pressure Within the Environmental TEM

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Synthesis of nanoparticles (NPs) with well controlled characteristics is crucial to better understand the behaviour of the active phase during reaction and to better correlate it with its catalytic performance. Among other self-assembly methods, the *di*-block copolymer approach is well suited to obtain monodisperse supported NPs which can serve as supported metallic catalysts on both flat (model catalysts) and powder (realistic catalysts) supports. In this approach, an amphiphilic *di*-block copolymer dissolved in toluene yields a system of inverse micelles of which the core can be charged with metallic precursors to ultimately yield networks with well-controlled characteristics (size, composition, inter-distance). Important questions must be addressed, in particular in the case of bimetallic systems, concerning the formation of unique NPs at the cores from the initially pre-formed bimetallic seeds or the stability of the NPs networks with increasing temperature in presence of

We have chosen to work with PS-*b*-P2VP *di*-block copolymer micelles that were functionalized with chloro-auric acid and palladium di-acetate precursors. The precursors selectively bind with N-functions in the P2VP cores to form (bi-)metallic seeds within the micelles' cores as it was previously established in the case of PdAg alloys. We have used an Environmental TEM (Titan ETEM G2, FEI/TFS) operated at 300kV under gas pressures up to 20 mbar to gain insight on their evolution/stability during heating under oxygen and CO (for CO oxidation catalysis). Temperature variation was achieved with a WildFire sample holder with dedicated heating MEMS-microchips (DENS Solutions) capable of reaching temperatures up to 1300°C. Monolayers of controlled $\text{Au}_x\text{Pd}_{1-x}$ core-metallized PS-*b*-P2VP micellar solutions were deposited by spin-coating (2000/4000 rpm) on the microchips. Special care was taken to minimize/prevent any influence of the electron beam on the observed events.

The Au-rich system ($\text{Au}_{80}\text{Pd}_{20}$) showed that, under oxygen, the (bi-)metallic seeds within the P2VP cores begin to sinter around 350° and unique NPs are eventually formed around 500°C which is consistent with the decomposition temperature range of the PS-*b*-P2VP copolymer associated with metallic nuclei. Further heating up shows that the NPs network is stable up to 900°C. Approaching the melting temperature of gold (1064°C) the NPs begin to shrink; concomitantly, smaller NPs (that grow even at 1100°C) form around the shrinking NPs. These smaller NPs are formed with Pd atoms from the initial bimetallic NPs.

In the case of the Pd-rich system ($\text{Au}_{20}\text{Pd}_{80}$), under oxygen, the seeds begin to sinter around 300°C and at 450°C demixing of the NPs is observed leading to Janus NPs (Au-rich/PdO, cf. Figure); the latter are readily reduced and homogeneous NPs reform upon CO exposure (cf. Figure).

The stability of the bimetallic NPs seems to be driven by the intrinsic properties of the metals composing them. Thanks are due to the METSA network for supporting this study and to CLYM for the access to the ETEM.

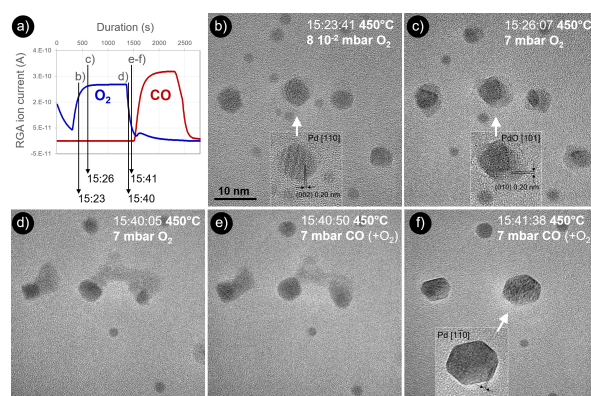


Figure 1: In situ ETEM oxidation of metallic Pd-rich AuPd NPs (b) under O_2 (c-d) and fast reduction under CO (e-f) at 450°C under 7 mbar according to the RGA profile shown in (a).

MXene-Supported Single-Atom and Nano Catalysts for Butadiene Hydrogenation

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In the last decades, 2D materials have gained great attention in catalysis, owing to their large specific surface area, mechanical robustness and flexibility, and unique physical and chemical properties [1]. MXenes, a burgeoning class of 2D transition metal carbides or nitrides, have a general formula of $M_{n+1}X_nT_x$ ($n=1-4$), where M is an early transition metal, X is C or N, and T_x indicates surface termination group(s) such as $-O$, $-OH$, $-F$ or $-Cl$, which depend on the etchants used in the synthesis process [2]. Since their discovery in 2011 with the Ti_3C_2 -based system [3], MXenes have shown great potential in various fields including electrocatalysis for evolution or reduction reactions [4]. However, the literature on the application of MXenes in thermal catalysis remains scarce. In this work, we have used butadiene hydrogenation under gas flow conditions as a simple model selective hydrogenation reaction - though of applied interest for polymerization. We have used two types of Ti_3C_2 MXenes, noted CMX and PMX, prepared with HF or LiF/HCl etchants, respectively, as supports for metal (Pt, Pd) single atoms or nanoparticles deposited by aqueous impregnation of metal salts (Fig. 1d). From SEM and STEM images, the MXenes present a multilayer structure (Fig. 1a) where each layer itself contains a few stacked nanosheets (Fig. 1b). Aberration-corrected STEM analyses of the as-prepared low-loading (0.1 wt%) Pt/MXene and Pd/MXene catalysts exclusively show single atoms on both MXenes (Fig. 1c for PMX). An increase in metal loading (1 wt%) leads to a fraction of nanoparticles.

Before the reaction, the catalyst was delaminated, dispersed on quartz wool, and reduced in hydrogen. The bare MXenes showed no hydrogenation capability. PMX-supported low-loading single-atom catalysts are less active than 1 wt% metal-loaded catalysts, but they exhibit a higher selectivity towards butenes (Fig. 1e), even at the same conversion. Depending on the metal, 1-butene (Pd) or 2-butenes (Pt) are the main products. Moreover, compared to conventional alumina-supported catalysts, the MXene-supported ones are much more selective to butenes. This could be due to the high thermal conductivity of MXenes [5], which prevents the appearance of hot spots in the catalyst bed during exothermic reactions. The structural properties and surface compositions of metal/MXenes powders were studied in detail by XRD, XPS, and DRIFTS to correlate them with the catalytic performances and assess the influence of the MXene synthesis etchant, as will be shown in this contribution.

Caption Fig. 1: a) SEM image of Ti_3C_2 PMX; b,c) HAADF-STEM images of Ti_3C_2 PMX (b) and Pt₁/PMX (c, arrows indicate single Pt atoms); d) Illustration of the process for the synthesis of metal/MXene; e) Catalytic performances in butadiene hydrogenation at 150 °C, 1 atm, $H_2:He:C_4H_6 = 10:88:2$ vol%.

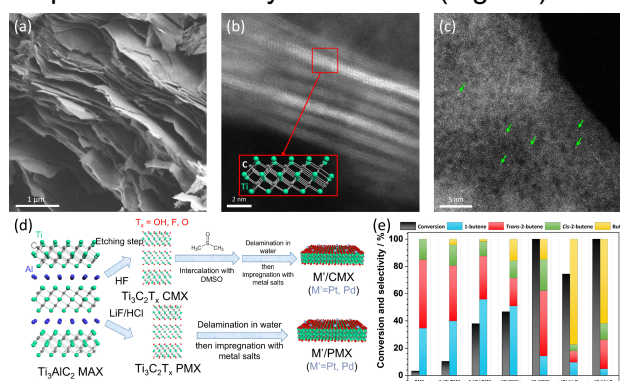


Figure 1: MXene preparation and characterization

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- [2] M. Benchakar et al, Appl. Surf. Sci. 530 (2020) 147209
- [3] M. Naguib et al. Adv. Mater. 23 (2011) 4248
- [4] H. Wang et al. J. Mater. Chem. A 8 (2020) 10604
- [5] L. Chen et al. Materials 11 (2018) 1701

Nickel Carbide Nanoparticles for Hydrogenation Reactions in Colloidal Suspension

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Finely divided nickel is one of the main heterogeneous catalysts for hydrogenation of nitro and alkyne moieties. However, it suffers from a lack of chemoselectivity and constitutes a major safety hazard due to its pyrophoric character.

Here, we investigated crystalline nickel carbide nanoparticles as catalysts in colloidal suspension for hydrogenation reaction under H_2 (7 bar), at 40 to 100 °C. First, we developed a robust synthetic route for the nanoparticles, which were characterized by x-ray diffraction on powder, transmission electron microscopy and x-ray absorption spectroscopy. A special attention was given to insure the full carbidization of the particles, a point that is sometimes overlooked in the carbide literature.

Then, we investigated the hydrogenation of two model substrates: nitrobenzene and phenylacetylene, and we showed that polar solvents are comparatively more favorable than less polar ones. Surprisingly, we found that the presence of water in the solvent mix was mostly favorable to the hydrogenation yield. We then showed that Ni_3C nanoparticles are comparatively as active as Ni nanoparticles of same diameter in the lower temperature range (40 – 80 °C) for the hydrogenation of phenylacetylene in ethylbenzene, a fact that directly confirms the interest of this phase vs. fcc Nickel.

We verified the absence of leaching, confirming that the nanoparticles are the active catalytic species. Complementarily, x-ray diffraction on powder was used to verify the structural integrity of the Ni_3C phase after catalysis. Lastly, we expanded the scope to a variety of aldehydes, ketones, esters, nitrile and unsaturated hydrocarbons and found a clear chemoselectivity of the catalyst, which gave either a quantitative hydrogenation or none at all, depending on the substrates. Altogether, this study highlights the interest of Ni_3C , a catalytic phase so far overlooked for these hydrogenation reactions, which actually works under fairly soft reaction conditions. We hope this will trigger an interest from the heterogeneous catalysis community to develop similar catalysts in supported forms, as well as from the theoretical chemistry community for modeling the active surface and explaining the chemoselectivity that we empirically identified.

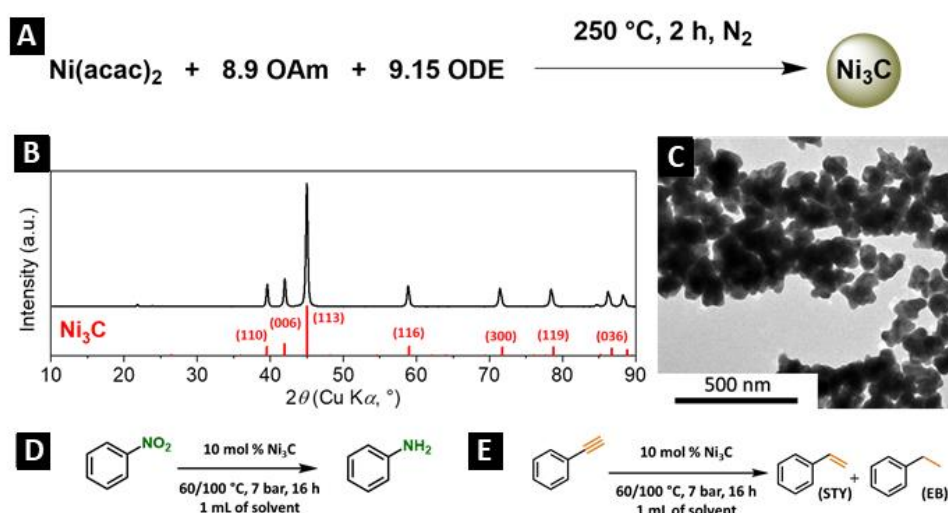


Figure 1: (A) Synthetic route for the Ni_3C nanoparticles. (B) Structural characterization by X-ray diffraction on powder. (C) Morphology by transmission electron microscopy. (D-E) The two main reactions investigated.

How the Products in Methane Dehydroaromatization Process Impact Its Stability?

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Introduction

Methane dehydroaromatization (MDA: $6 \text{ CH}_4 \rightleftharpoons \text{C}_6\text{H}_6 + 9 \text{ H}_2$) under non-oxidative conditions has received great interests over the past three decades. This direct route allows decarbonizing methane into benzene while simultaneously producing sustainable hydrogen, which offers great potential as future energy resource. MDA yet faces two major hurdles:

- (i) low activity, as the one-pass conversion into benzene is thermodynamically limited (~12% at 700 °C)
- (ii) rapid catalyst deactivation, as coke formation catalyzed by Brønsted sites is kinetically favored

Recently new deactivation modes emphasizing hydrocarbon pool formation or carbide molybdenum sintering were identified reinforcing the share of mystery remaining in the deactivation step. Numerous methods have been developed in the quest to mitigate the deactivation. However, low catalytic stability still remains a major issue and is considered the major challenge to make the process viable. In this communication, we present a kinetic study of the reaction focusing on the typical deactivation period observed during the MDA reaction. From these two different phenomena could be established: (i) poisoning of molybdenum active sites by aromatics and (ii) the acting of hydrogen as scavenger.

Experimental conditions 3wt. % Mo/HZSM-5 (Si/Al = 25) was prepared by traditional wetness incipient impregnation and further calcined under air at 500°C for 6 hours. Methane dehydroaromatization was performed at atmospheric pressure in a fixed-bed quartz reactor at 700 °C under continuous feeding with a (15/85) (v/v) N₂/CH₄ mixture. The gas hourly space velocity per gram of catalyst (M-GHSV) was subsequently adjusted from 1 to 29 LCH₄ h⁻¹ gcat⁻¹ (0.04s < τ < 2.04s). After 10 hours of reaction, the samples were recovered and deeply characterized by TGA-DTA, N₂-physisorption, Ir chemisorption of pyridine at 150°C, and Raman operando spectroscopy.

Results

Surprisingly, rather unexpected results were obtained. Indeed, the carbon amount deposited on the recovered catalyst was higher at low contact time. Monitoring CO₂ intensity signals with the help of mass spectra allowed us to distinguish two different cokes: - “soft” coke corresponding to the peak with lower oxidation temperature - “hard” coke referring to higher oxidation temperature. It appeared that the “soft” coke develops independently of the contact time while the “hard” is inversely related to it. These observations arouse our curiosity on the real nature of deactivation in the MDA process. Further advanced characterizations and products distribution analysis revealed the involvement of an organocatalytic intermediate called hydrocarbon pool. In addition, active sites inhibition by aromatics, which is attenuated in the presence of hydrogen, could be evidenced. To support our assumption theoretical modeling was performed. The adsorption energy of aromatics on molybdenum carbide was calculated (Figure1) confirming their strong interactions.

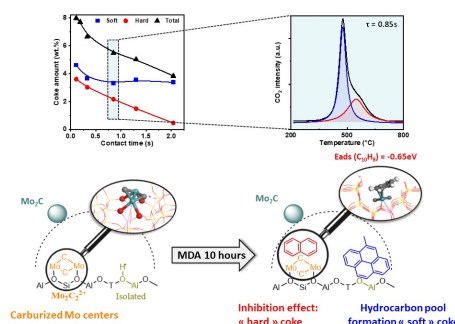


Figure 1: Coke content as function of contact time and TPO-CO₂ profile for one contact time: 0.85s and catalyst evolution after 10 hours of MDA

Conclusion

The strong aromatics inhibition effect of active species in MDA reaction is evidenced for the first time and give new approaches for preparing more stable catalysts crucial for developing a sustainable process

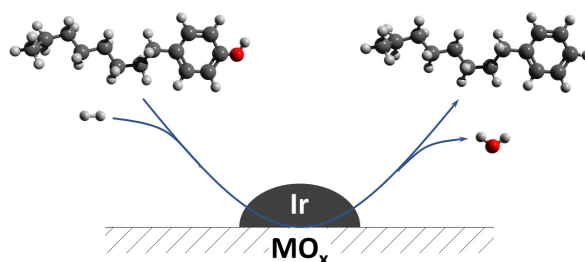
**Oral Communications 8 (OC8):
HDO - CO₂/CH₄**

Mechanism Investigation and Support Optimization for the Iridium-Catalyzed Hydrodeoxygenation of Phenols

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Lignin is a waste product of the pulp and paper industry, produced on a scale of tens of millions of tons annually. The hydrodeoxygenation (HDO) of lignin-derived phenols is an appealing source of renewable hydrocarbons, particularly aromatic hydrocarbons. Iridium supported on niobium oxide was recently established as a viable catalyst for this reaction under mild conditions. In this work, the mechanism and pathway of this reaction are investigated through in-situ sampling alongside GC-MS and NMR characterization. In light of those results, support optimization was performed, yielding iridium catalysts with greatly increased activity and selectivity for the HDO of model compounds.



Catalytic Hydrodeoxygenation of Benzyl Phenyl Ether as a Model Molecule for Lignin

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The bio-oil produced through fast pyrolysis of lignin is considered as a potential alternative source for the production of fuels and platform molecules. However, this bio-oil is chemically and thermally unstable, and its upgrading by hydrodeoxygenation (HDO), a reaction aiming at removing oxygenated chemical functions to produce hydrocarbons, is necessary. Surprisingly, the HDO of phenol-based aromatic ethers, such as benzyl phenyl ether $C_6H_5-CH_2-O-C_6H_5$ (BPE), has been less explored than that of phenol or anisole, even though these ethers stand as better model molecules for the linkages present in lignin. In this work, a series of 2 w.t.% Pd-based catalysts (see Table) were used to identify the most suitable system for the HDO of BPE. It will be shown that each catalyst transforms BPE following a specific network of reaction pathways.

The catalysts prepared by incipient wetness impregnation were characterized by ICP, XRD, N_2 physisorption, TEM and NH_3 desorption. The selection of results given here was obtained at 230 °C, 18 bar H_2 for 3 h, using decaline as solvent, in a Screening Pressure Reactor (Unchained Labs).

BPE was completely converted by all the tested Pd-based catalysts; the BPE conversion started with the hydrogenolysis of the Caliph-O

bond, producing phenol and toluene. Strong differences appeared in the subsequent steps, and the products distribution was affected by the choice of the catalyst. Pd/SiO₂ and Pd/Nb₂O₅, two catalysts presenting the same particle size (7 nm, TEM) performed the hydrogenation of the aromatic rings from the primary products, phenol and toluene, yielding cyclohexanone/cyclohexanol and methyl cyclohexane. Compared

with Pd/SiO₂, Pd/Nb₂O₅ allowed moving one step further, because the presence of acidic sites (170 μmol g⁻¹, NH_3 desorption) promoted the dehydration of cyclohexanol to a cyclohexene intermediate that led, on the one hand, to cyclohexane by hydrogenation, and, on the other hand, to oxygen-free 1,1-bicyclohexyl, through the acid-catalyzed alkylation of cyclohexene. In contrast, Pd/TiO₂ and Pd/Al₂O₃ did not hydrogenate toluene, and these catalysts rather provided deoxygenated and oxygenated dimers, in particular 2- and 4-benzylphenols. These molecules may originate from the acid-catalyzed electrophilic substitution of benzyl alcohol onto phenol, themselves produced by a parallel hydrolysis reaction of BPE. These two catalysts exhibit the same number of acidic sites as Pd/Nb₂O₅, but differ by their larger average particle size (9 and 24 nm, respectively). Likewise, Pd/ZrO₂ and Pd/HZSM5 mostly promoted the formation of oxygenated alkylated products, in line with their high number of acidic sites (251 and 700 μmol g⁻¹, respectively) and large particle size.

In conclusion, Pd/Nb₂O₅ was the only catalyst that performed a deep deoxygenation of BPE, yielding a mixture of monomeric and dimeric cycloalkanes. It can be inferred that, in order to complete the hydrogenation of toluene and avoid the formation of oxygen-containing dimers, the HDO of phenol-based aromatic ethers requires a catalyst that exhibits both small metal particles and moderate acidity.

Catalyst	X_{BPE} (%)	CB (%)	Yield (%)							Akyl. Deoxyg.	Akyl. Oxyg.
			(ANE)	(MCH)	(TOL)	(BENZ)	(OL)	(ONE)	(PHOL)		
Pd/SiO ₂	100	54	4	21	6	-	11	8	-	-	3
Pd/Nb ₂ O ₅	100	67	18	35	-	-	-	-	-	12	-
Pd/TiO ₂	100	68	7	1	37	-	-	-	1	13	7
Pd/Al ₂ O ₃	100	65	6	1	22	-	-	-	9	-	28
Pd/ZrO ₂	100	56	4	1	2	-	-	1	3	2	41
Pd/HZSM5	100	84	2	1	2	1	-	-	6	-	72

Figure 1: Conversion of benzyl phenyl ether (X_{BPE}), carbon balance (CB) and yield of products on palladium-based catalysts in decaline

Hydrotreatment of HTL Micro-Algal Bio-Oil Over Sulfide, Nitride, and Phosphide Catalysts

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Microalgae is a potential raw material for third-generation fuel production due to their high growth rate, the potential for CO₂ fixation, and high lipids content which can provide a high biofuel yield. Hydrothermal liquefaction (HTL) is a thermochemical process that has been used for the conversion of microalgae in bio-oil. However, the HTL micro-algal bio-oil contains a high amount of heteroatoms such as N, O, and sometimes S which causes harmful emissions upon combustion and also reduced the quality of the fuel. Therefore, an upgrading step is required before the commercialization of biofuel to reach transportation fuel specifications. Being part of the Rafbioalg project (ANR-18-CE43-0009) that explores the production of biofuel from algae growth until fuel combustion with an LCA analysis of the all value chain, we investigated the catalytic upgrading step of the HTL algal oils. The whole algae, *Chlorella Sorokiniana* grew at CEA Cadarache, was converted to a bio-oil using a continuous reactor at 300 °C, under 10 MPa for 15 min at Liten laboratory in CEA Grenoble. The bio-oil was upgraded using a batch reactor at 375 °C under 10 MPa (H₂), over NiWS/Al₂O₃, NiMoN, and Ni₂P/Al₂O₃. The nitride and phosphide catalysts were prepared using a methodology described in the literature. The produced HTL and HDT oils were characterized by CHONS, XRF, ICP-OES, GPC-RID/DAD, ¹³C-NMR, SIMDIS, and GCxGC-MS/FID. The hydroconversion experiments performed with nickel phosphide showed the same conversion as an experiment without catalyst, indicating that, even though Ni phosphides have been reported in the literature as a good candidate to replace sulfide catalysts, this active phase is not efficient for algal oil. However, the W sulfide and Mo nitride catalysts were permitted to reduce O, N, and S content and thus improved the quality of bio-oil. The main compounds formed after the upgrading step were C15, C16, C17, and C18 from carboxylic acids hydrogenation (HDO) or decarboxylation/decarbonylation (DCO). More than 60 wt% of upgraded bio-oil eluted on the diesel range, which corroborates the potential of microalgae as a feedstock for biofuel production. The degree of deoxygenation and denitrogenation were, respectively, 91% and 67% for sulfide catalyst, 93% and 46% for nitride catalyst, and 84% and 6% for phosphide. Therefore, NiWS/Al₂O₃ had a higher hydrodenitrogenation (HDN) ability than NiMoN and Ni₂P/Al₂O₃ catalysts. GCxGC-MS/FID analysis revealed that fatty amides were first converted into nitriles and then in alkanes. The experiments performed over Ni₂P/Al₂O₃ and without catalyst showed a family of nitriles that are completely converted with nitride and sulfide systems. Besides, it was also observed that NiWS/Al₂O₃ converted more cyclic nitrogen compounds, such as, pyrroles, indoles, and carbazoles than NiMoN which is associated with a higher hydrogenation ability of this catalyst, since these nitrogen molecules should be hydrogenated before the HDN reaction. The HHV increased from 36 MJ/kg in the HTL micro-algal bio-oil to 47 MJ/kg in the upgraded bio-oil over sulfide catalyst, and the average molar mass reduced from 363 to 265 g/mol indicating that heavy molecules were converted during the upgrading step.

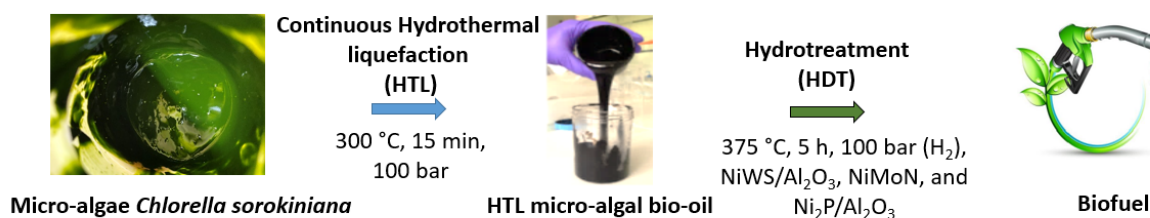


Figure 1: Hydroconversion of HTL micro-algal bio-oil over different catalysts

Operando Investigation of Ni Exsolution from LaNiO₃ Perovskites for Improved CO₂ Methanation Catalysts

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Among the most viable strategies to produce value added chemicals from CO₂, Sabatier's reaction (CO₂ + 4H₂ → CH₄ + 2H₂O) is gaining increasing interest. Ni-based catalysts are mostly envisaged for the reaction owing to their affordable price, but suffer from low activity at low temperature and fast deactivation. Consequently, an amelioration of the catalyst formulation is needed to envisage industrialization of this process. While poorly studied, Ni/La₂O₃ catalysts were found to be promising for methanation owing to Ni nanoparticles stabilization by La₂O₃ thus limiting sintering. Moreover, the presence of La₂O₃ has been shown to prevent coke deposition on nickel through La₂O₂CO₃ generation during reaction. However, lanthanum-supported catalysts still suffer from poor activity as compared to ceria-based materials and need further improvement. In this work we present the use of LaNiO₃ to produce highly active and stable Ni/LaO_x catalysts through exsolution processes under reductive conditions. A novelty of this work is the use of a hard template (SBA-15) to prepare high-surface perovskites prior to Ni exsolution with the goal to obtain better dispersed particles on the finite material. We first compared the catalytic performances of "classical" LaNiO₃ prepared through citrate method (b-LNR) with its mesoporous counterpart prepared in SBA-15 (m-LNR) after pretreatment under H₂ at 400, 500 and 600 °C. While the bulk material is composed of large particles before pretreatment (~200 μm, Figure 1a), the mesoporous material exhibits smaller particles with important porosity after removal of the hard template (Figure 1b, S_{BET} = 55 m².g⁻¹).

The activity tests indicate that both the perovskite parent and the temperature affect the final methanation activity. By passing from a classical sample (b-LNR-400) to its bulk counterpart reduced at 600 °C, the temperature of half-conversion (T₅₀) was lowered by 60 °C (Figure 1c) with a high CH₄ selectivity (>99%). XRD measurements highlighted smaller Ni⁰ crystallites for the m-LNR (~8 nm) than for the b-LNR catalysts (12-16 nm). Complementary *ex situ* XPS measurements allowed the Ni and La quantification over the surface of the reduced samples. A linear correlation between the corresponding Ni/La ratios (Figure 1c) and the T₅₀ was observed which points that the differences in activity observed between the materials might be linked to the number of accessible Ni sites over this type of material. Synchrotron-based depth-dependent NAP-XPS measurements of the bulk sample (TEMPO beamline, SOLEIL) confirmed Ni surface exsolution and revealed the relation between the pretreatment temperature and the amount of surface Ni (Figure 1d). Long-term stability tests show that m-LNR-600 is not only the most performant but also the most stable, with a decrease of 10% after 65h against 20 and 43% for b-LNR-600 and a conventional material prepared by wet impregnation (25%wt.Ni/La₂O₃), respectively. Recent *operando* NAP-XPS study conducted over the mesoporous material at the BESSY synchrotron facility showed successive surface segregation of Ni under CO₂/H₂ media and re-encapsulation under H₂ by lanthanum species, highlighting specific metal-support interaction that may be the reason for its high stability.

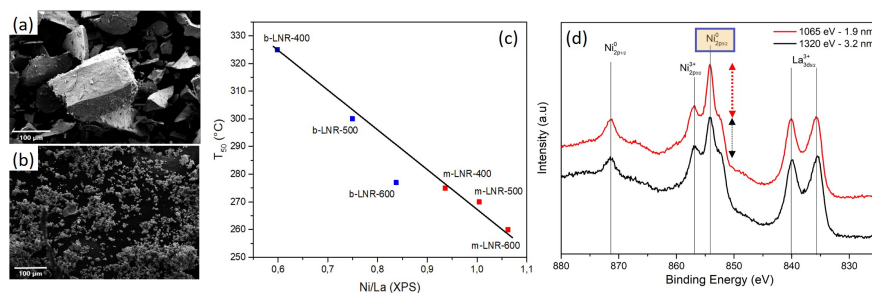


Figure 1. SEM images of fresh (a) classical and (b) mesoporous LaNiO₃. (c) Temperatures of half-conversion (T₅₀) as a function of the Ni/La atomic ratio (from Ni 3p and La 4p quantification in XPS) for reduced b-LNR and m-LNR samples during CO₂ methanation after reduction at 400, 500 and 600 °C (fix bed reactor, 100 mg of catalyst mixed in 100 mg of SiC, 20%CO₂ and 80%H₂, 1bar, Total flow: 2.5 L.h⁻¹.g_{catal}⁻¹). (d) Depth-dependent NAP-XPS measurements in 2 mbar H₂ after pretreatment at 600 °C, Ni 2p and La 3d spectra recorded at 1065 and 1320 eV.

Metal-Organic Framework as a Template to Form Co Nanoparticles in Porous Carbon Matrix for CO₂ Methanation

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CO₂ emission represents serious environmental issues since it is one of the greenhouse gases leading to climate change [1, 2]. Hydrogenation of CO₂ captured at point sources, towards methane, is considered an effective way to reduce net CO₂ emissions [3]. In this regard, several metal oxides-supported metals have been implemented. While noble metal-based catalysts are very active for this reaction at low temperatures, their high cost and limited availability led to a shift in the focus towards non-noble metals such as Ni and Co [4, 5].

In the field of heterogeneous catalysts, the number of organic reactions in which metal-organic frameworks (MOFs) and MOFs-derived materials have been employed is rocketing. MOFs-derived carbon (obtained by thermal treatments under inert atmosphere) have attracted significant attention because this strategy gives access to highly dispersed metal nanoparticles in a porous carbon matrix with high stability at high temperatures. Interestingly, MOFs-derived carbon has found their merits in CO₂ methanation reaction as well [6, 7].

Here, we disclose carbon-based Co catalyst obtained by the controlled thermal decomposition of 2D MOF: Co-ZIF-L. The latter is compared to the more conventional ZIF-67, which was already studied for CO₂ methanation[7]. Here, Co(NO₃)₂ and 2-methylimidazol are applied to synthesize the MOFs via ultrasonication (Co-ZIF-L) and at room temperature (ZIF-67). The resultant powders after drying, are carbonized at 800°C under Ar to form Co nanoparticles dispersed in porous carbon (CoNP-C). CO₂ methanation is performed in a fixed bed flow reactor with 100 mg of the catalyst while the molar ratio H₂/CO₂= 4/1, the GHSV=24000 ml/gcat.s and P=0.1MPa . Importantly, with this catalyst, the reduction step with hydrogen is skipped since CoNP are formed during the carbonization. Interestingly, at 400°C Co-ZIF-L-derived CoNP-C (C-Co-1) reaches CO₂ conversion as high as 62% with 53% selectivity towards methane. By comparison, ZIF-67-derived CoNP-C (C-Co-2) demonstrates 49% CO₂ conversion with 35% methane selectivity (Fig.1). We surmise that much higher performance exhibited by catalyst C-Co-1 is assigned the basic sites.

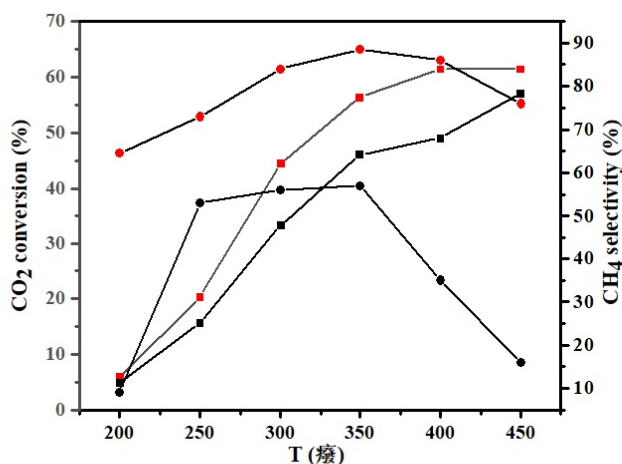


Figure 1: Fig. 1. Square=CO₂ conversion, Circle= CH₄ selectivity. Red= results for C-Co-1 catalyst and Black= results for C-Co-2 catalyst.

Coupling Plasma and Catalysis: Influence of Metal Oxides Properties for CH₄ and CO₂ Transformation

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The dry reforming of methane has been largely studied under non-thermal plasma discharge (NTP) and the coupling of plasma with catalyst was proposed to overcome the poor selectivity obtained with plasma only [1]. It is admitted that combining plasma and catalysis requires the development of specific materials able to interact with active species generated in gaseous phase under NTP.

In the present study a series of oxides possessing different physical and chemical properties were used: dielectric constant (from 2.8 to 2903), surface area (from < 1 to 312 m² g⁻¹) and different number of acid and basic sites.

The reaction was investigated at atmospheric pressure and at room temperature in a coaxial dielectric barrier discharges (DBD) reactor. The total flow rate was 40 mL/min with a ratio CO₂/CH₄ = 2 and a constant concentration in He: 75%, the corresponding contact time was equal to 1.6 s. The discharge power was fixed at 8 watts (sinusoidal power supply, 800 Hz, 13.5 kV). The oxides used in this study were commercial powders for CaO, MgO, BaO, TiO₂, La₂O₃, ZnO, SiO₂, CeO₂, Al₂O₃. Mesoporous alumina (surface area from 260 to 312 m².g⁻¹) were also prepared in the laboratory. All the materials were sieved before experiments in the range: 355- 650 μm.

The best performances in terms of methane and CO₂ conversion are obtained for oxides possessing low dielectric constant such as γ-Al₂O₃, MgO and CaO while a very low CH₄ and CO₂ conversion is observed with TiO₂. It is proposed that a high localized electric field is created at the junction of oxide grains with oxides possessing a high dielectric constant. Consequently, the efficient volume of discharge is reduced and the reactants transformation is limited. Besides Al₂O₃ materials, the highest conversions are reached with a commercial γ-alumina, possessing a surface area of only 65 m² g⁻¹ but exhibiting a higher amount of acid and basic sites compared to the mesoporous materials with higher surface area. Methane conversion reaches 31.3% for γ-Al₂O₃ against 23.4, 22.6 and 25.4% for alumina with surface area of 312, 301 and 260 m² g⁻¹ respectively. It is suggested that the active sites localized into the mesoporosity of alumina are not accessible to CH₄ and CO₂ under NTP. A correlation between the number of acid and basic sites of alumina has been shown [2]. This study confirmed experimentally that the coupling of plasma with catalyst depends strongly on the nature of surface active species (presence of OH) but in a lower extend to the amount of active sites as soon as there are located in small pores. A possible reaction pathway for CH₄ and CO₂ transformation at the surface of Al₂O₃ is proposed. A deep discussion on selectivity to products (CO, hydrocarbons, oxygenates...) will be performed. Moreover, structural modifications of oxides, such as CaO under plasma discharge will be shown and a mechanism of carbonation will be proposed.

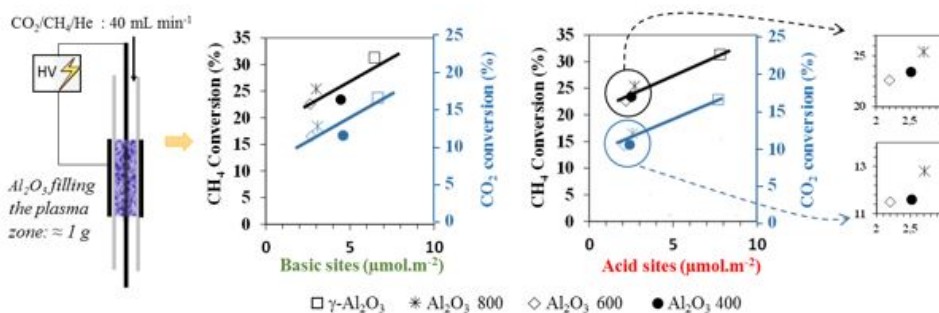


Figure 1: Effect of acid and basic sites under non-thermal plasma

[1] Neyts, E.C. et al. Chem. Rev. 115, 13408 (2015)

[2] Bouchoul, N. et al. Appl. Catal. B : Env. 298, 120262 (2021)

**Oral Communications 9 (OC9):
Bifunctional and acid-base catalysis**

On the Intimacy of Bifunctional Catalysts for the Conversion of Syngas to Light Olefins

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Context and objectives

Light olefins (C₂–C₄) are key building-block chemicals mostly produced either by steam cracking or fluid catalytic cracking of oil resources, two highly energy-consuming processes. Among alternative processes, the syngas via methanol to olefins (SMTO) and the OX-ZEO single step processes are very promising since very high selectivity to light olefins can be reached. They combine one hydrogenating catalyst to synthesize either methanol or ketene and one acidic zeotype to convert the intermediate into light olefins. In both cases, the intermediate has to diffuse from the first catalyst to the other and their intimacy can significantly influence the catalytic performances.

In this work, Cu/ZnO/Al₂O₃ or MnO_x was used as hydrogenating catalyst and SAPO-34 as acidic zeotype. The role of intimacy has been investigated by modulating the density of contact between the two functions in different bed arrangements and the distance through preparing MnO_x@SiO₂ core shell structures or diluting the two catalysts in SiO₂.

Material and methods

Cu/ZnO/Al₂O₃ was commercial catalyst while MnO_x and MnO_x@SiO₂ were prepared from MnCO₃ powder or monodispersed suspension by different routes. SAPO-34 powders with different acidities were prepared by hydrothermal method. The catalysts were characterized before and after reaction by various techniques, including ICP/XRF, BET, H₂ and CO-TPR, NH₃-TPD, XRD, SEM, STEM-HAADF, NMR as well as by in situ DRIFT and Raman spectroscopies. Catalytic performances were compared using a fixed-bed reactor with a feed H₂/CO/N₂:62/23/15 at 390–450 °C and 25 bar.

Main results

For both catalytic systems, methanol was shown to be a key intermediate from catalytic data and from the in situ DRIFT observation and evolutions of formates (Fig. 1a) which are formed before methoxy species. The two catalytic systems were active and selective (>50%) to C₂-C₄ hydrocarbons with a low Olefin/Paraffin (O/P) ratio (<0.3) when using Cu/ZnO/Al₂O₃ and high (up to 8) using MnO_x with SAPO-34. Different parameters such as the pre-treatment temperature, the SAPO-34 acidity and the conversion were shown to strongly influence this ratio. After optimizing the mass balance for the two systems, it was shown that the conversion raised increasing the number of catalytic bed layers and hence the density of contact. It was further increased for random mechanical mixtures but only without milling. On the contrary, the disappearance of contact depositing even a thin shell of SiO₂ over MnO_x cores or strongly diluting MnO_x into SiO₂ led to a drop of conversion associated with a strong increase in CH₄ selectivity. Crossing NH₃-TPD and SEM images, the conversion was shown to depend on the surface interaction between Cu/ZnO/Al₂O₃ and SAPO-34 generating particular active sites. For MnO_x+SAPO-34, a strong morphological modification under feed was evidenced by SEM (Fig1b and c) revealing intimacy was in situ generated. Attempts to strengthen this intimacy was unsuccessful.

Major conclusions

This work evidenced the key role of intimacy of bifunctional catalysts for the conversion of syngas to light olefins. For both Cu/ZnO/Al₂O₃ and MnO_x catalysts associated with SAPO-34, the conversion was maximal for simple mechanical mixtures. It arises from two totally different phenomena.

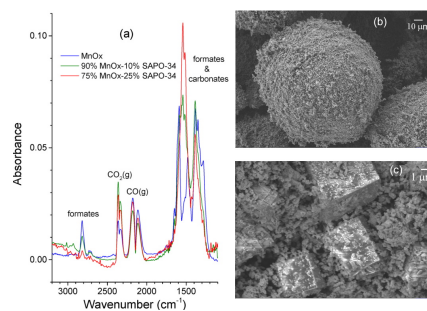


Figure 1 : (a) In situ DRIFT spectra of MnO_x, 90%MnO_x-10%SAPO-34 and 75%MnO_x-25%SAPO-34 samples recorded at 410 °C under 20 mL.min⁻¹ of 2.5%CO/7.5%H₂/90%He flow, (b) SEM image of MnO_x before reaction and (c) SEM image of 80%MnO_x-20%SAPO-34 after

Insights on Acid and Metallic Site Proximity in Pt/ γ -Al₂O₃-Cl Bifunctional Catalysts

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Highly dispersed platinum supported on γ -alumina doped with chlorine is widely used as a bifunctional catalyst for catalytic naphtha reforming, combining hydro/dehydrogenation metallic function and isomerization acid function (Brønsted acidity enhanced by Cl). For such catalytic systems, an “intimacy criterion” indicates the maximum diffusion time, correlated with a distance allowed between the two types of sites so that inter-site diffusion is not a limiting step [1]. This work focuses on the evaluation of this key distance between metallic and acidic sites by building an atomic scale geometric model of the catalytic system fed by NMR, HR-HAADF-STEM and DFT data obtained in our previous works identifying the precise locations of Pt nanoparticles (NPs) and of Cl atoms on the γ -alumina crystallites [2, 3].

A series of catalysts with varying wt%Pt (0.3 to 1%), wt%Cl (0.1 to 1.4%) and varying support crystallite size and morphology was thoroughly characterized at the atomic level. We have demonstrated that Cl is preferably located on the edges of alumina crystallites [2] and an advanced electron tomography study revealed a great majority ($\approx 80\%$) of Pt NPs to be located on the edges of the support's crystallites [3].

With these atomic scale insights on active site location, a geometric model of the Pt/ γ -Al₂O₃-Cl catalyst was built to estimate the distance between metallic and acidic sites [4]. The model enables the impact of three key physico-chemical parameters on inter-site distance to be assessed: 1) the chlorine loading, 2) the morphology of the alumina platelet, and 3) the platelet size (specific areas from 150 up to 450 m²/g).

The estimated inter-site distance ranges from about 1 nm to over 6 nm (Figure 1). Inter-site distance decreases with increasing chlorine loading. Platelet morphology has two impacts: on the one hand, larger facets (T-flat) lead to larger inter-site distances, on the other hand a higher edge to surface ratio (P-egg) results in a higher chlorine loading at which edge sites are saturated with Cl. However, the impact of support morphology on inter-site distance is revealed only for chlorine contents smaller or equal to edge saturation.

We finally show how this geometrical model may provide guides to better quantify how the nature and location of active sites and their proximity in naphtha reforming catalysts as a function of experimental parameters. This work is the first step towards a catalyst improvement route based on tuning of active site location.

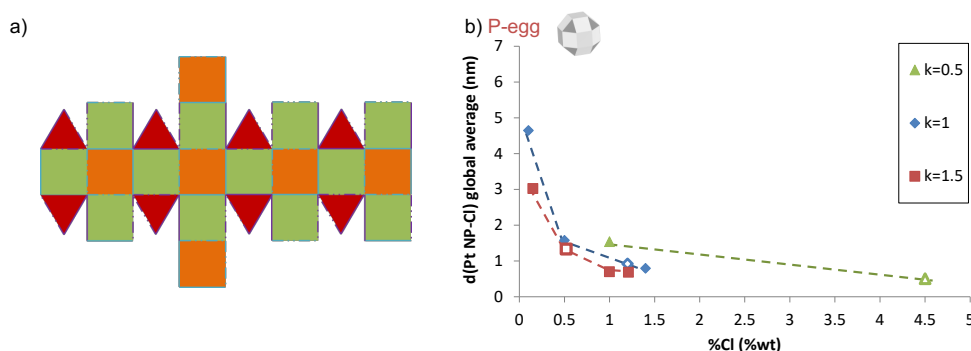


Figure 1: a) Polyhedral net for P-egg crystallite morphology used in the geometric model; b) Inter-site distance (global average) for platelet morphology P-egg in function of chlorine loading (%Cl) for three size factors k . The points corresponding to edge

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Bifunctional Metal/Acid Zeolites with Hierarchical Porosity as Catalyst in Synthesis of Alkyl-Branched Fatty Acid Methyl Esters

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Interest in valorization of lipid biomass as replacement of fossil oil supply has been increasing in the last years. Taking that into account, the interest on the use of acid porous materials for the valorization of lipid biomass increases too. Among different ways to transform lipid biomass in high added value products, synthesis of alkyl-branched fatty acid methyl esters [1] through isomerization/hydroisomerization reactions has been studied. These reactions have been widely studied on saturated long-chain hydrocarbon moieties to get branched molecules with improved properties using bifunctional metal-acid catalysts [2]. Although high yields (>80%) have already been obtained in the isomerization reaction of unsaturated fatty acids [3], the difficulty remains in obtaining similar yields for the hydroisomerization reaction on the saturated fatty acid chains [4].

In this work, the use of metal/acid zeolitic catalytic materials with hierarchical porosity is proposed in the isomerization of unsaturated fatty acid methyl esters and hydroisomerization reaction of saturated ones.

Properties of bifunctional recrystallized zeolites show that a new mesopore systems have been created in Ferrierite and zeolite Y (see figure 1) by recrystallization procedures. In both isomerization and hydroisomerization reactions, the added mesoporosity improves the diffusion of methyl esters to the zeolitic acid sites, leading to higher conversion values as well as slower deactivation compared to non-hierarchized porous materials. Although higher selectivities to alkyl branched products in isomerization of methyl oleate was obtained using recrystallized materials, a lower selectivity to branched products as well as higher amounts of undesired products was obtained in hydroisomerization of methyl palmitate. All these results will be discussed during the conference.

The use of bifunctional metal/acid zeolites with hierarchical porosity as catalysts in the synthesis of alkyl-branched fatty acid methyl esters through isomerization/hydroisomerization reactions can represent a way to improve the profits from lipid biomass with high levels of saturated fatty acids, which have lower market prices.

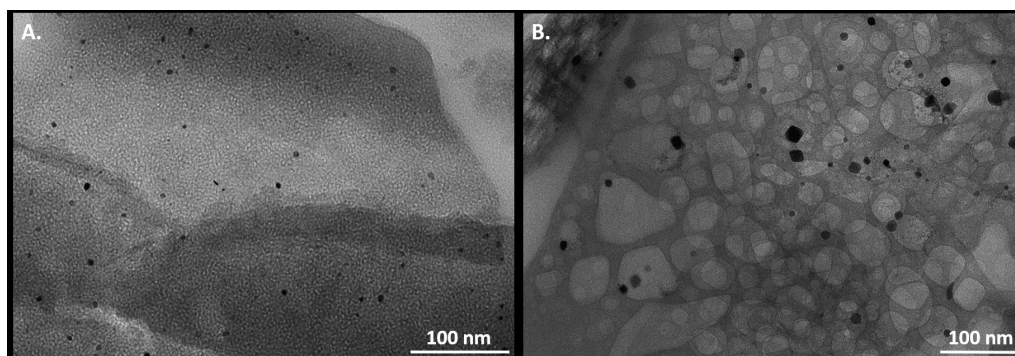


Figure 1: TEM images of hierarchized zeolite Y (a) and hierarchized ferrierite (b) samples impregnated with platinum

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Nanometric Metal Oxo/Hydroxo Fluoride Catalysts Prepared by Anion Exchange Method for Dihydroxyacetone Conversion in Aqueous Phase

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Metallic oxo/hydroxo fluoride based heterogeneous catalysts were prepared by anionic exchange between commercial supports $\text{MO}_x(\text{OH})_y$, where $\text{M} = \text{Ti, Zr or Nb}$, with trifluoroacetic acid (TFAH) as a fluoride precursor. The water tolerance of the acid and basic sites of these catalysts calcined at 300°C and 400°C were studied by a model reaction in aqueous phase i.e., dihydroxyacetone (DHA) conversion. It was found that the conversion of DHA reached 98% for the $\text{NbO}_x(\text{OH})_y$ catalyst after 5h of reaction and that the exchange with TFAH had little effect on the DHA conversion and on the selectivity in LA (catalysed by Lewis acid sites) and PA (catalysed by both Lewis and Bronsted acid sites). This is consistent with the TGA, FTIR and ^{19}F MAS-NMR analyses which evidenced that the Nb support retained a low amount of F species. For the Ti and Zr supports which entrapped higher amounts of F species, in particular the Zr support, however, this led to an overall decrease of the catalysts' reactivity in water irrespective of the calcination temperature. Moreover, in the case of $\text{TiO}_x(\text{OH})_y$, the exchange with TFAH decreases both the selectivity in PA and LA, independent of the calcination temperature. In the case of $\text{ZrO}_x(\text{OH})_y$, which retains the highest amount of F species, the exchange with TFAH increased only the selectivity in PA. These results are consistent with the formation of Bronsted acid sites as shown by the FTIR studies of Pyridine adsorption. The two previous catalysts also showed water tolerant basic sites yielding C6 sugars formed via aldolic condensation of the C3 substrat (DHA and its isomers, glyceraldehyde).

New results will be presented with regards to the characterization of the acid-base properties established with usual techniques in gas phase such as probe molecules adsorption (pyridine, CO_2 , NH_3) monitored by FT-IR and calorimetry to study the original acid and basic properties in terms of nature, number and strenght in absence of moisture.

Magnesium Hydroxide Fluorides: A New Family of Heterogeneous Acid-Base Catalysts for Aldol Condensation

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The development of new generation of catalysts is a very important topic because of the implementation of new catalytic processes due to the treatment of diversified feedstocks. Lignocellulosic biomass can be valorized in biorefinery through different routes including aldol condensation. Furfural is considered as a very promising biomass-derived platform molecule, especially because such molecule can lead to the synthesis of new types of biofuels. The condensation of furfural and acetone leads to products containing either 8 (FAcOH and FAc) or 13 carbon atoms (F₂Ac) as shown in Fig. 1a. Fluorine magnesium hydroxides were prepared by sol gel method and exhibited very high specific surface areas and interesting catalytic properties without using activation step. Indeed, this high energy consuming step is often required to activate basic sites of these catalysts by removing of the (hydrogen) carbonate species formed previously by reaction with atmospheric carbon dioxide.

The aim of the present study is to evaluate the effect of the presence of fluorine in magnesium hydroxide on activity, selectivity and stability for the aldol condensation between furfural and acetone. Thus, a series of MgF_{2-x}OH_x catalysts were prepared. Interestingly, the presence of fluorine allowed to increase the specific surface area in hydroxide fluorides, equal to 600, 380 and 280 m² g⁻¹ for MgFOH, Mg(OH)₂ and MgF₂ respectively. On the other hand, ¹⁹F NMR investigation allowed to evidence three distinct F local environment whose proportions gradually vary with OH content (Fig. 1b). The local environments of three Mg²⁺ cations in the vicinity of F⁻ anions are affected by the occurrence of hydroxyls as first neighbors which are at the origin of the basic character of such catalysts. Moreover, the conversion of furfural is favored in presence of magnesium hydroxyfluoride catalysts compared to magnesium hydroxide (Fig. 1c). This result can be explained by the presence of dual acid-base active site, as highlighted by adsorption of CO (acid site) and CO₂ (basic site) followed by IR. Obviously, such sites are not formed in Mg(OH)₂, this catalyst having only basic sites with high strength that react with CO₂ of air just after synthesis, explaining the lower activity of this catalyst. In addition, MgF₂ was inactive due to the absence of basic sites. The selectivity of catalysts can be estimate by the C13/C8 ratio which is the ratio between the quantity of F₂Ac (target molecule for biokerosene synthesis) and those of FAcOH and FAc (molecules having 8 C atoms). As expected, irrespective the catalysts, this ratio increased with the conversion of furfural since F₂Ac was obtained from consecutive reactions (Fig 1a), its value being higher than 1 for conversion greater than 25%. Moreover, the presence of fluorine clearly favored the stability of the active phase. Indeed, when both synthesized solid samples were left in the open air during 56 days, the conversion of furfural dropped by 25% over MgF_{1.5}OH_{0.5} and about 70% over Mg(OH)₂. This change can be explained by thermal analyses which highlight an important water uptake on Mg(OH)₂ compared to MgF_{1.5}OH_{0.5} leading to a partial deactivation.

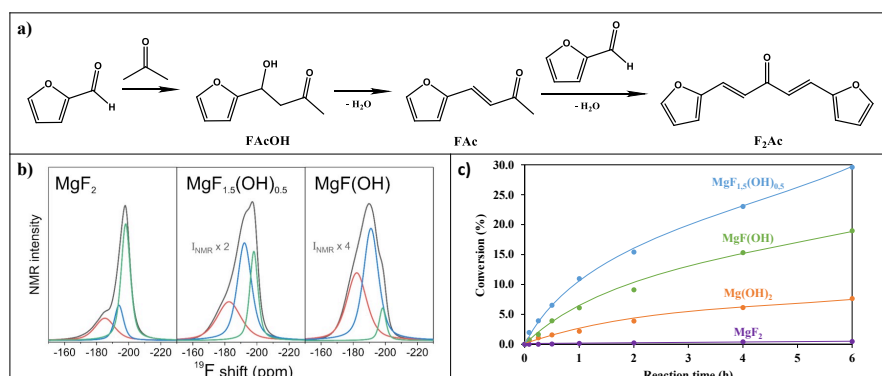


Figure 1: (a): reaction scheme of aldol condensation of furfural by acetone; (b): ¹⁹F NMR spectra of various magnesium hydroxyfluoride samples; (c): Influence of reaction time on the conversion of furfural by aldol condensation over magnesium hydroxide, magnesium hydroxide fluoride and magnesium fluoride catalysts.

**Oral Communications 10 (OC10):
Depollution**

Adsorption - Oxidation Process (Ad-Ox) for Bisphenol a Removal from Polluted Water Using Green Activated Carbon and Pd-Doped Transition-Metal Catalysts

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Extensive use of Bisphenol A (BPA) in packaging has increased its concentration in water beyond health standards while it is associated with cardiovascular diseases and diabetes and has been evidenced as an endocrine disruptor. To definitively remove BPA from water, a hybrid Adsorption - Oxidation process (AD-OX) was developed. The adsorption step was achieved using a green activated carbon prepared from agricultural waste i.e. olive kernels (OK). By concentrating the pollutant on the adsorbent, catalytic wet oxidation (CWO) becomes a cost-effective process, especially if the catalyst used is based on transition metals. Our research work aimed to (i) optimize the preparation of an efficient bio-sourced adsorbent, (ii) study its BPA adsorption performance and (iii) explore the BPA desorption in aqueous solution while CWO is simultaneously performed using an optimized heterogeneous catalyst.

Our first and second objectives were achieved by preparing an activated carbon ($1472 \text{ m}^2 \cdot \text{g}^{-1}$) capable of removing 92% of Bisphenol A at an initial concentration of 20 mg/L in wastewater. The preparation was optimized by controlling parameters such as the activating agent (AA) nature, mass

ratio (AA: OK) and activation temperature. Our bio-sourced sorbent reached a BPA adsorption capacity equal to 464 mg/g according to Langmuir model, which is higher than those reported for most carbon adsorbents. Concerning CWO, our results evidenced that the BPA desorption from activated carbon and simultaneous oxidation can be achieved using a 0.44 L batch reactor loaded with 160 mL of aqueous solution, 0.3 g of catalysts and 0.25 g of activated carbon containing 116 mg of BPA at 25 bars of oxygen and 140 °C. Water samples collected over time and analyzed by HPLC pointed out that a 90% conversion rate is reached after 1 h using a first series of heterogeneous catalysts containing 10 wt. % $\text{MO}_x\text{-Al}_2\text{O}_3$ (M = Cu, Ce, Mn, Mg, W) prepared by sol-gel technique. Unfortunately, the total organic carbon abatement was lower than expected, with a range of 25 - 40%. Thus, a second series of catalysts was prepared by introducing a very small Pd amount, i.e. 0.1 wt. %. To ensure a strong interaction with the transition metal, Pd was added by surface redox method except for $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst, which was prepared by wet impregnation method. This second series of Pd- $\text{MO}_x/\text{Al}_2\text{O}_3$ catalysts was tested in CWO of BPA. The most active and stable catalyst was PdCuO/ Al_2O_3 , as a total conversion of BPA was reached in the first 10 min with a significant increase in TOC abatement up to 75 % after 3 h (Fig 1). Moreover, the interaction between Pd and the transition metal oxides avoids metal leaching. This improvement was explained by an alloy formation evidenced by TEM-EDS. A LC-MS study revealed that the degradation mechanism is quite similar regardless of the catalyst. However, the Pd addition increases the reaction rate constant, leading to drastic reduction of end-of-reaction products.

Thus, the proposed AD-OX system enables the BPA removal from water and its successful catalytic oxidation using a low-cost and energy-efficient process.

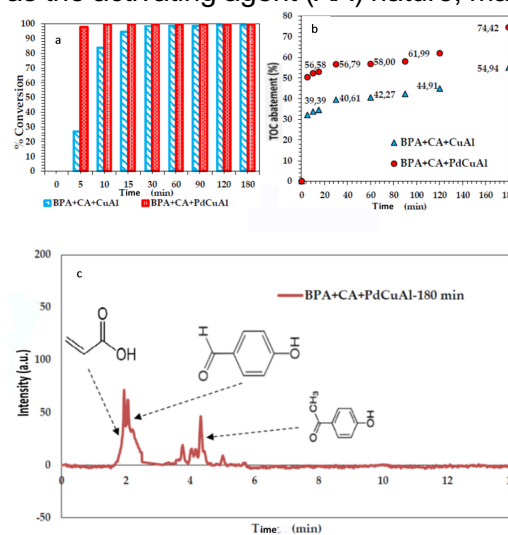


Figure 1: Conversion rate of BPA (a) and total organic carbon abatement (b) using CuAl or PdCuAl catalysts. Degradation products of BPA after 3H by using PdCuAl oxidation catalyst, the molecules structures were identified by LC-MS analyses (c).

Direct Valorization of Recycled Precious Metals as Heterogeneous Catalysts for Toluene Total Oxidation

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With the development of a modern economy based on an optimal use of natural resources, and thus on recycling, this research project addresses an innovative aspect of the development of short economic circuits. We are studying the direct use in heterogeneous catalysis of precious metals recovered from electrical and electronic equipment waste (WEEE), for the elimination of volatile organic compounds (VOCs). Latter are recognized as major contributors to air pollution, either through their toxicity and/or as precursors of ozone and photochemical smog. This concept has already been developed in our group in the field of homogeneous catalysis with Suzuki-Miyaura cross coupling reactions. The recycling of metals from WEEE through hydrometallurgical processes represents an attractive way to manage the increasingly low abundance of precious metals. However, the exploitation of e-waste remains limited, mainly because of the high variability and the high complexity of the waste flows. In parallel, the demand for precious metals for chemical applications is increasing, due to their performance in catalysis, both homogeneous and heterogeneous. While existing hydrometallurgical processes allow the ultimate purification of precious metals, the main challenge of this project is to prepare oxide supported precious metals catalysts with a minimum of purification steps, leading to multi-metallic catalysts. Many studies have revealed the high catalytic performance of supported precious metals (Au, Pd, Pt, etc.) on oxide supports in a wide range of oxidation reactions. Bimetallic Au-Pd based catalysts and monometallic Pd catalysts with or without impurities (Cu, Ag) supported on various oxide (CeO_2 , TiO_2 , Al_2O_3) have been prepared, characterized (TEM, H_2 TPR, TPD, ATG-MS, phys- N_2) and evaluated for the total oxidation of toluene, as a model reaction.

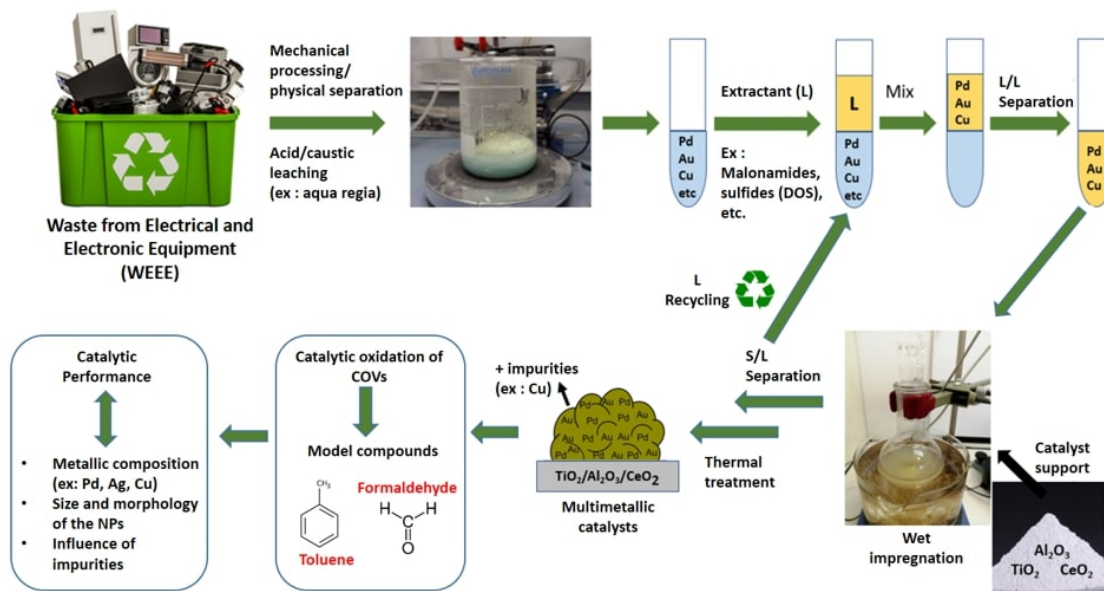


Figure 1: Overall strategy for the direct valorization of precious metals from WEEE as heterogeneous catalysts

Total Oxidation of Toluene on Cu/Al₂O₃ Catalyst Prepared by Dielectric Barrier Discharge Plasma

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1. Introduction

The development of transition metal catalysts is a major challenge for total oxidation catalysis of Volatile Organic Compounds (VOCs) because the use of noble metals (very active components) in the catalyst composition is limited by their scarcity and cost. For their preparation, whether the catalysts are bulk or supported, a thermal treatment is generally employed to decompose the transition metal precursors which leads to aggregation of metal transition oxide particles, reducing the efficiency of the catalyst. Our present work explores the non-thermal plasma technique for the decomposition of impregnated-dried copper nitrate on alumina pellets as an alternative method for the preparation of an efficient CuO/Al₂O₃ catalyst for the removal of toluene from industrial off-gases.

2. Experimental

CuO/Al₂O₃ materials with 10 wt% of copper loading were prepared by wet impregnation in deionized water, using Cu(NO₃)₂ · 3H₂O as copper source and Al₂O₃ pellets as support. After impregnation and evaporation of water, the sample was dried in an oven at 80°C overnight. The sample (~ 2g) was treated in a DBD reactor whose description was previously reported elsewhere. The duration time was allowed to vary between 15 min to 90 min and the delivered power from 6 to 50 W in dry flowing air (0.1 L·min⁻¹). For comparison purposes one part of the dried impregnated pellets were also calcined at 450°C for 5h in a muffle furnace under static air. The catalytic performances of the plasma treated or calcined catalysts as fine powder placed in a fixed bed reactor were evaluated for total oxidation of toluene. The catalysts were activated under flowing air at 200°C for 1h (5°C/min ramp) before to be submitted to the reactive gas mixture comprising 1000 ppm of toluene in 100 mL/min of air. The toluene conversion into CO₂ was assessed for 2h at that temperature and throughout three additional isotherms (250°C, 275°C and 300°C) of same duration.

3. Results and discussion

Variation of the power and duration of the NTP discharge allows to determine a minimum value of 23 W and 45 min for the power and duration, respectively, to get CuO/Al₂O₃ as final material using XRD and FTIR-ATR characterizations. The CO₂ yield obtained in toluene total oxidation is presented in Figure 1. The results demonstrate that the plasma treated catalyst exhibits a much higher CO₂ yield in comparison with the yield obtained in the presence of calcined sample. This improvement is mainly due to a better dispersion of copper oxide species on the alumina surface determined by XPS with a Cu/Al atomic ratio twice as high to that of the calcined sample.

4. Conclusions

Non-thermal plasma treatment has been successfully used to prepare CuO/Al₂O₃ catalysts faster (90 min against 5h for calcined sample) with less energy consuming (estimated at 0.03 kW.h against 14 kW.h for calcined sample). The plasma treated catalysts show significantly improved catalytic activity in toluene total oxidation. It is believed that the higher CuO dispersion on Al₂O₃ surface induced by plasma treatment is the reason for the enhanced catalytic performances.

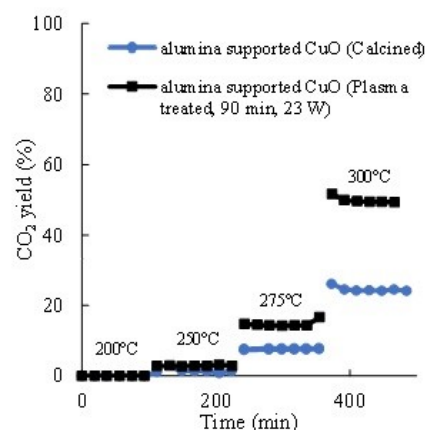


Figure 1: CO₂ yield obtained in the course of toluene oxidation in the presence of calcined CuO/Al₂O₃ and plasma treated CuO/Al₂O₃ (90 min, 23 W)

Cu-Hierarchical-SAPO-34 Catalysts with Enhanced Low-Temperature NO_x Removal and High Hydrothermal Stability

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Current and future regulations for NO_x emissions spotlight the strong limitations of catalytic systems used in industrial applications. In particular, under cold start conditions, the temperature of the exhaust gas is not high enough to ensure a good catalytic performance. To overcome this issue, we develop Cu-hierarchical SAPO-34-based catalysts by soft-template hydrothermal crystallization method. The hierarchical catalysts are targeted to allow an efficient gas diffusion through mesopores, improving NO_x efficiency at low temperature. To demonstrate the potential of our catalytic systems, this study was focused on the analysis of the catalysts' performance for NH₃-SCR of NO_x. The catalytic activity of fresh and hydrothermal aged (HT, treated in air with 10% H₂O at 750°C for 16h) catalysts was assessed in a broad temperature range, i.e. from 100 to 450°C. The composition of the feed gas mixture was 650 ppm NO_x, 650 ppm NH₃, 5% H₂O and 6% O₂ using Ar as the balance gas. The total flow rate was set at 730 mL min⁻¹, which corresponded to a gas hourly space velocity (GHSV) of 120.000 h⁻¹ and 0.15 g of catalyst. The NO, NO₂, NH₃ and N₂O concentrations at the reactor exit were monitored online with a Fourier transform infrared multigas analyzer (MKS 2030).

Fresh Cu-hierarchical catalyst presented a slight increase in catalytic activity at low temperature (zoomed part in Figure 1b), which could be attributed to the incorporation of mesopores into the solely microporous SAPO-34 structure, improving reactant diffusion. However, Cu²⁺ ions exchanged into micro-SAPO-34 framework favor the standard NH₃-SCR of NO_x at medium temperature range. Note that these Cu²⁺ cations were not clearly detected by NH₃-DRIFTS in the fresh Cu-hierarchical catalyst. After HT, nevertheless, the Cu-hierarchical catalyst presented a more abundant presence of Cu²⁺, which enhanced the catalytic activity related to that of conventional catalyst in an extended temperature range. This improvement is attributed to the migration of copper species on the catalyst surface to SAPO-34 framework. At high temperature, however, a competition between the desired NH₃-SCR reaction and the NH₃ oxidation reaction is clearly observed (Figure 1a), which are mostly presented on hierarchical catalysts. Moreover, a more significant amount of N₂O was formed at medium temperature for hierarchical catalysts. To reach high performance keeping the low temperature catalytic activity of developed Cu-hierarchical catalysts, a Fe-based shell was synthesized onto the Cu-based core using a self-assembly method followed by a secondary hydrothermal growth promoted by a seed precursor solution. The main risk is to achieve only low control on core-shell attractions and secondary growth due to the cross-influences between different synthesis parameters. To minimize this risk, further optimization of pH conditions and well-controlled compositions for self-assembly and seed precursor is in progress in our laboratories. Targeted hierarchical core-shell structures are expected to open a uniquely ample temperature window of efficient activity, leading to a joint abatement of NO_x and N₂O, with the copper and iron phase being specifically selective to each of these pollutants.

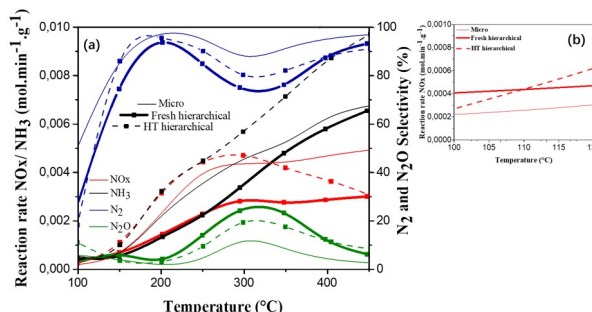


Figure 1: a) NH₃-SCR standard catalytic performance of Cu-micro (solid line) and Cu-hierarchical fresh (solid square line) and HT (dash square line) catalysts; b) NO_x reaction rate at low temperature range for Fresh Cu-micro and hierarchical catalysts (solid lines)

Poster Session 1

Green Synthesis of Heterogeneous Catalysts by Solvent-Free Reactive Extrusion

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Catalyst applications diversity and the environmental challenges facing industries and our world are leading to a rapid growth in the catalysis market (+4.4%/year according to Catalyst Market Growth & Trends 2020). This competitiveness can be achieved by improving the performance through the catalytic process, the improvement of the properties of the catalytic material and the improvement of the processes for its synthesis.

In this project, we want to manufacture catalysts in a sustainable development approach. Obviously, we want to improve the materials but it is becoming increasingly important to rethink the production

of these materials by saving raw materials, energy and reducing wastes production. The crucial work focuses to improve the modes of synthesis to make catalysts in greener way.

Our strategy consists in coupling the sol-gel process with the principle of reactive extrusion as a method for the simultaneous production and shaping in one step of the active phase and catalysts support at room temperature, in a continuous mode, and in solvent-free conditions. Reactive extrusion has been developed mainly for the synthesis and processing of polymeric materials, a path that is just beginning with metal oxides. It combines the performance of chemical reactions with classical forming steps by mixing and extrusion.

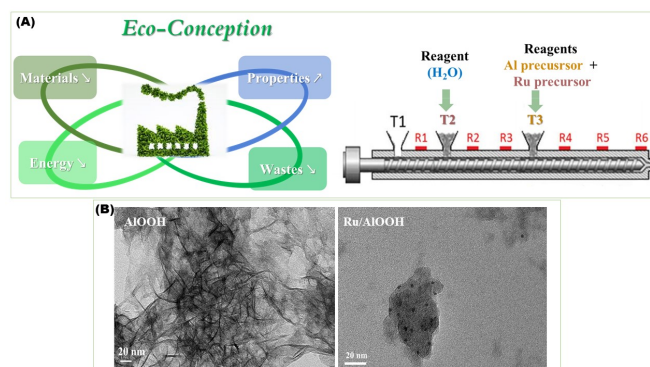


Figure 1: The principle of the synthesis at left and the scheme of the experimental set-up of Reactive extrusion at right; (B) TEM images of γ -AlOOH synthesized by solvent-free reactive extrusion at left and Ru/AlOOH (Wt% Ru = 4%) prepared by solvent-free synthesis

First, we focused on the synthesis of bohemite (γ -AlOOH) which is converted upon calcination into mesoporous alumina (γ -Al₂O₃) with high specific surface area. The developed material exhibits good catalytic properties with ethanol dehydration activity comparable to those observed in literature. This oxide is widely used in industry as catalyst and catalyst support. Secondly, we developed reactors and processes for the synthesis of Ruthenium-based catalysts supported on γ -AlOOH and γ -Al₂O₃ for CO₂ methanation. In order to quickly evaluate the influence of the experimental parameters (concentrations, temperature and hydrolysis), the simultaneous synthesis of the support and the active phase of the catalyst was developed in a stirred reactor tank (outside the extruder), as preliminary study.

The Ru precursor (solid) is mixed with the alumina precursor (viscous liquid), without the addition of solvent and hydrolyzed. Ru/AlOOH and Ru/ γ -Al₂O₃ catalysts with different weight contents of Ru (Wt%Ru: 1, 2, 4 and 6%) relative to the γ -Al₂O₃ support were prepared. As obtained materials were treated under air and dihydrogen at different temperatures.

The physical and structural properties of the catalysts were determined by X-ray diffraction, transmission electron microscopy, showing well dispersed Ru based particles of 2-3 nm on aluminum hydroxide and oxide nanoplatelets. The specific surface area increases with decreasing amount of Ru (from 506m²/g for Wt%Ru=6% to 818m²/g for Wt%Ru=1%). The most interesting samples will be evaluated in CO₂ methanation catalysis (A.Kim et al. 2019).

Direct Functionalization of UiO-66 Metal-Organic Framework as an Effective Way Towards UiO-66-SO₃H - An Active Solid Acid Catalyst for Fructose Dehydration

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Metal-Organic Frameworks (MOFs) are a class of hybrid crystalline microporous solids. Their combined architecture provided by inorganic nodes (clusters or ions) and organic ligands allows for unique framework organizations in 1, 2 or 3 dimensions. With around 10 000 denominations known so far, MOFs have found application in gas storage and transportation, sensing making them a “hot topic” in materials science. UiO-66 (Universitetet i Oslo) is one of the well-known MOFs nowadays. Built of Zr-oxoclusters and terephthalate linkers, UiO-66 exhibits a continuous 3D structure with pronounced textural properties and a surface area surpassing 1000 m² g⁻¹. Moreover, free metal sites on the Zr-oxoclusters enables Lewis acidity which together with the MOF's chemical and thermal stability allows for applications in various media. Besides, the UiO-66 framework is known to be easily tuned via either direct or post-synthesis functionalization. Either way leads to grafting functional acidic (-COOH, -SO₃H) or basic (-NH₂) groups onto the framework. Thus, newly formed Brønsted sites can expand the application of UiO-66 to a variety of acid- or base-driven processes such as catalysis, toxic gas removal or wastewater treatment.

Therefore, the goal of the present work is to show an easy direct functionalization way for insertion of -SO₃H groups onto the UiO-66 framework and to test the so-formed UiO-66-SO₃H in fructose dehydration into hydroxymethylfurfural (5-HMF) (Fig. 1). A special attention will be given to comparing two functionalization processes performed in water to the one performed in DMF (N,N-dimethylformamide), traditionally used hazardous solvent for UiO-66 and its derivatives. On the other hand, fructose dehydration is carried out in DMSO (dimethyl sulfoxide), a known solvent which possesses activity towards fructose dehydration. Therefore, reaction optimization was performed to diminish the solvent effect and study the impact of the catalyst alone. Thus, at 100 °C UiO-66-SO₃H demonstrated complete (> 98 %) fructose conversion after 0.5 h while the blank (no catalyst) test reached complete conversion after 3 h. This highlights the positive effect of framework functionalization and insertion of Brønsted sites on fructose dehydration. At the same time, at 80 °C the blank test and a test over UiO-66 showed no conversion after 3 h while UiO-66-SO₃H reached decent 81 % (Fig. 1). The catalyst reusability test revealed its structural stability for at least 9 consecutive cycles with a gradual drop of fructose conversion down to 40 % due to coke deposition on the catalyst surface. Lastly, additional results concerning the effect of the solvent (DMF or water) used for framework functionalization on the structural and textural properties as well as catalytic activity will be discussed.

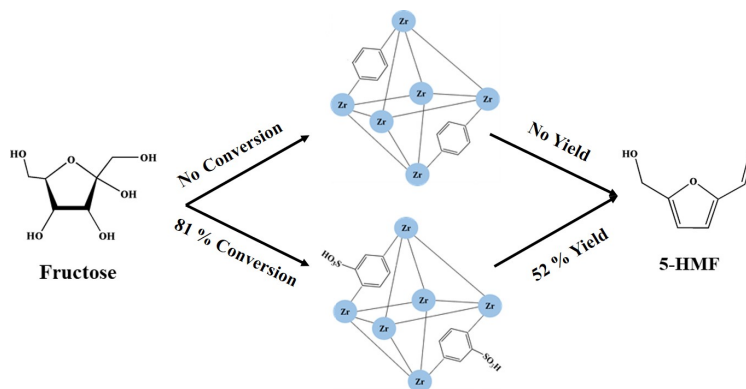


Figure 1: Fructose dehydration over UiO-66 and UiO-66-SO₃H at 80 °C after 3 h

Depolymerization of Hemicelluloses Through Mechanocatalytic Process Using Aquivion, a Perfluorosulfonic Acid Polymer, as Catalyst

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Oligosaccharides are raw materials that find many applications as prebiotic functional food ingredients for instance. They are currently obtained by extraction from natural resources by chemical or enzymatic routes. Currently, the enzymatic pathway is receiving the largest interest but very dilute aqueous media, costly downstream purification processes and low enzyme stability, decrease their competitiveness. Other chemical alternatives as the use of acid-catalyzed processes suffer from a lack of selectivity. Recently, we, and others, explored the mechanocatalytic-depolymerization of cellulose using a heterogeneous-acid-catalyst as solvent-free process. To our knowledge, this concept has never been applied to hemicelluloses, despite these abundant and renewable resources are nowadays poorly valorized. Together with previous results on cellulose, transposition of the mechanocatalytic process to hemicelluloses would complement the scope of lignocellulosic biomass waste, an abundant and cheap renewable feedstock, for the synthesis of oligosaccharides. In this research, they were obtained starting from hemicelluloses from two different biomasses: maritime pine (Pine-HEM) and bleached pulp waste (Pulp-Hem). The depolymerization process was done using a perfluorosulfonic acid polymer (Aquivion®) as acid catalyst and a planetary ball mill. The product was analyzed by HPLC-SEC after removing the catalyst by solvent washing.

First, the mechanocatalytic depolymerization of Pine-HEM was investigated. The effect of wetness on hemicellulose, catalyst amount, and reaction time were evaluated in order to maximize the oligomers production. An amount of oligomers with degree of polymerization (DP) < 7 of 67 wt. % was obtained with 3.5 wt. % wetness on Pine-HEM, 100 wt. % of catalyst and 12 h. The catalyst Aquivion PW98 was recycled using similar conditions (Fig.1-A). Yield in oligosaccharides with a DP<7 significantly dropped to 37wt. %, due to a partial neutralization of Aquivion by remaining trace of NaOH (difficult to fully removed) used for the extraction of Pine-HEM. Secondly, the mechanocatalytic depolymerization of Pulp-HEM led to 56 wt. % of oligomers with DP < 7 of 59 wt. % using 3.5 wt. % wetness of Pine-HEM, 100 wt. % of catalyst and 12 h of ball milling. This lower yield in oligomers is due to its higher recalcitrance in comparison with Pine-HEM. In order to check the catalyst recyclability, Aquivion was recycled (Fig.1-B). Yield in oligosaccharides DP<7 keep constant in a second, and third cycles. We will show that the difference in the recyclability of the catalyst is due to the extraction and purification process of hemicellulose which dramatically impact the catalyst stability.

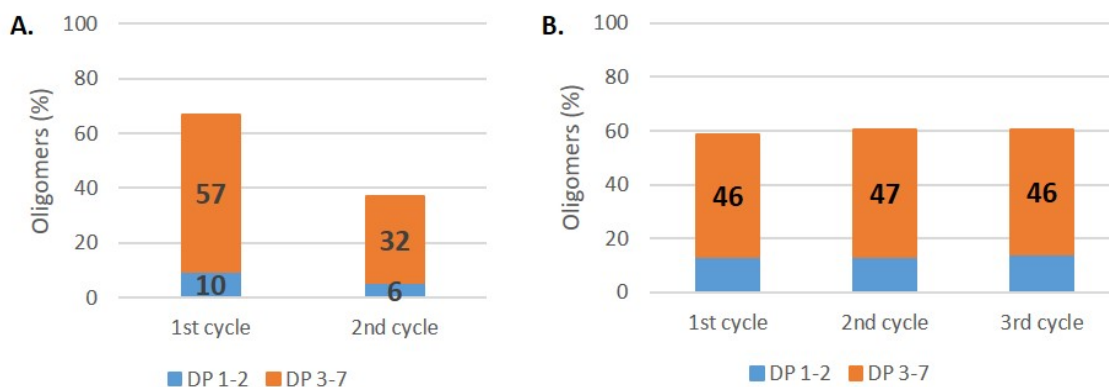


Figure 1: Catalyst recycling tests of Aquivion® as acid catalyst on the mechanocatalytic-depolymerization of (A) Pine-HEM and (B) Pulp-HEM.

Catalytic Fast Pyrolysis on H-ZSM-5 Zeolite: Activity and Stability of NNN Pairs of Al Atoms During Anisole Transformation

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Introduction

Petrochemical products are pervasive in our daily lives and are set to account for more than a third of the growth in oil demand to 2030 and more in 2050, and the landscape for petrochemical, oil, and gas industries is evolving to develop more “high-value chemicals” (aromatics).

The majority of BTX aromatics originate from catalytic reforming and FCC units located in refineries. The catalytic fast pyrolysis (CFP) of biomass represents an interesting production pathway for green aromatics (+olefins) by mimicking the FCC of crude oil. Pyrolysis is conducted in a dual fluidized bed on a zeolite catalyst. The oxygenated volatiles formed by biomass pyrolysis diffuse to the zeolite's acid sites to form the targeted products (aromatics, olefins), but also coke and gas (CO, CO₂). Despite growing interest, biomass CFP is still in its infancy compared with other thermochemical technologies (gasification, combustion), notably requiring more stable catalysts with increased BTX selectivity; thus, understanding and mastering deactivation is key to improve activity and selectivity over time, and provide cleaner and cheaper processes. Methoxy functional groups are very prevalent in biomass pyrolysis products (anisole, guaiacol, etc.). The methoxy group being the only functionality of the molecule, anisole is used as a model compound to investigate the reactivity of methoxy-based compounds present in the gas phase during lignin CFP.

Materials and Methods

The transformation of anisole was carried out over H-ZSM-5 (Si/Al=40) catalyst at 400°C under atmospheric pressure with partial anisole pressure of ≈0.048atm. The experiments were performed at different contact times (W/F), from 0.02 to 0.17h, to evaluate the deactivation and coking rates. In addition, the kinetic losses of porosity and acidity are evaluated by nitrogen and pyridine adsorption, respectively.

Results and Discussion

Anisole Transformation, occurring mainly by disproportionation reactions, follows an apparent first-order rate equation. Regardless of the reaction time, the plot of $|\ln(1-x)|$ as a function of the contact time (W/F) is a linear function (Figure 1a). Yet, the kinetic constants (k_r) decrease with time on stream, owing to coke formation. The deactivation function and coke deposit initially follow an exponential law, then reach a steady-state (Figure 1b). After only two minutes, the initial activity is reduced by four, and the coke content is already more than 4 wt. %. After 1 hour, regardless of contact time, the coke amount is less than 8 wt.% and causes losses of micropore volume and concentration of Brønsted acid sites (BAS) of only 50-65%, and 14-24%, respectively.

These results suggest that a large part of framework aluminum is resistant to coking. The proportion of deactivated BAS corresponds to Al atom fraction in the next nearest neighbors (NNN) position in H-ZSM-5 with a Si/Al of 40, i.e., 0.25. Moreover, from activity loss and residual acid sites percentage, it is possible to assess that NNN pairs of Al are 10 times more active in disproportionation reaction than isolated Al.

The transformation of the anisole highlights the significant role of the distribution of aluminum in the zeolite framework for the activity and the stability of the catalyst

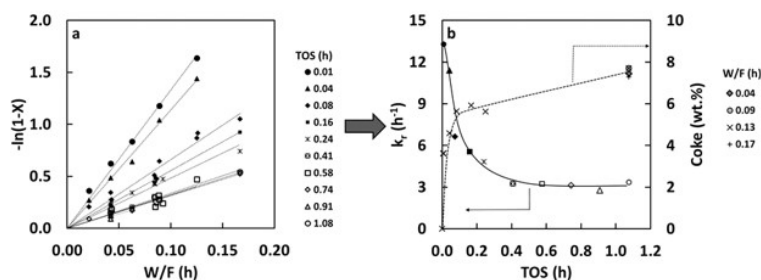


Figure 1: (a) Linear determination of reaction rate (k_r) for different TOS. (b) Reaction rate decrease, compared to coke formation, as a function of TOS

Effect of Al Content on the Reaction Pathways of m-Cresol Transformation over Pd/Al-SBA-15 Catalysts

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The hydrodeoxygenation (HDO) reaction of lignin-derived compounds is an important step in the bio-oil upgrading obtained from pyrolysis of lignocellulosic biomass. In order to evaluate the catalysts properties in the HDO reaction mechanism, model molecules are often used. In the present work, the effect of support acidity is investigated, by testing a series of Pd supported on SBA-15 functionalized with aluminium (Al = 0, 5, 20 and 40 wt.%) on the deoxygenation of m-cresol as a probe molecule.

SBA-15 support was prepared by the conventional procedure using template while Al-SBA-15 were prepared by two-steps pH-adjusting method. Pd (2 wt.%) was thereafter impregnated using incipient wetness impregnation with Pd(NO₃)₂ and calcined at 400 °C for 3 h (2 °C min⁻¹). The transformation of m-cresol was carried out in a fixed-bed reactor, operating at atmospheric pressure and 300 °C. Catalysts were reduced in situ under pure H₂ flow at 300 °C for 1 h prior to reaction.

The results showed a satisfying incorporation of aluminium up to 20 wt.% over SiO₂. The aluminium distributed over silica porosity slightly affected the PdO size and distribution, nanoparticles being mostly located inside the mesoporosity. At higher loading (40 wt.% Al), accumulation of Al₂O₃ and pore clogging were observed with most of PdO localized onto the Al₂O₃ phase situated outside of the SBA-15 grains or at the pore mouths.

The activity and product distribution were significantly changed with the insertion of Al over silica. For the Pd/SBA-15 catalyst, 3-methylcyclohexanone (62%) and toluene (38%) were the main products. The incorporation of 5 wt.% Al strongly enhanced the selectivity to the deoxygenated product, toluene (77%) with the HDO rate being the highest on this catalyst. However, it was also observed the formation of o-cresol, phenol and xylenols obtained by isomerization and disproportionation reactions. Further increase in the aluminium content (20 and 40 wt.%) allowed to increase the selectivity into these oxygenated products, whereas the selectivity into toluene strongly decreased (from 77% with 5 wt.% Al to 22 with 40 wt.%).

Three reaction pathways were proposed: (i) tautomerization of m-cresol with further ring hydrogenation to produce 3-methylcyclohexanone (catalyzed by metal particles) or hydrogenation of the carbonyl group to produce toluene (Pd-acid site interface); (ii) isomerization toward ortho and para-cresol (acid sites); (iii) disproportionation with formation of phenol and xylenols (acid sites). The calculated reaction rates showed a pronounced increase in the HDO rate with addition of 5 wt.% Al and thus a continuously decrease accompanied by increase in the isomerization and disproportionation rates increasing Al content. This was attributed to the aggregation of PdO particles and formation of alumina layer outside SBA-15 grains with consequent reduction in the number of Pd-acid sites interfaces leading to the inhibition of the deoxygenation route and the promotion of isomerization and disproportionation reactions. Therefore, the results obtained demonstrated that adjusting the metal/acid site balance is an efficient way to control product distribution and improve the deoxygenated aromatic compound yield during the upgrading of bio-oils containing phenolics compounds.

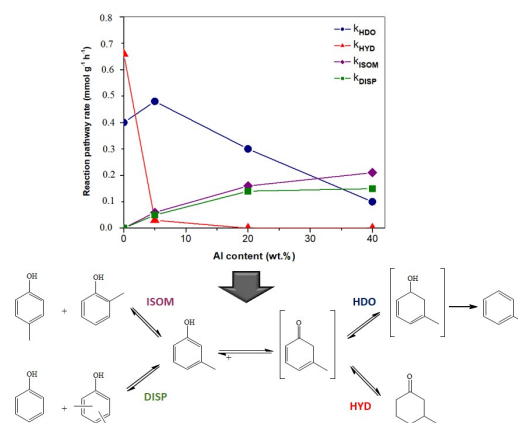


Figure 1: Reaction pathways proposed for the transformation of m-cresol over Pd-based catalysts and the respective reaction rates as a function of Al content.

Controlling Ni Nanoparticles Size within SBA-15 Porosity toward Selective HDO Reaction of m-Cresol

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One of the effective methods to valorize the biomass feedstock is by pyrolysis process, where a bio-oil is produced. The bio-oil is having high potential to obtain green fuels by hydrodeoxygenation (HDO) reactions in the presence of a catalyst. The key factor in achieving good activity and selectivity in HDO is the choice of the catalyst. It was shown that the formulation and the design of the catalyst are definitive to reach high performances. In the HDO reactions were used a large variety of catalyst such as: sulfides and phosphide solids, transition metal oxides, supported noble or non-noble metals. Among them, supported catalyst based on transition metals (TM) are presenting good results for the conversion of phenolic compounds (phenol, cresol, guaiacol) into benzene, toluene and BTX. Even if there are a lot of methods for the preparation of supported catalysts, is still difficult to control with precision the size and the dispersion of the NPs onto porous supports and at the same time to maintain a high thermal stability.

We are proposing in this work to investigate the influence of the nickel nanoparticles (NPs) size in the HDO reaction of m-cresol. With this aim, we prepared catalysts with Ni NPs size precisely controlled of 1 nm, 3 nm and 9 nm, in order to evaluate the selectivity-to-size influence over m-cresol HDO reaction. The 10 wt% nickel based materials were prepared using the infiltration methods. The fresh and spent materials catalysts were completely characterized by XRD, N₂ physisorption, TPR, TEM, in order to collect information for their structural, morphological and reductive properties. The HDO reaction of m-cresol was performed in vapor phase at 573 K and under atmospheric pressure. The XRD patterns and TEM images confirmed that we successfully obtained the Ni NPs size of 9, 3 and respectively, 1 nm. The results were strengthened by the TPR profiles, which showed the absence of large and external Ni NPs and the presence of confined NPs for 10%Ni-9 nm and high dispersed NPs in high interaction with the support for 10%Ni-1nm. Deoxygenation of m-cresol towards toluene was found to be Ni-particle size dependent. Decreasing of Ni particle size from 9 to 1 nm greatly improved the HDO reaction rate by 9 times (Figure 1). Moreover, the catalysts were characterized after test to prove their resistance toward sintering and coke formation.

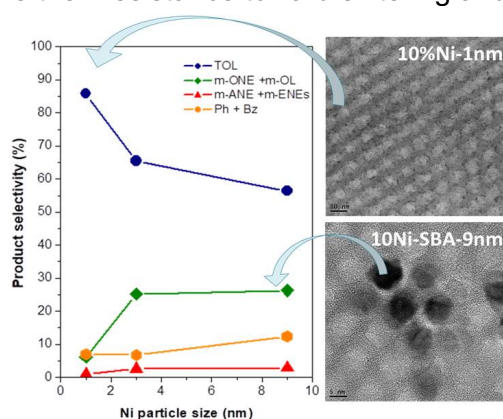


Figure 1: Figure 1. HDO reaction, selectivity in function of Ni NPs size.

[1]. S.A. Oudraogo, P.R. Bhoi, J. Clean. Prod. 253 (2020) 119957.

[2]. F. Yang, D. Liu, Y. Zhao, H. Wang, J. Han, Q. Ge, X. Zhu, ACS Catal. 8, 2018, 1672-1682

OH-Oligomers by Lignin Catalytic Depolymerization

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In recent years, catalytic depolymerization of lignin has been widely performed to obtain aromatic monomers under reductive or oxidative operating conditions [1]. However, starting with a recalcitrant technical lignin, co-produced in pulp industry or cellulosic biorefinery, the depolymerization only lead to poor monomers yield that prevent a valuable process. Another option to valorize technical lignin is to use it as a macromer in polymer applications. For instance, lignin can be used to replace polyol in polyurethane synthesis [2]. Other approaches were proposed using either lignin or lignin-derivatives to be incorporated into polymer synthesis [3]. Lignin derivatives might be more interesting

than lignin if they are well-defined and possess higher amount of OH groups that can be further functionalized. Thus, one approach would consist in depolymerizing softly the lignin to create OH- groups that are phenolics or aliphatics. This can be done by cleavage of the ether inter-units linkages in lignin (β -O-4, α -O-4 or 4-O-5) and also by demethylation of the methoxy groups in the syringyl and guaiacyl units of the macromolecule. In literature, catalysts with lewis acidity have been found to have an effect on this type of transformation. Until now, the most efficient demethylation method proposed is using HI acid formed in situ by using Iodocyclohexane in DMF [4]. We thus undertook a study to develop heterogeneous catalysts able to cleave selectively ether bonds of a technical lignin. In order to make a large screening of catalysts having various hydrogenolysis and acido-basicity properties, we have chosen Pd/C already successfully used in lignin depolymerization to get monomers, CoMo catalysts in oxide and sulfide forms active under reductive conditions, tungstated alumina (AIW) [6], silica-supported phosphotungstic acid and a well-known H-ZSM-5 zeolite.

One of the main questions in this approach is to determine whether the operating conditions influence the lignin conversion and depolymerization. It has been observed that the yield of oligomers recovered in THF (THF-solubles) is varying according to the nature of the catalyst. For instance, much higher yield was obtained with Pd/C (92 wt%) compared to other catalysts (around 60 wt%). Furthermore, the content of aromatic OH groups in the THF-soluble fraction evaluated by ^{31}P NMR allowed to evidence that both catalysts and temperature might have a strong influence on the structure of the lignin-derivatives (Figure 1). Catechols groups that may form by demethylation of guaiacyl are more difficult to characterize in oligomers and are included in phenols or guaiacyl groups. Compared to initial lignin (3.6 mmol/g), the phenolic OH content in the products reached 4.6 mmol/g. Higher amount of phenolic OH were obtained with CoMo(S)/Al₂O₃ and AIW. Increasing the temperature from 250°C to 280°C led to increase the OH content with CoMo catalysts and the yield also increased around 72 wt%. On the contrary, increase of the residence time is fewly affecting the OH content and increase the monomers to oligomers ratio obtained by precipitation in acetone/heptane mixture.

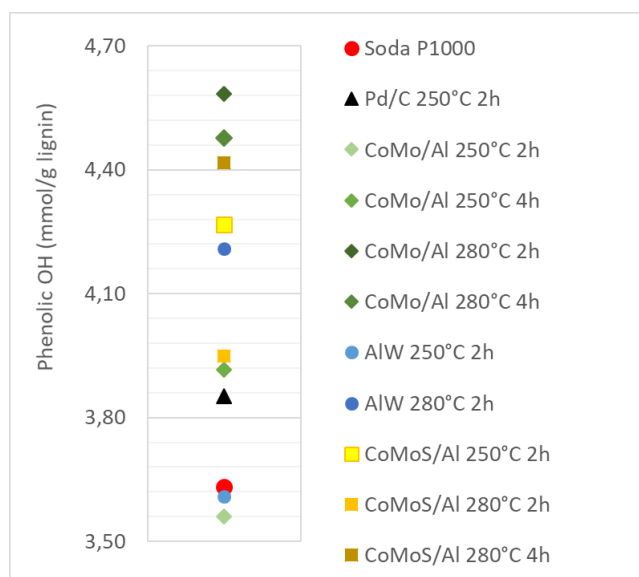


Figure 1: Phenolic OH groups in THF-soluble fractions compared to initial Soda lignin

Sequential Fractionation of Pine Wood to Bioproducts in Supercritical Methanol by Using Heterogeneous Catalysts

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In the late 1970s, the use of sub- and supercritical fluids in the processing of lignocellulosic biomass appeared in the literature. Supercritical fluids offer possibilities for the liquefaction and fractionation of lignocellulosic biomass into bio-oils or even directly into chemicals. In earlier works performed in batch reactor, we have shown that using a mixture of supercritical methanol (SC-MeOH) with water, SC MeOH-10%H₂O, enhanced the rate of cellulose liquefactions. The liquefaction of pine in supercritical methanol using a semi-continuous fixed bed reactor allows separating the methanolysis and the further catalytic conversion into value added molecules. Our work is in line with the previous one. We therefore study the sequential liquefaction of pine in SC-MeOH free of H₂ addition, in the presence of the bifunctional copper dispersed on Hydrotalcite catalyst (10 wt% Cu/MgAlOx), in semi-continuous flow reactor, filled with a fixed bed of pine sawdust or a mechanical mixture of pine sawdust and CuMgAlOx (Figure).

The preliminary results already highlighted that:

- The presence of the catalyst mixed with the pine sawdust improves the yield of light products analyzed by GC-MS. The total yield of light products using pure SC-MeOH flowing through the pine /catalyst mixture up to 280°C for 6h is in the same order of magnitude than products yield reported in the literature starting from isolated lignin using a similar semi-continuous plug flow reactor.
- Other parameters were disclosed to influence strongly the total yield of value added products analyzed by GC-MS such as the configuration of the fixed beds, biomass vs catalyst, catalyst/biomass mixture, the rate of temperature increase, the presence of water in the feed, the impact of biomass pre-treatment using SC-CO₂ and the metal/basic site balance.

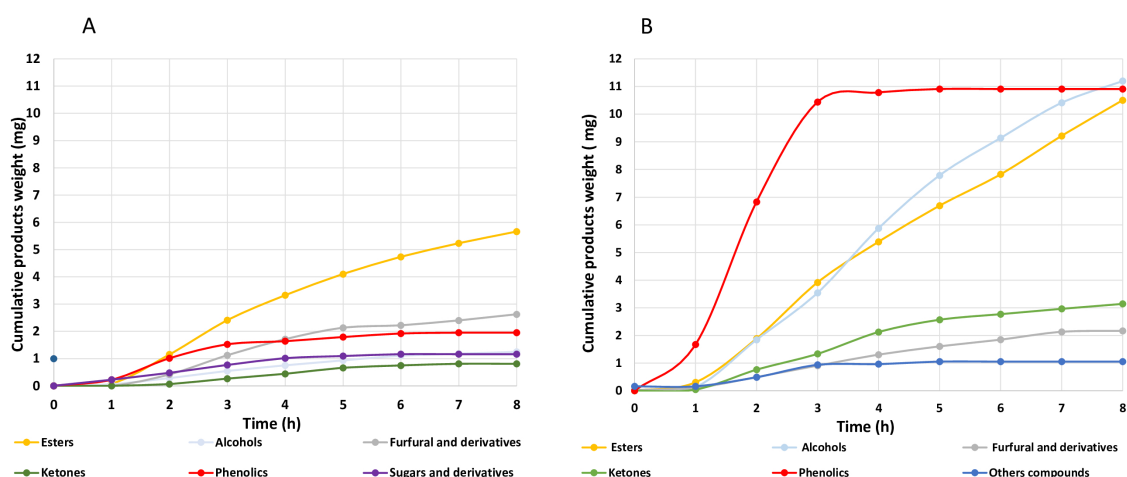


Figure: Light products families from pine wood liquefaction in semi-continuous reactor using SC-MeOH

Conditions:

- (A) 1 g pine wood, 280°C, 0.1mL/min MeOH,
 (B) 1 g pine wood, 280°C, 0.1mL/min MeOH, 0.3 g of 10 wt% Cu/MgAlOx

Figure 1: Light products families from pine wood liquefaction in semi-continuous reactor using SC-MeOH

Black Liquor Valorization Via Reactive Distillation and Heterogeneous Catalysis

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In the industrial production of paper and pulp, the remaining compounds resulting from the biomass degradation conform a solution known as the black liquor (BL). This solution contains an important fraction of carboxylic acids ($\approx 30\%$), which are burned and valorized as energy through the BL combustion. Alternatively, this fraction can be exploited as renewable feedstock for chemical valorization and biosourced chemistry. Among the processes reviewed for recovering of aliphatic acids from BL, reactive distillation (RD) stands out as one of the most promising technologies. RD can facilitate the recovery of carboxylic acids by broadening the relative volatility between the compounds through the transformation of the carboxylic acids into their derivative esters. In this project, the inclusion of active structured column internals is also considered (Figure 1). Using this type of packing has a significant effect on process intensification; however, it is also a challenging strategy because the efficiency of the process can be compromised by the hydrodynamics of the column and catalyst deactivation.

Before developing a process for the reactive distillation of crude black liquor, it is necessary to consider the operational conditions, a screening for possible catalysts, reaction kinetics and the correct selection of the column internals. All these parameters were studied taking the esterification of glycolic acid with ethanol as a model reaction. Additionally, various support materials for the chosen catalyst (mixed oxides) were also considered, among them aluminum-based were retained as the best fit for the catalyst induction. Regarding the form, the structure for the column internals, foams with different pore sizes (10, 20 and 30 ppi) were chosen and compared to glass beads internals ($\phi \approx 7$ mm).

The greatest advantage of foams over beads is that foams may potentially reduce the problems associated with pressure drop, column flooding as well as allowing catalyst deposition over the full length of the packing and limiting internal mass transfer effects. Various catalyst induction strategies were evaluated and a wash coating type protocol of the catalyst on the structured packing was defined. Continuous RD and hydrodynamic characterization tests were carried out in a laboratory distillation column ($\phi 32$ mm*1 m). The impact of the column internals in the RD was studied on esterification and separation of different acids representative of BL. Additionally, a strategy is currently being developed for the pretreatment of crude BL in order to extract the carboxylic acid fraction, conceiving the study of BL esterification in batch and RD.

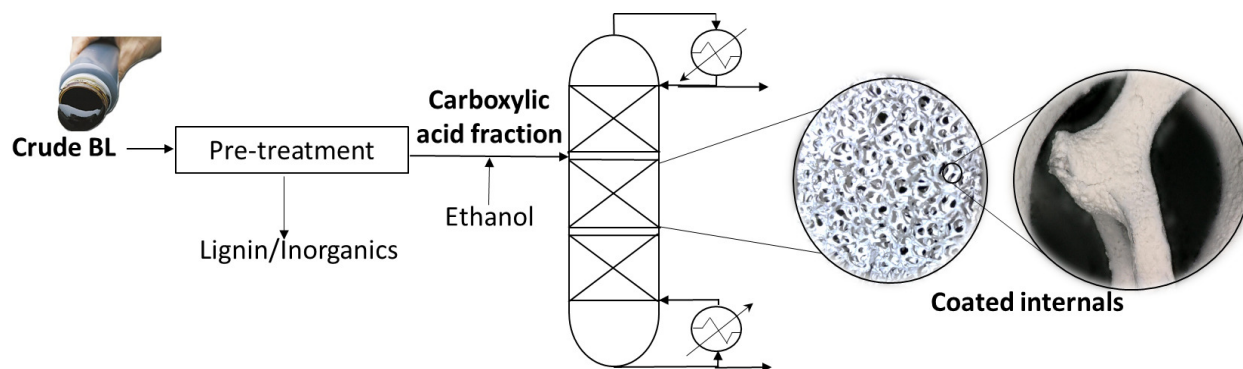


Figure 1 : Envisaged strategy for the carboxylic acid recovery from BL

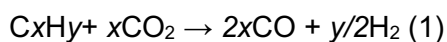
Consecutive Pyrolysis-Catalytic Dry Reforming of Plastics to Produce Synthesis Gas

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In recent years, the production and consumption of materials plastics has grown considerably due to their low cost, versatility, ease of manufacturing and their use in a wide range of application. "Plastics the facts" study in 2020 showed that out of the 29.1 million tons of plastic post-consumer wastes collected in Europe, 43% are used in energy production, 32% recycled, however, the remaining 25% are still deposited in landfills. This high percentage of landfilling poses a serious environmental problem and risks to the health of aquatic and terrestrial animals. A promising solution is the dry reforming process (1), where carbon dioxide is used, in the presence of a catalyst, to crack the high molecular weight hydrocarbons to produce synthesis gas (also known as syngas: mixture of CO and H₂).



However, this reaction is highly endothermic and requires a catalyst to increase its efficiency. In this work, the catalysts were prepared by impregnating Ni or Ru-Ni over alumina. They were then tested in the two-stage pyrolysis-catalytic dry reforming of plastics reaction. The process involves a two-stage fixed bed reactors (Fig. 1), where the pyrolysis of the plastics occurs in the first stage, and the resulting hydrocarbons are sent into the second stage to be reformed in the presence of CO₂ and the synthesized catalyst. The catalytic performance of the different γ -Ru_xNi/Al₂O₃ catalysts was evaluated. The number of moles of hydrogen produced increased with active phase loading (maximum theoretical moles of H₂ = 0.14 mole).

Novel Bio-Inspired Catalytic Tools for Versatile Applications

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Commercially available polyurethane open cell foams are functionalized with mussel-inspired Polydopamine (PDA). Two ways are presented (i) active-PDA coating or (ii) robust nanoparticle immobilisation at the surface of PDA on the foam. The resulting catalytic tools are efficient for three different applications: H₂ product (from hydrides alkaline solution), photocatalytic degradation of VOCs and show antibacterial effect for wastewaters. A novel type of robust structured catalytic support, easily accessible via an inexpensive and green bio-inspired process is thus described.

Based on the adhesive properties of marine mussels (*Mytilus edulis*), Lee et al¹ have proposed to use a naturally molecule with similar redox groups, named dopamine, which can polymerise spontaneously in a slightly alkaline aqueous solution thanks to dissolved dioxygen of air: the Polydopamine-PDA. This PDA layer presents similar adhesive and redox properties than mussel's protein. Inspired of our previous works (Fg1), we present the different routes for synthesis the catalytic foam: (i) one step, with a simple pre-functionalised PDA by dip coating on commercial polyurethane open cell foam (OCPUF@active-PDA) or (ii) two steps, functionalization of PDA film by nanoparticles deposition on its surface for versatile catalytic foam, namely OCPUF@PDA@Nps. Finally, we explain why OCPUF is an ideal candidate for different catalytic applications: the specific surface area is important, the large pore allow high light intensity through the foam (for photocatalytic application) and the pressure drop is very low due to high foam's porosity. Three applications with bio-inspired catalytic open cell foam are presented:

(i) For OCPUF@PDA@Nps:

- First, commercially available OCPUF have been successively functionalized with cobalt nanoparticles. The resulting catalytic foam (OCPUF@PDA@Co) has been used as a highly efficient tool for the release of dihydrogen from a commercially available alkaline sodium borohydride solution at room temperature. With a diluted solution containing 0.4 wt% NaBH₄ and 0.4 wt% NaOH, the hydrogen generation rate was of 76.4 ± 3.18 L.h⁻¹/gcat after stabilization of the catalytic activity. The catalytic tool could be used for 10 runs.

- Next, we show that a simple thin polydopamine film coating on the foam surface plays a "sunscreen" role, protecting the polyurethane foam from UVA or UVC degradation and inhibiting volatile organic compounds' emanation. Furthermore, when loaded with TiO₂ particles, these functionalized foams (OCPUF@PDA@TiO₂) allowed developing an efficient photocatalytic system for the formic acid degradation in water and the mineralization of acetaldehyde, n-heptane, toluene and acetone in air.

(ii) for OCPUF@active-PDA:

- For the first time, the impact of pre-functionalised OCPUF with active-PDA on the growth of pathogenic microorganisms found in wastewaters are presented. It is show that OCPUF@PDA significantly reduces the growth rate of *Staphylococcus aureus* and the bactericidal effect of OCPUF@active-PDA (pre-functionalised with copper) was assessed after 24h

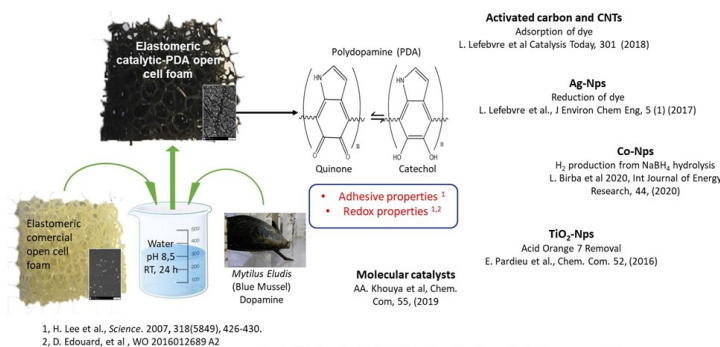


Fig 1, Bio-inspired (PDA) functionalisation of elastic open cell foam and catalytic applications

Figure 1 : Bio-inspired catalytic open cell foam and applications

Photocatalytic Direct Methane Conversion to Acetic Acid with Water as Oxidant

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Methane as one of the most abundant energy reserve feedstocks on earth, its direct catalytic functionalization to value-added chemicals holds great interest to modern scientific community. To obtain acetic acid, an important industrial chemical, the direct conversion routes generally involved with the oxidative condensation or carbonylation of methane, using oxygen or strong acid as oxidant. However, from a safety perspective, potential risks may exist by mixing methane with these strong oxidants at high pressures. Consequently, realizing a milder oxidative transformation of methane to produce acetic acid would be of great significance. Herein, we show that under the irradiation of UV light, CH₄ and CO can be catalytically converted to acetic acid, with H₂O as the sole oxidant at room temperature. The photocatalyst that we developed for this new process is TiO₂ supported polyoxometalate clusters anchored with isolated Pt₁ atoms (Pt₁/POM/TiO₂), synthesized via a spontaneous monolayer dispersion strategy. Under the condition of 2 bar CO, 8 bar CH₄ and 10 mL H₂O, Pt₁/POM/TiO₂ shows a acetic acid production of 197 μmol/g after 12 h irradiation, with CO₂ as the only carbonaceous side-product. We find that each phase of this ternary material is indispensable for the reaction. Referential catalysts without Pt, polyoxometalate clusters or TiO₂ all show negligible activity in the catalytic production of acetic acid. Additionally, control experiments in the absence of UV light, CH₄ or H₂O also show no production towards acetic acid, indicating the methane conversion to acetic acid is essentially a photo-induced H₂O oxidative carbonylation process. Based on the current understating, it is proposed that the C-H activation of CH₄ and subsequent carbonylation was occurred at the Pt₁ sites, facilitated by the photo-generated holes from TiO₂; in the meantime, with the assistance of photo-generated electrons, the underlying polyoxometalate cluster served as a reactive oxygen reservoir, realized the oxidation of methylcarbonyl intermediate via a H₂O-mediated MvK mechanism. Moreover, under the optimized condition, our Pt₁/POM/TiO₂ shows superior stability in over 50 h reactions, producing 3.39 mM acetic acid solution with the liquid-phase selectivity up to 94.2%.

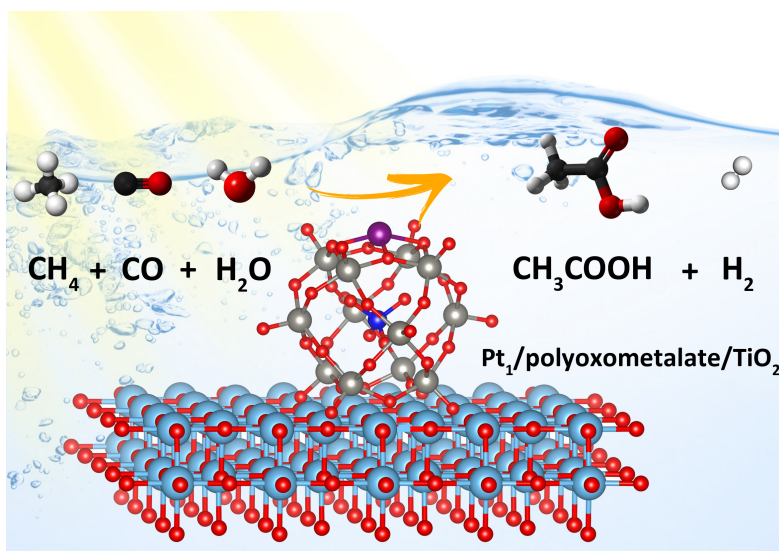


Figure 1: Graphic illustration of the photo-induced methane direct transformation to acetic acid route over Pt₁/POM/TiO₂ photocatalyst

Reduction of Alkenes by Hydrazine Produced from Ammonia Under High Frequency Ultrasound

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When a liquid is subjected to an ultrasonic irradiation at a high frequency, cavitation bubbles are formed. Inside the cavitation bubbles, extreme conditions of temperature and pressure are reached. As a result, gaseous molecules diffusing inside cavitation bubbles are instantaneously pyrolyzed, leading to the formation of radicals. At the bubble collapse time, these radicals are propelled into the solution where they can be recombined or react with other compounds in the solution to initiate chemical reactions.

In a previous work, we demonstrated the possibility to use high frequency ultrasound for the activation of ammonia and its subsequent conversion to hydrazine. Here, we extended this concept for the reduction of alkenes by in situ generated hydrazine, directly using ammonia as a source of hydrogen.

A typical experiment was performed using a 5 wt% aqueous solution of ammonia containing alkene (octene for model reactions) supported on activated charcoal. The solution was subjected to an ultrasonic irradiation at 525 kHz in a high frequency ultrasound reactor. The solution was maintained at 30°C. The reduction of octene to octane was monitored by GC-FID. Under these conditions, the hydrogenation reaction occurred, and octane was formed in 40% yield. In the same system but with gaseous H₂ bubbled in water instead of an ammonia solution, less than 5% of octene was reduced. This is partly due to the low solubility of hydrogen in water, that makes it less available for the hydrogenation reaction. This demonstrates that ammonia can be used as a hydrogen source for an efficient hydrogenation of alkenes in these conditions.

To have more insights on the mechanism of the reaction, the influence of different parameters was studied.

First, various reaction conditions were tested to maximize the yield of the reduction reaction in this system: the amount of ammonia, the charge of the alkene on the activated charcoal, the amount of activated charcoal.

Then, the role of the support and the gas atmosphere (air, argon) of the reaction were investigated. It has been observed that without activated charcoal as a support, the reduction reaction does not occur. This shows that the support has a key role in this reaction. Moreover, hydrazine is not able to reduce directly a C-C double bond, it has first to be oxidized to diimide N₂H₂ to be able to reduce the alkene to the alkane, and release nitrogen. (Figure) According to experiments performed under argon atmosphere to remove oxygen, hydrazine may be oxidized at the surface of the activated charcoal, by oxygen from air or OH radicals from sonolysis of water.

The reduction of alkenes is usually performed by hydrogenation with gaseous hydrogen, which is extremely flammable, and in the presence of a catalytic amount of transition metal catalyst. Here, we demonstrated that under high frequency ultrasound, it was possible to use ammonia as a source of hydrogen for the reduction of alkenes. Indeed, the acoustic cavitation phenomenon enables the formation of hydrazine from ammonia, an intermediary to the diimide which reduces the alkene.

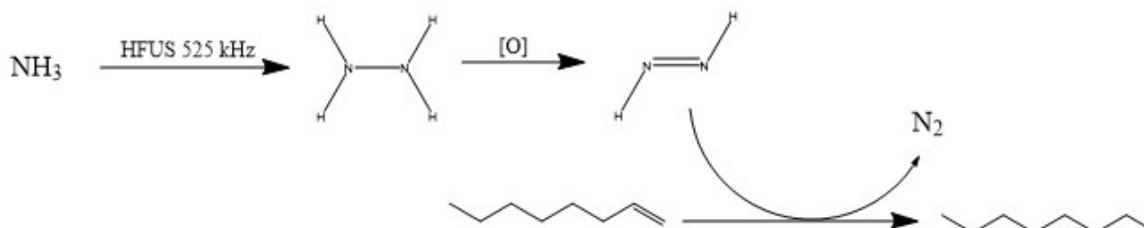


Figure 1: Hydrogenation of octene in presence of ammonia under high frequency ultrasound

Ru/RScSi Intermetallic Materials for Eco-Efficient Synthesis of Ammonia at Low Pressures

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Introduction

Ammonia, one of the most synthesized chemical compounds in the world [1] is used in many industrial sectors such as fertilizers, but also probably as an energy carrier (hydrogen storage molecule) in a near future. The usual ammonia synthesis process (Haber-Bosch process, $N_2 + 3H_2 \rightarrow 2NH_3$) requires high temperatures (400-600°C) and high pressures (150-200 bars). It is responsible for 1 to 2 % of the world's annual energy supply. The performance of historical iron-based materials could be improved by the addition of ruthenium (Ru) and/or by promotion with basic oxides (CaO, MgO) or activated carbon [2]. These materials are electron donors towards the metal (Ru), which promote the weakening of the triple $N\equiv N$ bond of adsorbed N_2 on ruthenium. However, the operating pressure of the Haber-Bosch process remains high, leading to deactivation due to hydrogen poisoning of Ru.

One promising solution is the use of Ru supported electride materials whose electron-donating effect is expected to boost the N_2 conversion [3]. This work aims to study the influence of rare earth in Ru/RScSi (R=rare earth: La, Ce, Pr, Nd, Sm, Gd) intermetallic materials for the eco-efficient synthesis of ammonia. Transient experiments were conducted to investigate the ammonia synthesis mechanism on this materials.

Experimental

The synthesis of intermetallics were performed by melting the pure elements R (R=rare earth: La, Ce, Pr, Gd, Nd), Sc and Si in stoichiometric quantity in an arc-melting furnace. Obtained materials were annealed in a sealed quartz ampoule at 800-1100°C. Ru ($\approx 1.8\text{wt}\%$)/electride samples were prepared by using a solvent-free preparation method by chemical vapor deposition from $Ru_3(CO)_{12}$ sublimation under vacuum. Catalytic tests (300-450°C; 1-5 Bars) were performed under N_2 - H_2 mixtures adjusted by mass-flow controllers. The ammonia synthesis activity was evaluated by the continuous measurement (every second) of the produced NH_3 by means of an infrared gas analyzer (MKS Multigaz 2030). The use of a real-time (1 Hz) analytical reaction monitoring system allows the examination of the catalyst behavior under transient conditions by alternating pulses of N_2 and H_2 under flow (H_2/N_2). Transient experiments are helpful to assess reaction pathways.

Results and discussion

The influence of the nature of the rare earth of intermetallics RScSi-supported Ru (1.3 to 2.1 wt%) for the NH_3 synthesis reaction has been studied at 300-400°C under 1-5 bar total pressure (Figure 1A). Compared to a 2.1wt%Ru/MgO reference catalyst, the Ru/RScSi materials allow a remarkable production of ammonia at 400°C at atmospheric pressure. Especially, a significant ammonia production rate is obtained at 300°C at atmospheric pressure with Ru/CeScSi sample.

Preliminary transient study performed at 300°C over Ru/LaScSi catalyst reveals higher NH_3 emission during N_2 pulses under H_2 flow (Figure 1B – dot line), compared to H_2 pulses under N_2 (Figure 1B – solid line). These results illustrated different H_2 and N_2 activation during NH_3 synthesis over electride sample. This breakthrough points out promising results in optimizing catalyst formulation.

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Bio-Ethanol Dry Reforming Over Ni-Co Catalysts for Hydrogen Production

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Nowadays the problems of fossil non-renewable resources (coal, oil, gas) and emission of greenhouse gases (GHG) are of vital interest. Renewable energy sources are studied for obtaining strategic energy vectors – syngas and hydrogen. Ethanol dry reforming (EDR) is one of the attractive processes for syngas and hydrogen production. The process uses biomass derived ethanol as a renewable fuel on the one hand and captured carbon dioxide, a dangerous GHG, on the other hand. Syngas obtained from EDR can be used directly as a raw material, or it can be treated further for pure hydrogen production [1, 2].

In this collaborative work, bimetallic Ni-containing materials supported on ceria-zirconia were studied as EDR catalysts. It is well known that Ni is an active metal in reforming reactions and is more suitable than noble metals due to cost and environment issues. Unfortunately, the stability of Ni-containing catalysts is affected by coking and active sites sintering. To overcome these problems, it is proposed to use bimetallic catalysts to stabilize the metal active sites. Additionally, ceria-zirconia supports are known to reduce coke formation due to high oxygen mobility.

Ceria-zirconia with ratio Ce/Zr=1 and Ce/Zr=3 was synthesized in a supercritical medium (isopropanol as solvent) at 400 °C and 120 atm [3]. Bimetallic catalysts containing 2.5 wt% Ni and 2.5 wt% Co were prepared by incipient wetness impregnation of ceria-zirconia. Monometallic 5 wt% Ni and 5 wt% Co catalysts were also prepared for comparison using the same supports and preparation method. All materials were characterized using XRD, H₂-TPR, H₂-TPD, BET, XPS and electron microscopy. All catalysts were reduced before reaction in 5% H₂/Ar at 650 °C, 1 h hold. EDR studies were carried out in a fixed-bed reactor at 650 °C, contact time 7.5 ms, 2 vol% EtOH + 2 vol% CO₂, N₂ balance.

The catalysts comprise of ceria-zirconia fluorite phase, NiO and Co₃O₄ phases. The specific surface area (SSA) was determined to be 12-14 m²/g for materials based on Ce/Zr=1 and up to 20 m²/g for materials based on Ce/Zr=3. XRD and TEM data show the presence of oxides nanoparticles of size 15-20 nm. The metallic surface area is dependent of the support composition as well as the presence of Co. Bimetallic materials have larger metallic surface areas, supposing that cobalt improves the metal-support interactions and modifies the Ni species on the surface. Monometallic cobalt-containing materials were not active in the EDR reaction, which confirms the structural rather than catalytic role of cobalt. Bimetallic catalysts were more active and more stable in EDR than nickel monometallic catalysts. The effect of the Ce/Zr ratio in the support, the presence of Co, and the Ni-Co interaction on catalytic activity was shown.

This work was supported by Russian Science Foundation, grant 18-73-10167, and Ostrogradski Stipendship 2021 from French Government.

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Preparation and Characterization of a Nickel-Based Catalyst Supported by Silica Promoted by Cerium for the Methane Steam Reforming Reaction

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Natural gas currently represents a raw material of choice for the manufacture of a wide range of chemical products via singas (mixture of CO + H₂). Among the ways of transforming methane into singas: The steam reforming reaction of methane

This work focuses on the study of the effect of cerium on the nickel-based catalyst supported by silica for the methane steam reforming reaction, with variation of certain parameters of the reaction. These parameters are: The reaction temperature, the H₂O / CH₄ ratio and the flow rate of the reaction mixture (CH₄+H₂O).

Two catalysts were prepared by impregnation of Degussa silica with a solution of nickel nitrates and a solution of cerium nitrates [Ni (NO₃)₂ 6H₂O and Ce (NO₃)₃ 6H₂O] so as to obtain the 1.5% nickel concentrations for both catalysts and plus 1% cerium for the second catalyst.

These Catalysts have been characterized by physical and chemical analysis techniques: BET technique, Atomic Absorption, IR Spectroscopy, X-ray diffraction.

Atomic absorption shows that the nickel and cerium nitrates have well impregnated the silica. The X-ray diffraction spectra performed before the reaction show the presence of the NiO and Ce₂O₃ phases. After the reaction, in addition to the two previous phases, the Ni⁰ phases are observed. BET surfaces show a decrease in silica surface without being affected.

The catalytic tests carried out on the two catalysts for the steam reforming reactions show that the addition of cerium to the nickel improves the catalytic performances of the nickel. We find for Ni/SiO₂, the overall transformation rate, the CO selectivity and the coke deposit for Ni/SiO₂ respectively: 17.06%, 11.78% and 5.62%. For Ni-Ce/SiO₂ the values are clearly improved and goes to 30.94%, 32.96% and 3.1% respectively.

These performances also depend on the parameters of the reaction namely the temperature, the rate of the reaction mixture. and the ratio(H₂O/CH₄). The temperature variation, the flow rate of the reaction mixture and the H₂O/CH₄ ratio show that the best respective performances reach at 700°C, 0.9l/h and 2.446.

Impact of the Sulfiding Agent on the Activation of a CoMoP Hydrotreatment Catalyst Under Industrial Conditions

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Improving the performance of hydrodesulfurization catalysts remains a challenge for the deep refining of lower quality feedstocks. These catalysts, generally based on Mo or W sulfides, promoted by Ni or/and Co and supported on γ -Al₂O₃, are obtained by sulfidation of an oxidic precursor, a step of crucial importance scarcely studied. In industrial units, the activation is carried out directly by the petroleum charge spiked with a liquid sulfiding agent such as dimethyl disulfide (DMDS). The catalyst is sulfided by the H₂S released during the sulfiding agent decomposition. It has been shown that adding booster molecules in the catalyst formulation induced a modification of the kinetics of DMDS decomposition and consequently of the supply of H₂S and of the temperature at which the sulfidation of the catalysts occurs. It could then influence the morphology of the MoS₂ crystallites and their promotion by cobalt, through closer sulfidation temperature of Mo and Co. Nevertheless, the choice of the liquid sulfiding agent is never considered. This study thus focuses on the impact of this choice on the active phase formation and on the catalyst performances. A CoMoP/Al₂O₃ hydrotreating catalyst was prepared and then loaded (10 mL) in a high pressure up-flow microreactor to perform both activation and hydrodesulfurization. The oxide precursors were sulfided using a mixture of straight run gas oil (SRGO) spiked with 1 wt% of DMDS (or sulfur equivalent for 4 others sulfiding agents) under H₂ (35 bar, 5 NL/h). The catalysts were first soaked with this mixture at 30°C at a liquid hourly space velocity (LHSV) of 10 h⁻¹. The LHSV was then decreased at 2 h⁻¹ and the temperature increased from 30°C to 350°C at a rate of 20°C/h and stabilized for 5 h. After this sulfidation step, the liquid feedstock was switched to pure feedstock (same operating conditions) and samples of desulfided feedstock were collected at 350°C, 360°C and 370°C.

The off-gas emission during the sulfidation was followed by μ -GC (Figure 1). Differences in the H₂S breakthrough were observed depending on the decomposition temperature of each sulfiding agent. Different decomposition products were also detected. DMDS decomposes first in methanethiol (MeSH) in equilibrium with dimethyl sulfide (DMS) to finally give methane (CH₄) and H₂S while bigger polysulfides such as di-tert-butyl polysulfide (TBPS) give first a tert-butylthiol and sulfur that may react to give the final iso-butane/iso-butene mixture and H₂S. Among the different agents tested, DMDS, DMS, TBPS 54* and 44* (*wt% of sulfur) and dimercapto-3,6-dioxaoctane (DMDO), a dithiol, the use of DMDS gave the best performance in the hydrodesulfurization of a SRGO, the lowest one being obtained with TBPS 54. In order to understand the observed differences, XPS and TEM characterizations of the sulfided catalysts were performed by collecting the catalyst at different temperatures of sulfidation for each agent, temperature carefully chosen depending on the sulfidation profile. Those analyses will allow a better understanding of the differences involved by the choice of the sulfiding agent and an identification of the key moments of the sulfidation for each agent.

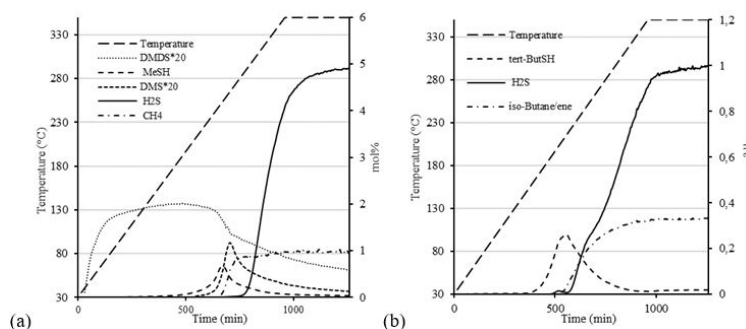


Figure 1: Follow-up of the off-gas emitted during the liquid phase sulfidation of a CoMoP catalyst using (a) DMDS and (b) TBPS 54 as sulfiding agent

Poster Session 2

Sorption-Enhanced Fischer-Tropsch Synthesis

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Fischer-Tropsch synthesis (FTS) converts bio-synthesis gas ($H^2 + CO$) into a wide range of hydrocarbons that can be further refined into drop-in fuels like diesel and jet fuel. To reduce the operational costs of the potential BTL-FT plant and to efficiently use the syngas in a once-through concept, it is beneficial to operate at high CO conversion levels. However, at high conversion, the gas phase in an FT reactor contains more than 50% of water, acting as a significant diluent. In addition, it has been reported that water deactivates Co-based FT catalyst by hindering the reduction of cobalt oxide, inducing sintering of the active metal catalyst, the formation of inactive cobalt aluminate, and re-oxidation of metallic cobalt to FT inactive cobalt oxides. The present paper presents the application of a tailored dynamically operated FT reactor where the produced water is systematically removed by solid water adsorbents (Step 1 in Figure 1). The H_2O -sorption active site is then regenerated in a separate step (Step 2 in Figure 1), allowing for cyclic operation. This will lead to increased selectivity to higher hydrocarbons (wax) while protecting the catalyst from an excessive oxidation rate

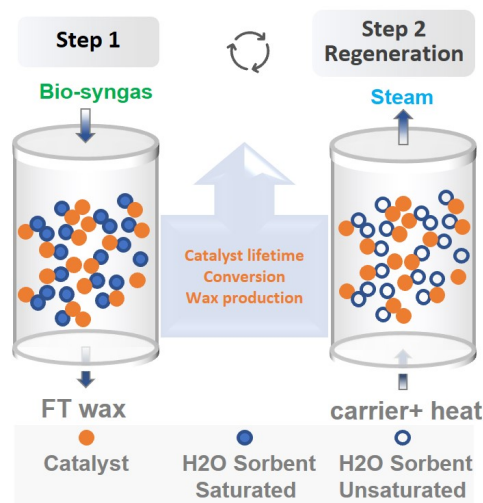


Figure 1: Sorption-Enhanced FTS

A Re promoted Co alumina-based FT catalyst is synthesized using one-step incipient wetness impregnation and characterized using following techniques such as X-ray diffraction (XRD), Brunauer- Emmett Teller (BET), temperature-programmed reduction (TPR), H_2 chemisorption. $20Co/0.5Re/Al_2O_3$ has a surface area of $144.7 \text{ m}^2/\text{g}$, pore volume of 0.5 nm and average pore diameter of 13.6 nm with the dispersion of 6.9% . Multi-cycle stability and water adsorption capacity of the selected zeolites (13X, 4A) were tested for up to 100 cycles with an in-house designed thermogravimetric analyzer (TGA) at relevant conditions for FTS ($210 \text{ }^\circ\text{C}$). The 4A showed stable water adsorption capacity ($7.8 \text{ g-H}_2\text{O}/100\text{g-sorbent}$) after 100 cycles while 13X showed decreased capacity from 9.6 to $6 \text{ g-H}_2\text{O}/100\text{g-sorbent}$. It was also observed that increasing temperature decreases the sorption capacity of the zeolites.

The catalyst and sorbent material will be mixed and tested in a fixed bed reactor to determine catalyst activity, selectivity and stability. The influence of operating parameters (temperature, H^2/CO ratio, pressure, and conversion) on the Co-based FT catalyst will also be studied. The same reactor will be used to optimize the operating parameters of the regeneration conditions. In addition one-particle system approach, where development of a hybrid material, which combines the water adsorption functionality with the catalyst functionalities in one, will be tested.

Preliminary impact assessment will be based on the lab-scale testing and process simulation of the implementation of the technology. Process efficiency, catalyst lifetime extension and optimal thermodynamic operational conditions (temperature, pressure), with the main advantages over traditional FT synthesis will be studied.

Syngas Production by Various Reforming of Methane Processes

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Currently, the economic and environmental problems related to the use of traditional energy sources such as coal, petroleum and natural gas are highly addressed. The consumption of these fuels generates two of the main greenhouse gases, methane and carbon dioxide, which are later released into the atmosphere. Both gases are key factors in a dangerous phenomenon called global warming. Studies are currently focusing on developing alternative, clean and renewable sources of energy.

In this context, the valorization of biogas, produced by anaerobic digestion of organic wastes, is a very interesting prospect. It is mainly composed of CH_4 and CO_2 , but can contain different concentrations of oxygen and water, as well as other minor compounds. Using reforming reactions, this gas can be transformed into a mixture of hydrogen and carbon monoxide, known as synthesis gas (syngas). This mixture can then be converted into molecules with a higher chemical and energy potential. The main reactions include dry reforming (CO_2), steam reforming (H_2O), and partial oxidation (O_2) of methane. Given that all four of these molecules are found in biogas, a process called tri-reforming of methane can occur simultaneously.

this process is endothermic and requires high temperatures to operate. In order to increase the kinetics at lower temperatures and to favor the formation of the desired products, these reactions usually occur in the presence of a catalyst. Transition metals such as nickel and cobalt have previously shown high activity towards reforming reactions. However, they are prone to deactivation by poisoning, sintering, and carbon formation. Therefore, other metals can be added to the formulation in order to increase the resistance to catalyst deactivation. Magnesium increases the basic character and aluminum enhances the specific surface, which improves the resistance to carbon formation and to sintering, respectively.

The objective of this work is to evaluate the feasibility of the tri-reforming of methane reaction on CoNiMgAl based materials. In this context, we aim to identify the effect of real concentrations of H_2O and O_2 on the catalytic performance of materials in the dry reforming of methane reaction. First, the concentrations of CH_4 , CO_2 , H_2O and O_2 in a biogas originating from an anaerobic digestion plant as well as a landfill gas were determined. Then, a series of stability tests was performed on CoNiMgAl catalysts derived from hydrotalcite precursors. The catalytic efficiency was evaluated in the absence (dry reforming) and presence of H_2O (bi-reforming), O_2 (oxy-reforming), and both H_2O and O_2 (tri-reforming). The concentrations selected for all reactants are in accordance with the amount found in biogas. Physicochemical characterizations such as X-ray diffraction and thermal analysis were carried out on the calcined, reduced, and used catalysts.

In general, the presence of H_2O and O_2 increased the conversion of methane. Moreover, carbon formation was reduced in the presence of both molecules. However, the presence of high concentrations of oxygen led to a progressive catalytic deactivation caused by the reoxidation of active sites.

CH₄ and CO₂ Adsorption Over Ni/Al₂O₃ Catalyst in Dry Reforming of Methane Reaction: A DFT Investigation

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Recently, dry reforming of methane (DRM) has been emerged as an effective process to reduce methane (CH₄) and carbon dioxide (CO₂) emission and convert them into more value-added energy or chemical raw. Understanding the adsorption mechanism of CH₄ and CO₂ on the catalyst surface in DRM reaction can significantly help to improve catalytic activity, and guide future research towards the development of stable and high-performance catalysts. Ni/Al₂O₃ system has been widely investigated with different Ni cluster sizes due to their activity and metal-support interaction. However, CO₂ and CH₄ activation on Ni dimer (Ni₂) supported Al₂O₃ surface has not compared. In this work, we have performed DFT investigation on the adsorption mechanism of CH₄ and CO₂ over Ni dimer supported clean alumina surface Ni₂/Al₂O₃, Ni dimer supported hydroxylated alumina surface Ni₂/Al₂O₃-OH, clean alumina surface Al₂O₃ and hydroxylated alumina surface Al₂O₃-OH. The metal-support interaction has been studied. The obtained adsorption energies showed that the Ni dimer supported alumina surfaces enhances the interaction between the investigated species and the catalyst. Hydroxyl groups appear to reduce the gas-catalyst interaction. Compared to the other Ni supported systems and extended surfaces, it was found that the Ni dimer supported alumina surface shows a higher activity towards CH₄ and CO₂ adsorption. The obtained results may help in the design of novel catalysts with high activity performance towards DRM process. Keywords: Carbon dioxide, Ni-based catalyst, Density functional theory, adsorption.

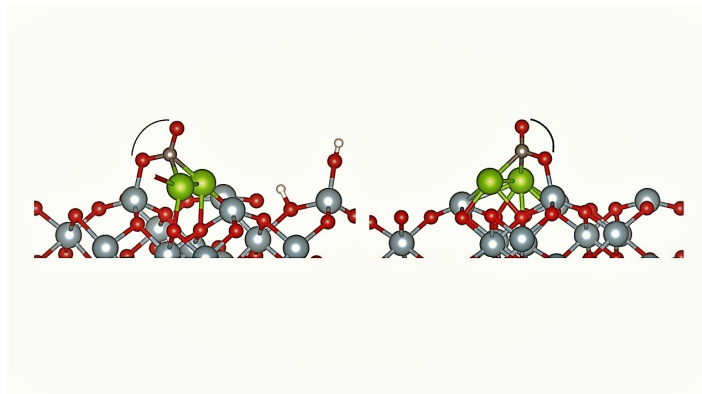


Figure 1: CO₂ adsorption on Ni₂/Al₂O₃

Mixed Oxides Catalysts Derived from Layered Double Hydroxide: Application in Methane Dry Reforming

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The methane reforming with CO₂ is a promising reaction for producing syngas by the use of two greenhouse gases. However, on most nickel-containing catalysts the formation of coke is to be suppressed to develop efficient catalysts for the reaction. To find alternative catalysts, Ni-M (M = transition metal) Layered double hydroxide was investigated.

In this experimental study, Ni-M-LDH was prepared by coprecipitation method at pH~10. The powders were calcined at 500 and characterized by TGA-SM, HT-XRD, B.E.T, PXRD, Raman, FTIR, SEM-EDS and H₂-TPR. According to PXRD and Raman analysis, the structure was observed at room temperature and was stable up to 250°C. The interlayer space decrease when the temperature increases with lattice parameter and space interlayer of 3.02Å and 7.53Å, respectively. It fully decomposed into oxide after calcination at 500 °C. Only NiO was observed and no other oxide was detected showing that M(III) is dispersed in NiO rocksalt phase as a solid solution. The specific surface area values were much greater than those obtained for primary structure. The catalytic activity in DRM reaction showed a considerable activity of the systems. This could be related to the high reducibility and the high specific surface area of the catalysts. A contribution of reverse water gas shift reaction was observed for synthesized samples. At 650°C, it showed substantial carbon deposition and this amount is decreased when the reaction temperature decreased to 550°C. These good catalytic performances are to be correlated to the textural and structural properties and reducibility of the catalysts.

(Al)MOF-Derived Catalysts: A Promising Strategy for the Synthesis of Highly Stable and Active Catalysts for Methane Reforming and CO₂ Methanation

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1. Introduction

Because of its lower cost, nickel tends to replace noble metals in the formulation of catalysts for dry reforming of methane (DRM) a reaction that transforms CO₂ and CH₄ into CO and H₂ (a key syngas mixture for the further production of sustainable energy) and CO₂ methanation (CM), a chemical process which involves reacting renewable H₂ (electrically produced by water splitting) with CO₂ to produce CH₄ as energy storage system. Although promising, the application of Ni⁰ as active phase for DRM and CM is however hampered by stability issues related to nickel sintering and to the formation of carbonaceous deposit. In this contribution, we will present a new way of synthesizing highly stable Ni/alumina catalysts made of nickel active phases dispersed on a lamellar porous alumina with high surface area. The strategy relies on the use of an Al-containing MIL-53 metal-organic framework used as sacrificial template.[1-3] The physicochemical characteristics and performances of the new MOF-derived materials for DRM and CM will be compared to those of more conventional catalysts of similar Ni content supported on various oxides. Finally, we will show how it is possible to reduce the ecological impact of the synthesis of these new catalysts by using depolymerized PET trash as organic linkers source in the synthesis of the sacrificial (Al)MIL-53.[4]

2. Experimental

(Al)MIL-53 samples were impregnated with a nickel precursor solution, then calcined to remove the organic linkers and subsequently reduced under H₂ stream to form the reduced nickel active phase. (Al)MIL-53 crystals were synthesized via solvothermal treatment using microwave irradiation (MW). Environmentally friendly syntheses of the catalysts were achieved by replacing in the synthesis mixture the commercial terephthalic acid commonly used as source of organic linker by polyethylene terephthalate (PET) flakes from trash PET bottles.

3. Results and discussion

At the step of calcination, this procedure results in the intimate mixing between the nickel phase and the oxide support and thereby in formation of a uniform spinel phase (NiAl₂O₄) nanospecies embedded in an amorphous alumina matrix (Ni/alumina), as deduced from XRD, EDX and TPR analyses (high reduction temperature (800-900°C)).[1-2] TEM and SEM reveal that the (Al)MIL-53 nanocrystals obtained by MW synthesis results after Ni-impregnation, calcination and Ni reduction in small Ni⁰ nanoparticles homogeneously dispersed in interwoven alumina nanosheets (Fig 1A). Mesoscopic Ni⁰/alumina lamellae are obtained with the conventional solvothermal employed with PET (Fig 1C). DRM results demonstrate superior performances of these new catalysts compared to Ni⁰/alumina catalysts prepared by conventional nickel impregnation of preformed alumina supports (Fig 1B). Also, the PET-made MIL-53 displayed as high activity as that of the catalyst derived from the MW-synthesized MIL-53.[4] The performances of MIL-53(Al)-derived samples for CM catalysis were shown to be higher than those of more conventional Ni-based catalysts (Fig 1D).[3]

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Influence of Nitrogen/Carbon Structure on the Stability of Immobilized Ruthenium Catalysts for CO₂ Hydrogenation to Formate

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Carbon dioxide (CO₂) is believed to be largely responsible for climate change and global warming. As a result, the direct hydrogenation of CO₂ to formic acid has garnered considerable attention as a promising strategy for achieving a sustainable circular-carbon economy by utilizing industrial CO₂ emissions. However, owing to its thermodynamic stability and chemically recalcitrant nature, CO₂ transformations are very challenging and usually proceed with the assistance of a catalyst. Accordingly, several homogeneous catalysts with exceptionally high activity have been reported for this transformation but the difficulties associated with the separation of homogeneous catalysts from the product mixture have greatly hindered their industrial adaptation. On the other hand, heterogeneous catalysts, which offer advantages of easy separation and reuse have received attention only recently and their development lags significantly behind. Hence, developing an efficient, simple, and affordable heterogeneous catalyst is a crucial task in the industrial realization of the CO₂ hydrogenation process to produce formic acid/formate.

Herein, we studied the catalytic behavior of nitrogen-doped carbon (NC)-immobilized ruthenium (RuCl₃) catalysts for CO₂ hydrogenation to formate. The NC supports were prepared by a facile one-step ionothermal carbonization process using adenine as the carbon and nitrogen source and MgCl₂ as the solvent/template. A well-mixed mixture of adenine and MgCl₂ (1:3, w/w) was subjected to carbonization in the temperature range of 700-900 °C under flowing N₂ for 1 h using the heating rate of 3°/min followed by washing and drying to get the NC supports. Ruthenium-loaded catalysts were prepared by impregnating NCs with RuCl₃ (2 wt. %) in refluxing methanol for 24 h, followed by washing and vacuum drying at 120 °C for 18 h. The catalysts were labeled as 2Ru/NC_x, where x indicates the carbonization temperature.

The total N content and pyrrolic-N structures decreased with increasing carbonization temperature, whereas the graphitic-N structures increased. CO₂ hydrogenation was carried out in a batch reactor using triethylamine as the basic additive to shift the reaction equilibrium in the forward direction. The effects of NCs' carbonization temperature, reaction temperature, and base concentration on the reaction activity were systematically investigated. The optimized 2Ru/NC750 catalyst showed excellent turnover numbers of 4468 in a 2 h and 18212 in a 12 h reaction at 120 °C and 8.0 MPa, and good stability, maintaining its original characteristics when recycled. The HRSTEM and XPS analyses revealed that ruthenium existed as highly dispersed atomic-scale Ru³⁺ species on the NC supports. The stability of prepared 2Ru/NC catalysts was also tested over five cycles. Deactivation of the catalysts was attributed to (1) loss of Ru³⁺, (2) migration of Ru³⁺, and (3) reduction of Ru³⁺ to Ru⁰ as evidenced by ICP and TEM analyses. Moreover, the catalyst stability decreased with increasing carbonization temperature which was ascribed to the loss of pyrrolic and pyridinic-N metal-binding sites at higher temperatures as determined by DFT calculation results. Thus, the superior performance of the 2Ru/NC750 catalyst was attributed to the strong binding of Ru to pyrrolic and pyridinic-N sites.

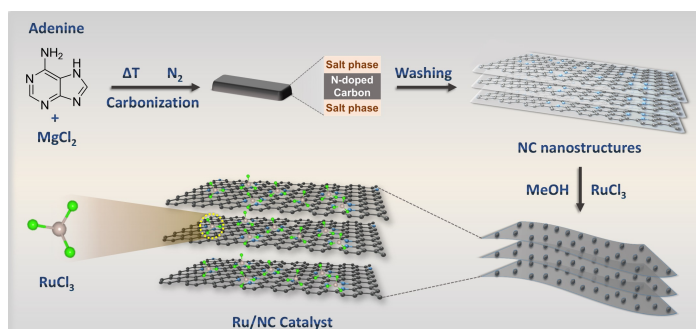


Figure 1: Catalyst's Synthesis Scheme

Single Catalytic Extrudate Reactor for Kinetic Studies of the Oxidative Coupling of Methane

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The conversion of abundant (bio)CH₄ resources into ethane and ethylene is an actual alternative to conventional petrochemicals paths. Ethylene is a key building block in the chemical industry and one of the most produced chemical intermediates with approximately 200 million metric tons in 2020. The oxidative coupling of methane (OCM) has been mainly studied these last decades with diluted methane concentration and powder catalyst. While optimized catalyst formulation can achieve promising CH₄ conversion and C₂ selectivity (25% and 60% respectively), kinetic and reactor design studies have been hampered by the lack of relevant data in relevant conditions. The OCM reaction is characterized by two features which makes reactor design a challenge:

1/ Its high intrinsic exothermicity ($2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$, $\Delta_r G^\circ_{1073\text{K}} = -153\text{ kJ}\cdot\text{mol}^{-1}$). More favored thermodynamically reaction is the total methane oxidation into carbon dioxide ($\Delta_r G^\circ_{1073\text{K}} = -800\text{ kJ}\cdot\text{mol}^{-1}$). In the case of CO₂ selectivity would increase, the heat release would create hot spots which may turn in reactor temperature run away.

2/ Gas phase reaction in the porosity of catalyst/bed. OCM reaction occurs at temperature above 800°C and up to 950°C. At this temperature gas phase contribution may dominate (radicals formation), especially at higher pressures. The complex interplay between radicals reactions and the catalytic surface reactions makes the prediction of the effects of diffusion limitations difficult.

As a matter of fact, measurement of intrinsic kinetic parameters shall be carried out i) in isothermal conditions and ii) with real catalyst pellet which size and porosity are relevant and representative of the industrial application.

In this study, we investigate the miniaturization of catalyst bed starting from a string pellet reactor configuration (Fig. 1 a) to a single extrudate reactor made of Mn-Na-W OCM catalyst on α -alumina support. A series of ceramic made reactors was designed to allow the testing of a string packing of pellets (4-6, representing 27- 42 mg) down to a single pellet under relevant conditions of contact time, temperature, feed composition and pressure (up to 10 bars). The set-up was miniaturized with only one extrudate of catalyst and a very low inlet flowrate, in order to approach isothermal condition. Results show on Fig. 1b, that the shaped catalyst on α -alumina presents the same conversions and activity than the powder catalyst, with a slight increase in C₂ selectivity.

We believe that the miniaturization of the reactor to a single extrudate shall allow the measurements of intrinsic catalytic parameters, especially for exothermic reaction operating at very high temperature such as OCM.

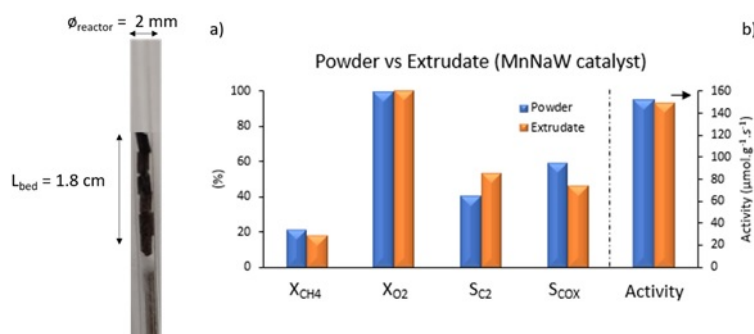


Figure 1: a) Example of a string pellet reactor configuration (with 6 pellets) allowing the decreases of the gas phase reaction and b) Comparison between powder and shaped catalysts at 3 bar and 800 °C, with an inlet feed of CH₄:O₂:N₂:CO₂ - 60:15:15:10.

Predicting the Stability of Single-Atom Alloy Catalysts Under Hydrogen Reactive Media

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Single-atom alloys (SAAs) are emerging materials containing isolated metal atoms dispersed on host metal surfaces, exhibiting unique reactivity compared with the corresponding monometallic counterparts. However, the stability of the SAA systems has hardly been studied, although, bulk segregation and/or sintering phenomena of the isolated atoms in the host metal have been commonly observed under reaction conditions. The aim of this work was to accurately predict the stability of single-atom Pt anchored on various metallic nanoparticles. Density Functional Theory (DFT) calculations coupled with environmental segregation energy analysis were performed to map the segregation trends of 22 different Pt-SAA surfaces under various hydrogen conditions (Figure 1). The results (recently published in *Appl. Surf. Sci.* 2021, 548, 14917) show the high stability of single-atom Pt in Ni, Co, Rh and Ir host metallic surfaces while no stability is predicted on Au and Ag surfaces. For Pd and Cu host supports, the single-atom Pt is found to be stable on specific surface facets and within definite temperature and pressure conditions. Through this presentation I would show how this environmental segregation model brings an important understanding of SAA systems through the prediction of surface atomic ordering changes under operating conditions which related to the reactivity will ultimately allow the design of more efficient catalysts.

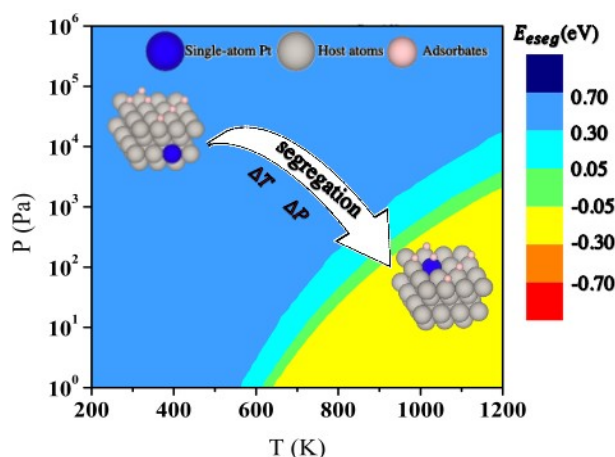


Figure 1: Schematic presentation of the scanned Environmental Segregation Energy evolution as a function of temperature and hydrogen pressure.

Multi-Elemental Analysis of Catalysts at ppm-Level and High-Speed Acquisition: Elemental Laser Microscopy

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Catalysis is of paramount importance in most industrial processes. Increasing reaction yields, helping to develop new sources of energy and reducing toxic manufacturing waste products are just the tip of the iceberg

Accurate characterization of catalysts improves the modeling of catalytic processes and provide information to unravel increasingly complex industrial problems. At present, chemical studies of catalysts are mostly based on bulk analysis, which lack spatial resolution. However, it is widely known that the elemental distribution of active elements is far from being homogeneous and thus valuable information is being missing. Current technology strives to achieve ppm concentration level at the micrometer scale and always at the cost of longer analysis time.

Even though, assuming longer analysis time does not solve one of the biggest challenges of catalyst characterization: the detection of light elements such as carbon.

Herein, we present the micrometer spatial distributions of active elements or poisons in internal diffusion-limited catalysts at the pellet scale. Elemental laser microscopy based on Laser-Induced Breakdown Spectroscopy (LIBS) technology has been used allowing an extreme sensitive multi-elemental and spatially-resolved analysis over industrial catalysts surfaces.

Carbon quantification at 60 times lower concentration limits than those of Electron Probe Micro Analysis (EPMA), at much higher speed and out of vacuum conditions are just some of the unique features of this technology for catalysis science. Our results provide a simultaneous monitoring of the distribution of the metallic precursor, organic additive and support impurities toward a better understanding of catalysts preparation processes; however, this is just one of the multiple envisaged applications. Spatially-resolved elemental information over a large dynamic range of concentration (from wt% up to few ppm) may change many other existing paradigms.

The extent to which elemental laser microscopy will impact catalysis science is yet to be defined and will be influenced by the ability of researchers to ask the good questions for which LIBS Elemental laser microscopy has a solution.

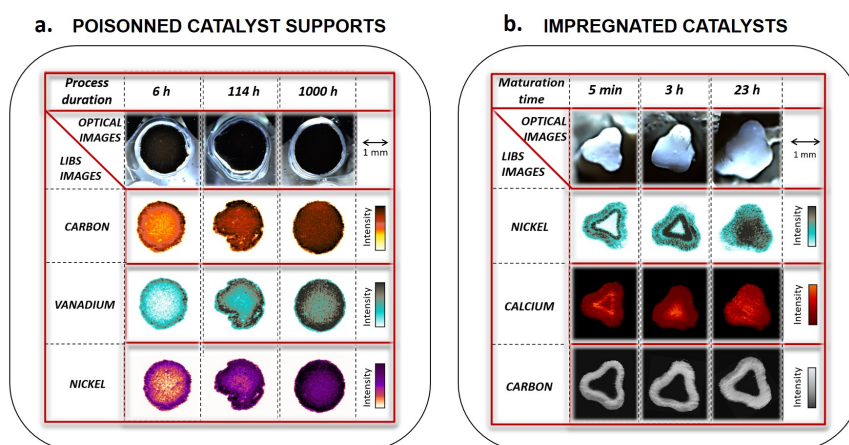


Figure 1: Example of elemental LIBS imaging of: a) Poisoned hydrotreating catalyst supports; b) Freshly impregnated catalysts

Acidity of Naphta Reforming Catalyst: 2,6-di-tert-Butylpyridine, a New Probe Molecule

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Introduction

Acidity of the naphtha reforming catalysts is crucial to promote the desired isomerization or dehydrocyclization reactions and reaction steps involving acidity. To do so, alumina is chlorinated up to 1 wt% to obtain a mild acidity [1]. Acidity is adjusted to be able to perform catalytic conversion while avoiding excessive cracking of the feed.

To this day, there is a lack of information concerning low acidity solids like alumina in the literature. Standard characterization methods such as infrared spectroscopy or thermodesorption of classic basic probe molecules are not suited for those kind of solids. 2,6-Di-tert-butylpyridine (2,6DTBPy) has already been used to quantify external acidity of zeolites[2], and will be performed in this study.

In addition to characterization, model reactions can be performed permitting a closer to reality analysis of catalysts and to further deepen the understanding of those kind of catalysts [3,4].

The isomerization of 3,3-dimethylbut-1-ene (3,3DMB1) is a great model reaction for the kind of solids mentioned previously. It has been found that this molecule fits a large panel of acidic solids with broad acidity range [5]. Its intermediate carbenium is formed onto Brønsted acid sites which fits the reaction pathway obtained during the reforming process.

Results and Discussion

Quantification of BAS was successful using 2,6DTBPy as shown in figure 1.a). The combination of this characterization and catalytic activity from the model reaction as pictured in figure 1.b), gives crucial informations about the samples. It appears that chlorine density (DCI) is the primary factor affecting the amount of acid sites of samples even though it is not the only one.

The second impacting factor is tin. It has already been shown through the reforming process that tin inhibits strong acid sites on the reforming catalyst. This study manages to show its influence through characterization with a decreasing number of BAS for Sn loaded catalysts. Furthermore, table 2 showing TOF of specific solids for the 3,3DMB1 isomerization indicates that Sn inhibits mainly inactive BAS. Indeed, a higher TOF for Sn loaded catalyst implies that despite BAS lowering, the activity of the catalyst does not decrease proportionally.

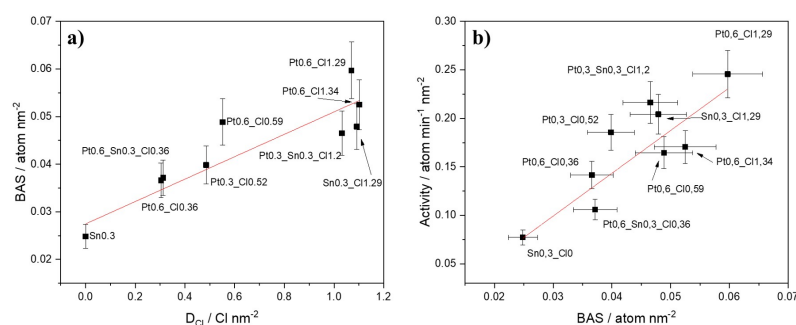


Figure 1: a) Number of BAS against density of chlorine. b) Activity of 3,3DMB1 isomerization against the number of BAS for each catalyst.

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Better Understanding the Structural Dynamics of Pt/CeO₂ Catalysts

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Context and purpose

Pt/CeO₂ catalysts are widely used in many redox reactions such as the oxidations of CO and hydrocarbons for automotive exhaust depollution and the water gas shift reaction. Their catalytic properties strongly depend on the coordination environment of Pt atoms. Pt can be dispersed during an oxidative treatment at moderate temperature while a reducing treatment triggers 3D particle formation. Even if such a structural dynamics has been extensively evidenced at the nanometer (crystallite) scale by transmission electron microscopies, its intra (surface, subsurface, bulk) and inter-crystallite Pt diffusion (grain, aggregate) length scale is poorly known. In this work, the latter has been investigated by an original method using mechanical mixtures of Pt/CeO₂ and CeO₂ to study inter-crystallite Pt diffusion scale.

Material and methods

A 0.83 wt% Pt/CeO₂ catalyst was prepared by wet impregnation using Pt(NH₃)₄(NO₃)₂ as a precursor and high surface area CeO₂ as a support, followed by calcination in air at 500 °C. Different mechanical mixtures of this solid with pure CeO₂ were prepared by sieving the powders between 10 and 50 μm and treating them under O₂ flow at 500 °C (OX500), then under H₂ flow at 500 °C (RED500). They were characterized before, during and after redox treatments by H₂-TPR and spatial characterization techniques such as SEM-EDS, in situ microRaman mapping and XPS.

Main results

As expected from the difference of Pt loading, energy-dispersive X-ray spectroscopy analysis of 50%Pt/CeO₂-50%CeO₂ revealed, at the initial state, a bimodal distribution of the Pt concentration (Fig. 1A). It validated the choice of the granulometry and the mixture composition to follow Pt diffusion. After redox cycles (OX500/RED500/OX500 for 1 h each), both populations were still observed, revealing the absence of Pt diffusion (no homogenization) at the ceria grain/aggregate scale. This feature was confirmed for a longer treatment (OX500/RED500/OX500, for 10 h each, Fig. 1A), showing a thermodynamic or a kinetic limitation of Pt diffusion.

As SEM-EDS results, in situ microRaman mapping of 50%Pt/CeO₂-50%CeO₂ showed, upon redox treatments at 500 °C, a bimodal distribution of the intensity of the ν(Pt-O) band at the oxidized state (Fig. 1B) and the Ce³⁺ electronic Raman band at the reduced state. A statistical treatment confirmed that the spatial repartition of Pt/CeO₂ and CeO₂ did not change. However, the presence of peroxo species was systematically evidenced on bare CeO₂ grains after reduction at 500 °C (map in Fig. 1C), which implies a slight reduction of CeO₂.

Moreover, H₂-TPR curves of different Pt/CeO₂ and CeO₂ mechanical mixtures presented two reduction peaks, corresponding (at increasing temperature) to Pt/CeO₂ and CeO₂ surface reduction. The latter is attributed to long-range hydrogen spillover, even if a slight (under the detection limit) Pt diffusion at the grain scale cannot be ruled out.

Major conclusions

This original methodology revealed that Pt diffusion within Pt/CeO₂ catalysts does not occur at the grain scale or is very limited after redox treatments at 500 °C. However, a long-range hydrogen spillover is likely occurring from Pt/CeO₂ to bare ceria grains, highlighting the complexity of structural dynamics.

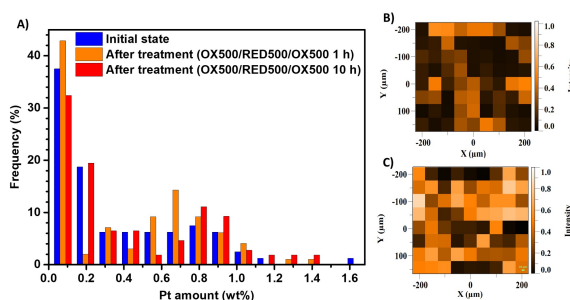


Figure 1: A) Pt loading distribution determined by EDS analysis of 50%Pt/CeO₂-50%CeO₂ mechanical mixture; B,C) Raman images of the relative intensity of the ν(Pt-O) band after oxidation at 500 °C (B) and of the band of peroxo species after reduction at 500 °C (C).

Room-Temperature CO Oxidation over Pt Particles Dispersed on $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_3$ Perovskites

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1-Introduction

Lately, perovskites have gained a lot of attention in the field of heterogeneous catalysis and have become the subject of many studies that focused on their use as active carrier materials [1-2]. Indeed, their intrinsic capacity to tolerate high levels of iron-exchange associated with the resulting electronic and ionic mobility make them very attractive as potential supports for catalytic applications. In the context of oxidation reactions, platinum-based catalysts have been highly investigated and were shown to be room-temperature active for CO oxidation when deposited on CeO_2 [3-4] and FeOx/TiO_2 [5] materials owing to oxygen supply from CeO_2 , TiO_2 , and FeOx as well as the formation of PtFe particles. Here we hope to achieve better performances than what has been reported so far by using an Fe-doped CaTiO_3 perovskite as a support for Pt particles.

2-Experimental part

$\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ perovskite materials, CTFX, with X=10, 30, 40, and 70% Fe, were synthesized via a modified Pechini method and the resulting gel was calcined at 600 °C. 1% wt. of Pt was then added to the perovskite by wet impregnation using a nitrate precursor. Subsequent to a second calcination at 400 °C, the following solids were obtained 1% Pt/CTF10, 1% Pt/CTF30, 1% Pt/CTF40 and 1% Pt/CTF70. These materials were then characterized by different physico-chemical techniques such as XRD, nitrogen sorption, TEM, H_2 -TPR, XAS. Finally, the samples were tested in CO oxidation reaction (2000 ppmv of CO in 10 000 ppmv of O_2), subsequent to a reductive pre-treatment at 300 °C under H_2 .

3-Results

The light-off curves of CO oxidation obtained for the prepared 1% Pt/CTFX catalysts are presented in Figure 1. It is clear that the catalyst with the highest doping of iron, i.e. 1% Pt/CTF70, is less active than the remaining 1% Pt/CTFX catalysts. More importantly, we notice room-temperature activity for 1% Pt dispersed on CTFX for Fe-doping levels ranging between 10 and 40%, with the better performance being noted for 1% Pt/CTF40 ($\approx 70\%$ CO conversion). Indeed, it would seem that until a certain level of iron doping ($\leq 40\%$), catalytic performances of perovskites are enhanced owing to an increase in the materials reducibility and oxygen mobility, as revealed through H_2 -TPR and XAS analysis.

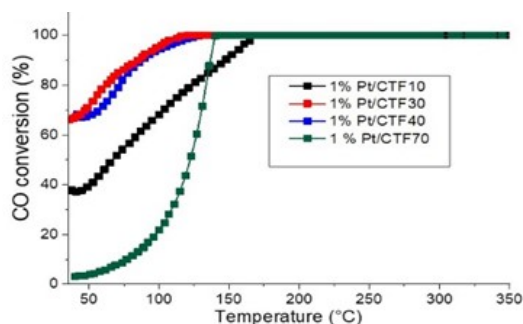


Figure 1: CO oxidation light-off curves of 1% Pt/CTF10, 1% Pt/CTF30, 1% Pt/CTF40 and 1% Pt/CTF70 after reduction at 300°C

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Effect of Cobalt Substitution on LaFeO₃ Catalysts for Propene Total Oxidation

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In recent years, volatile organic compounds (VOCs) have become one of the main contributors to air pollution [1]. Catalytic oxidation is one of the most efficient ways to eliminate VOCs. Perovskite oxides with the advantages of flexible composition, high thermal stability, superior redox capacities have been extensively applied in catalytic oxidation [2].

In this study, a series of B-site (cobalt, copper, and manganese) substituted LaFeO₃ perovskites were firstly synthesized by a citrate method and then tested in the total oxidation of propene, a model VOCs. As the outperformed dopant, the proportion of the cobalt was further varied. The physicochemical properties of the materials were fully characterized by TG/TDA, ICP analysis, FTIR, XRD, Raman, N₂ adsorption, H₂-TPR, and O₂-TPD. In addition, water influence, long-term stability, and kinetic study were also performed over the optimal catalyst.

The results showed that LaFeO₃-based perovskites were successfully synthesized by the citrate method, with specific surface areas of 6–10 m² g⁻¹ and average crystallite sizes of 26–49 nm. All catalysts could achieve 100% conversion of propene below 450 °C. Cobalt substituted catalyst showed higher activity than other B-site substituted ones. With increasing cobalt content from 0.1 to 0.3, the structure of LaFeO₃ was well maintained while the surface area decreased. Cobalt incorporation could greatly enhance the low-temperature reducibility and the oxygen mobility of the perovskite thus leading to better catalytic performance. A good correlation was established between the catalytic activity and the amount of the active oxygen species. As a cost-effective catalyst (T₉₀ = 337 °C, E_a = 58 kJ mol⁻¹), LaFe_{0.8}Co_{0.2}O₃ exhibited outstanding stability in cycling and long-term tests, as well as good water resistance, being a potential candidate catalyst for industrial applications. Moreover, the Power-Law model provided fairly good fits to the kinetic data (R² > 0.95) and suggested that the reaction order of oxygen and propene over LaFe_{0.8}Co_{0.2}O₃ were 0.2 and 0.3, respectively.

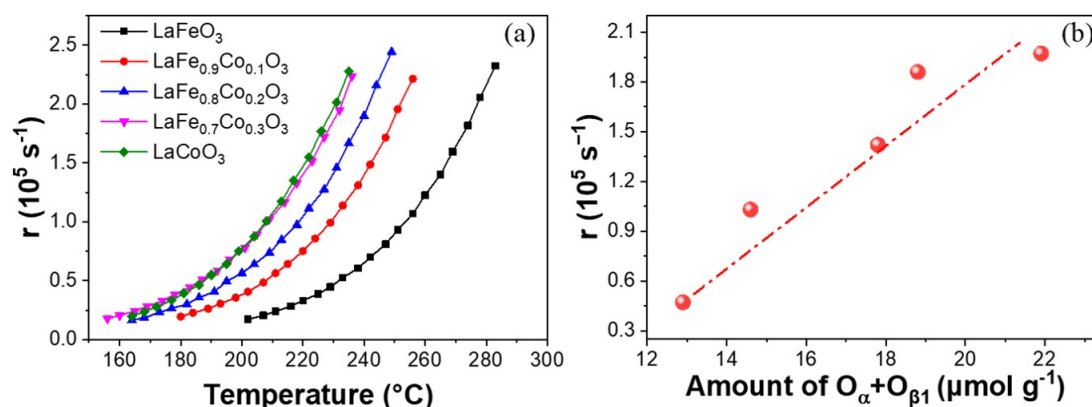


Figure 1: Figure 1 (a) Propene oxidation rate (r) of LaFe_{1-x}Co_xO₃ perovskites as a function of temperature (b) Correlation between r at 230 °C and the amount of desorbed oxygen species below 500 °C in O₂-TPD.

[1] C. He, J. Cheng, X. Zhang, M. Douthwaite, S. Pattison, Z. Hao, Chem. Rev. 119 (2019) 4471–4568.

[2] S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari, Chem. Rev. 114 (2014) 10292–10368.

Co-Mn-Al mixed oxides issued from Layered Double Hydroxide precursors for total oxidation of VOCs

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Volatile organic compounds (VOCs) are among the most common air pollutants emitted by the chemical and petrochemical industries. They are one of the main sources of photochemical reactions in the atmosphere, leading to various environmental risks for which severe restrictions, such as the European Parliament and Council Directive 2001/81/EC, have been established to regulate their emissions. As a result, the development of effective techniques to eradicate them is critical.

One of the most effective technologies for the elimination of VOCs is catalytic oxidation since it operates at much lower temperatures than conventional thermal treatment, resulting in energy savings. In addition, its high overall selectivity avoids the formation of by-products due to incomplete VOCs combustion, unlike other techniques such as thermal incineration. However, choosing the right catalyst for this type of treatment is a challenge. Mixed metal oxide catalysts are frequently used, apart from supported noble metals, as catalysts for the total oxidation of VOCs. An interesting way to obtain mixed oxide catalysts is the heat treatment of materials prepared by the "Layered double hydroxide"(LDHs) route under specific conditions. Indeed, after thermal treatment, mixed oxides are formed which have unique properties such as specific surface, porosity, thermal stability and good dispersion of metal oxides.

Among the metal oxides, manganese or cobalt oxides are the most interesting owing to their ability to reach variable oxidation states. Therefore, the synthesis of catalysts based on mixed oxides comprising these two elements seems to be very suitable for redox reactions and thereafter for VOCs oxidation.

In this work, a series of $Mn_xCo_{6-x}Al_2$ spinel oxides with x varying between 0 and 6 and keeping a molar ratio of $(Mn+Co)/Al$ equal 3, are synthesized via the LDH route by co-precipitation at constant pH. These materials were then characterized by different techniques such as X-Ray Diffraction (XRD), Thermal Analysis (TDA/TGA), Temperature Programmed Reduction by hydrogen (H_2 -TPR)

Because industrial use requires the shaping of catalytic materials, one of these mixed oxides was deposited on an alumina support in the form of pellets or foam using a simple dip-coating technique from slurry containing the powdered oxides and other additives to achieve their dispersion.

This presentation will elucidate the catalytic activities of the synthesized materials towards the oxidation of a VOC which is ethanol taken as model molecule as well as the physicochemical properties of our materials.

Effect of Gas-Treatments of Cu-Al Layered-Double Hydroxides on Catalytic Reduction of NO by CO Under Oxidative and Wet Conditions

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Removal of NO is an important step in flue gas purification processes which would otherwise corrode the inner walls of the gas transfer lines because of its acidic nature upon reaction with water and have a detrimental effect on the environment. NO removal can be achieved by catalytic selective reduction to non-toxic N₂, using reductants like CO, H₂ etc. Reportedly, CO and NO co-exist in flue gases like that from cement and steel industries. Therefore, NO reduction by CO (indicated as 'CO+NO') is an attractive approach for flue gas purification as it eliminates both CO and NO (both are toxic gases) simultaneously. Copper-based catalysts have reportedly exhibited good performance in CO+NO reaction thanks to the presence of Cu(+1), Cu(0) species. These active copper species are stabilized by partially reducing the predominant Cu(2+) species under inert and reducing gas atmospheres and/or oxidising pre-reduced copper species (Cu(1+) and Cu(0)) under oxidising gases at elevated temperatures.

In this study, Cu-Al mixed oxides are obtained from Layered Double Hydroxide (LDH) precursor (synthesized by co-precipitation) and activated under controlled atmospheres at 500°C: air, He, 1 vol% CO/He and CO₂ (indicated as CuAl-X where X represents the treatment gas). Moreover, under real operating conditions, CO₂, O₂ and H₂O co-exist with NO and CO in the industrial flue gases and considerably affect CO+NO reaction. However, not many authors have considered these gas components in the reactant gas mixture for their respective CO+NO studies. Therefore, the catalytic tests in this study were performed under wet and oxidative conditions (O₂ = 8.8 vol% and H₂O = 8.6 vol%).

The catalytic activity measurements (**Figure 1**) confirm different activities for CuAl-X materials under the presence and absence of water in the reactant gas stream. Water had a promotional effect on all CuAl-X materials favouring NO reduction except for CuAl-CO₂. Also, CuAl-CO₂ showed NO reduction activity in absence of water unlike the rest of the CuAl-X samples. To explain the trends observed in catalytic activities over the CuAl-X materials, different characterization experiments like XRD, H₂-TPR, N₂-physisorption and TGA were performed. Among the physical properties, dispersion of Cu(2+) governed the catalytic activities for CuAl-X samples. However, exceptional NO reduction yield observed for CuAl-CO₂ from the rest of the CuAl-X samples was attributed to probable interaction between carbonate species formed during CO₂-treatment and NO thereby outlying the effect of Cu(2+) dispersion in the sample. The characterization results and inferred correlations will be discussed in the presentation.

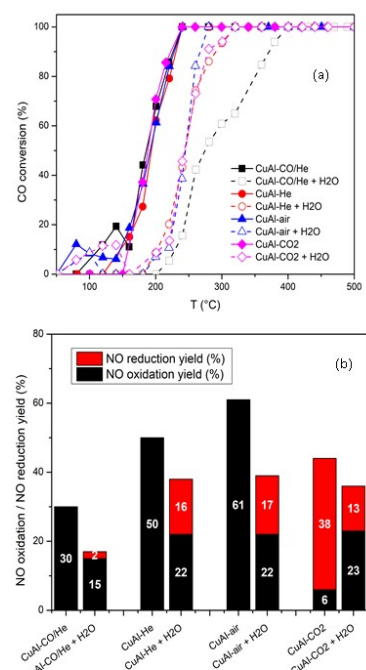


Figure 1: (a) CO conversion (b) NO oxidation and reduction yield for CuAl-X materials

Competitive Adsorption of NO_x and Ozone on the Catalyst Surface of Ozone Converters: In-Situ DRIFTS Measurements

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Pollution by ozone and NO_x is a major concern at ground level because of their impact on human health and natural environment. Both compounds are known to interact, linked by the cycle:



Ozone is also a major pollutant in aircrafts because the cruise altitude is at a level where the ozone concentration exceeds the upper limit level specified in Federal Aviation Regulations for long flights (100 ppbv). Catalytic converters, allowing the treatment of bleed air at 200°C, are classically used in aircrafts to reduce ozone. In future more electrical aircrafts, ozone converters will not benefit from the high temperature of bleed air and will have to work efficiently at temperatures below 100°C.

Besides this issue and depending on the altitude, ozone and NO_x can be present simultaneously or one after the other, and if the interaction between them is well studied in the atmosphere, the way they compete to adsorb and react at the catalyst surface is much less studied. Our group published a preliminary study showing that the presence of NO_x in the air is detrimental to the performances of the ozone converter at low temperature. Experiments at 40°C showed a stable conversion of ozone in pure air and a rapid decrease of the conversion in the presence of NO_x. However, the poisoning effect was found to be reversible; NO_x compounds were desorbed from the surface either when pure air was injected and were no more adsorbed when air + NO_x was injected at higher temperature (120°C).

Based on these preliminary studies, a deeper examination of the surface phenomena was necessary for the understanding of this competition.

After having synthesized several catalysts supported on alumina and containing Pd and/or MnO_x, they were exposed to ozone and/or NO with in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis. A series of in-situ DRIFTS analysis was effectively carried out under different consecutive gas sequences to further understand the above-mentioned ozone and NO_x competition and catalyst regeneration as well as to elucidate the main intermediates formed during the adsorption or co-adsorption of O₃ and NO_x.

It has proven that on palladium and manganese-based catalysts, the inhibition effect of nitrogen oxides was due to the formation of monodentate nitrites, monodentate, bidentate and bridged nitrates, which were all extremely hard to be transformed into gaseous NO_x, either by oxidation or by thermal treatment, and to desorb from the catalyst surface. Interestingly, monodentate nitrites could be eliminated if the catalyst went through a co-adsorption of NO_x and ozone prior to exposure in clean ozone flow as shown in the figure. This transformation could be the reason why the catalytic conversion of ozone could return to its original value before the poison effect of nitrogen oxides.

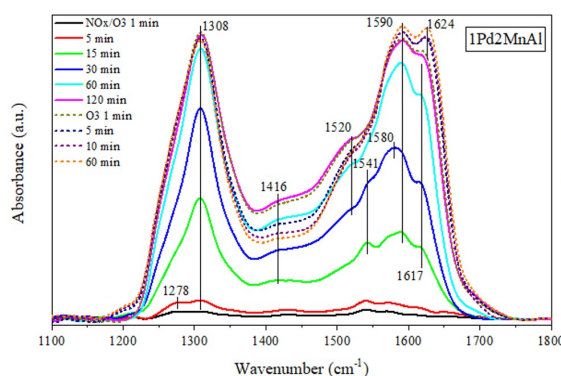


Figure 1: NO_x/O₃ co-adsorption for 120 min prior to O₃ exposition for 60 min

The Unexpected Role of NO_x During Catalytic Ozone Abatement at Low Temperatures

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Peaks in ozone concentration at ground level are increasing and constitute a major health issue of ambient air pollution. The ozone concentration in urban air at ground level is usually less than 100 ppb but it can exceed this threshold in polluted seasons.

It is therefore necessary to eliminate the ozone from the air to preserve human health. Decomposition of ozone can be done by thermal, chemical or catalytic treatment. The catalytic decomposition of ozone can be performed using various catalysts, and it is considered as the most widely used ozone elimination process due to the mild reaction conditions, high yield and low operational cost.

The catalytic decomposition of ozone was carried out at 40 °C over a 5wt%Pd/Al₂O₃ catalyst in the presence or absence of nitrogen oxides traces. NO_x were produced during generation of ozone from air. Two reactor set-ups were used to examine the possible effects of NO_x poisoning, namely, a fixed bed with a powder catalyst and a ceramic monolith coated with the same catalyst. It was shown that NO_x significantly poisoned the catalyst, resulting in a decrease of ozone conversion over time on stream. NO_x-free ozone feed can lead to the total recovery of the initial catalytic activity indicating a reversible poisoning effect (Figure 1).

Although a simple lab-scale solution is to use pure oxygen in the ozone generator, the phenomenon highlights the possible impact of ambient pollution on the efficiency and lifetime of actual ozone converters, especially at low temperatures.

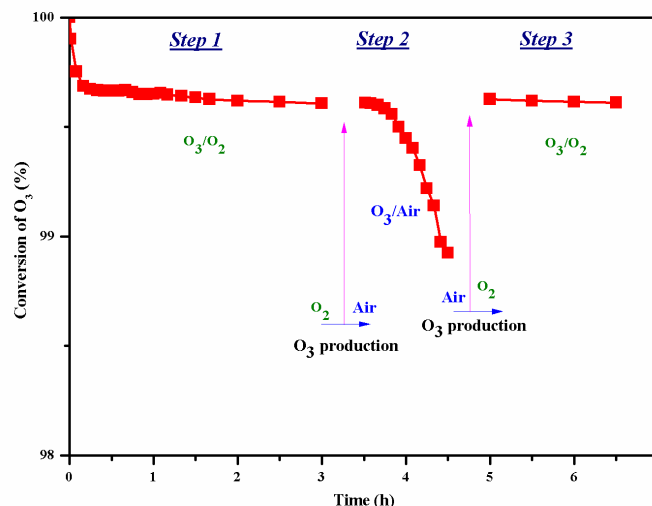


Figure 1: Consecutive ozone decomposition tests at 40 °C; O₃ alternatively generated from pure O₂, air and pure O₂ gas treatments of the catalyst.

Glass Furnaces Emissions Measurement: SO₂ Storage Catalyst Optimization for NO_x Electrochemical Sensors Protection

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Glass-melting furnaces emit more than 25 tons of nitrogen oxides (NO_x) per year. In this respect, the development of in-situ on-line, cheap and robust techniques, like electrochemical gas sensors, to on-board control NO_x emissions under harsh environments become urgent. One of the main issues is the presence of sulphur oxides (SO_x) in the stream, which can strongly poison the NO_x gas sensor. The objective of this study is to develop a "barrier" to sulfur oxides, located up-stream, to protect NO_x sensors from sulfur poisoning. Such materials must exhibit bi-functional properties, combining a good catalytic activity for the oxidation of SO₂ to SO₃ with a high SO_x storage capacity (SSC) into sulfates. Furthermore, the overall NO_x concentration in the stream must not be modified, excluding the NO_x adsorption and storage on the barrier material. Moreover, this latter must be periodically regenerated in air in a temperature range suitable with the application, typically below 700°C.

This study reports the SSC measurements of different catalysts at 500°C, a representative temperature of a glass-melting furnace exhaust. The exhaust stream was composed of 75 ppm of SO₂, 0.9% O₂ and 2% H₂O (overall flow: 30 L/h). The SO_x desorption was carried out during Temperature-Programmed Oxidation (TPO) measurements in 20 %O₂/He up to 600°C. On-line SO₂ analysis, performed with a multi-gas FTIR analyzer (MKS 2030), was used to quantify the SSC.

Barium oxide supported on alumina (surface specific area (SSA) = 193 m²/g), a material involved in NO_x storage catalytic systems and known for its sulfur adsorption ability, was chosen as a reference SO_x barrier. At 500°C, the SO_x adsorption is expected to be predominant with respect to NO_x one as the NO oxidation of NO₂ is thermodynamically limited at this temperature. Organized mesoporous silica materials (SBA-15 and MCM-41 calcined at 900°C), with high specific surface areas (406 and 1026 m²/g respectively) and porous volumes, were selected to support BaO and CuO active phases. A negligible SSC was observed on 20wt.%Ba/SBA-15 and 20wt.%Ba/MCM-41 (Fig. 1), which suggests that barium oxides cannot catalyze the oxidation of SO₂ to SO₃. Alumina can oxidize SO₂ and Ba/Al₂O₃ (20 wt.% Ba) displays a SSC value of 557 μmol_{SO2}/g (Fig. 1). SO_x storage is full for only 10 minutes, which could be related to the limited SSA of alumina. The addition of CuO on silica by wet impregnation promotes the formation of SO₃. High SSC values (Cads = 827 μmol_{SO2}/g) were achieved on 15wt.%CuO/SBA-15 (Fig. 1), higher than those reported in the literature for similar materials. After around 1 h of stream, the SO₂ concentration reaches a plateau at 12 ppm, suggesting that more than 80% of SO₂ is converted into SO₃ at 500°C on this catalyst. The impact of the Cu loading and its association with BaO on the SSC have been explored during successive storage/TPO cycles. In-situ DRIFTS measurements will be also performed to evaluate the NO_x impact on SSC.

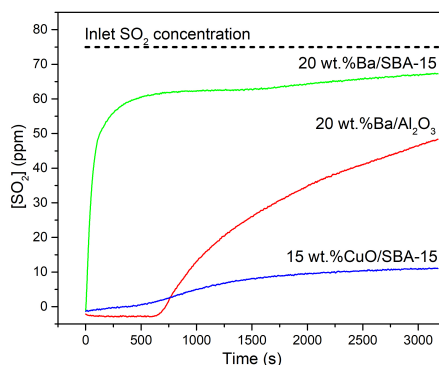


Figure 1: SO₂ breakthrough curves of samples Ba/Al₂O₃, Ba/SBA-15 and CuO/SBA-15 at 500°C. Feed gas: 100 ppm SO_x (75 ppm SO₂), 0.9% O₂, 2% H₂O in He