# **10th Czech-Italian-Spanish Conference (CIS-10)** on Molecular Sieves and Catalysis

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BOOK OF ABSTRACTS 9-12 June 2025 Liblice

# Program Book of Abstracts



## 10<sup>th</sup> Czech-Italian-Spanish Conference on Molecular Sieves and Catalysis (CIS-10)

Liblice Castle June, 9-12 2025



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![](_page_6_Figure_10.jpeg)

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![](_page_6_Figure_15.jpeg)

![](_page_6_Picture_16.jpeg)

![](_page_6_Picture_17.jpeg)

![](_page_6_Picture_18.jpeg)

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![](_page_7_Picture_2.jpeg)

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![](_page_7_Picture_6.jpeg)

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9. 6. 2	025		
18:00		Registration	
20:00		Welcome Party	
10. 6. 2025			
8:4	45	Opening	
	Chair:	Jiří Čejka, Girolamo Giordano	
9:00	PL1	<u>Cristina Martínez</u> DESIGNING ZEOLITE-BASED CATALYSTS FOR INDUSTRIALLY RELEVANT CHEMICAL PROCESSES	
9:45	OP1	<b>E. Giglio</b> , G. Ferrarelli, F. Salomone, E. Corrao, S. Bensaid, M. Migliori, R. Pirone, G. Giordano HIERARCHICAL ZEOLITES FOR DIMETHYL ETHER DEHYDRATION INTO LIGHT OLEFINS	
10:00	OP2	<b>P. Sánchez-Morena</b> , J. Jurado-Sánchez, C. Márquez-Álvarez, L. Gómez-Hortigüela, J. Pérez-Pariente EXCEPTIONAL CATALYTIC ACTIVITY OF GERMANOSILICATE GTM-4 IN THE OXIDATION OF CYCLOHEXENE WITH MOLECULAR OXYGEN	
10:15	OP3	<b><u>E. Shamma</u></b> , A. Seidlová, J. Přech, M. Opanasenko, M. Shamzhy XYLENE ISOMERIZATION OVER IWW ZEOLITE WITH A THREE-MODAL PORE STRUCTURE: THE EFFECT OF CRYSTAL MORPHOLOGY	
10	:30	Break	
	Chair:	Maksym Opanasenko, Rosa María Martín-Aranda	
11:00	OP4	<b>A. López Albero</b> , D. de la Calle, J. Cueto, M. Alonso-Doncel, D.P. Serrano SYNTHESIS AND CATALYTIC PROPERTIES OF ZSM-11 ZEOLITES WITH CONTROLLED NANOARCHITECTURES	
11:15	OP5	N. Uricochea, G. Morales, <u>M. Paniagua</u> , J.A. Melero ENHANCED ALDOL CONDENSATION OF BIOMASS-DERIVED LEVULINIC ACID AND FURFURAL USING METAL-MODIFIED ACID ZEOLITES FOR THE PRODUCTION OF AVIATION FUEL INTERMEDIATES	
11:30	OP6	<u>A. Olšovská</u> , M. Kamlar, J. Veselý, J. Čejka, M. Mazur ANCHORING Pd NANOPARTICLES TO ZEOLITE SURFACE SILANOLS TO DEVELOP HETEROGENEOUS TSUJI-TROST ALLYLATION CATALYSTS	
11:45	OP7	<u>M. Kubů</u> , V. Přibyl, M. Shamzhy SYNTHESIS AND CHARACTERIZATION OF -EWT ZEOLITE	
12:00		Lunch	
	Chair:	Pavla Eliášová, Enrico Catizzone	
14:00	OP8	I. Arnaiz, L. Perea, Y. Awoke, M. Sánchez-Sánchez, M. Grande-Casas, I. Diaz, C. Márquez-Alvarez, E. Sastre SYNTHESIS OF ZSM-5 FROM NATURAL MORDENITE FROM SPAIN AND THE APPLICATION IN MTH PROCESS	

14:15 ODO S Kolosár P.A. Diddams M. Mazur	S Kolocár D.A. Diddams M. Mazur		
SYNTHESIS OF ZEOLITE-SUPPORTED BIMETALLIC NANOPARTICLES FOR LIGNIN VALORISATION			
14:30 OP10 <b>R. de la Serna</b> , I. Arnaiz, J. Jurado, C. Márguez-Álvarez, J. Pérez-Parier	nte,		
L. Gómez-Hortigüela	,		
INVERSION OF CHIRALITY IN GTM-4 ENANTIO-ENRICHED ZEOLITE DRI	IVEN		
BY A MINOR CHANGE OF THE STRUCTURE-DIRECTING AGENT			
14:45 OP11 P. Bruno, E. Catizzone, F. Pietramale, M. Migliori, R. Mancuso, B. Gab	P. Bruno, E. Catizzone, F. Pietramale, M. Migliori, R. Mancuso, B. Gabriele,		
BIOGAS VOC VALORIZATION: THE CASE OF ZEOLITE-CATALYZED D-LIN	<b>IONENE</b>		
ETHOXYLATION			
15:00 OP12 J. Xie, J. Přech, M. Kubů, M. Mazur, J. Čejka			
PALLADIUM/ZEOLITE NANOCLUSTERS IMPROVE SELECTIVITY FOR PA	RTIAL		
HYDROGENATION OF ALKYNES			
15:15 OP13 D. de la Calle, J. Cueto, R.A. García-Muñoz, D.P. Serrano	OF		
FURFURAL AND CYCLOPENTANONE USING TITANIUM OXIDE-MODIFI	ED USY		
ZEOLITES			
15:30 OP14 Y. Zhang, C. Bornes, J. Přech, M. Shamzhy			
QUANTIFICATION OF Zr-ACID SITES IN ZEOLITES: IN SITU FTIR AND N	MR		
15:45 OP15 I. Arnaiz, C. Márquez-Alvarez, M. Zubimendi, M. Asunción Molina, A.I	M. Beale,		
CATALYTIC TRANSFORMATION OF DIALKYLUREAS INTO METHANE BY	' Ru-MOFs		
16:00 Excursion Lobeč Brewery			
20:00 Barbecue (if weather allows)			
11. 6. 2025			
Chair: David Serrano, Domenico Caputo			
9:00 PL2 Michal Otyepka			
2D-CHEMISTRY OF FLUOROGRAPHENE TOWARD FUNCTIONAL GRAPH	HENE		
DERIVATIVES FOR CATALYTIC APPLICATIONS			
9:45 OP16 M. Kamlar, S. Putatunda, I. Císařová, J. Veselý			
TYPE REACTION	IG CONIA-ENE		
10:00 OP17 <b>M. Pitínová</b> , A. Krnáčová, A. Shafiq, I. Danylo, I., Koláčný, I. Luxa, M. V	/eselý		
STYRENE HYDROFORMYLATION CATALYZED BY RHODIUM SUPPORTE	D ON 3D		
AND 2D TRANSITION METAL DICHALCOGENIDES			
10:15 OP18 M. Mancinelli, C. Bonadiman, R. Tassinari, B. Davide, D. Enrico, C. Ca	terina,		
A. Pavese, A. Martucci			
ASSESSIVIEINT OF ZEOLITE EFFICIENCY IN HEAVY IVIETAL REMOVAL FRO			

Chair:		Michal Mazur, Patricia Pizarro		
11:00	OP19	<u>C.A. Chirinos</u> , P.J. Megía, A.J. Vizcaíno, J.A. Calles, A. Carrero ENHANCED OXIDATIVE STEAM REFORMING OF BIO-OIL AQUEOUS PHASE USING NOBLE METAL-DOPED Co/CeO₂/SBA-15 CATALYSTS		
11:15	OP20	K. Knotková, S. Essid, J. Halamek, R. Bulánek THE ISSUE OF COPPER ENCAPSULATION IN MICROPOROUS MATERIALS		
11:30	KL1	Mariya V. Shamzhy FT-IR SPECTROSCOPY FOR CHARACTERIZATION OF SOLID CATALYSTS		
12:00		Lunch		
Chair:		Michal Horáček, Carlos Marquez Alvarez		
14:00	OP21	D. Valdivieso-Vera, I. Santos-López, I. Barroso-Martín, E. Rodríguez-Castellón, G.A. Flores-Escamilla, J. Cano, <u>M.O. Guerrero-Pérez</u> BIOFUEL SYNTHESIS FROM SHORT-CHAIN ALCOHOL CONDENSATION OVER Cu/MgAI CATALYSTS		
14:15	OP22	<b><u>G. Pérez-Martín</u></b> , J. Cueto, M. Paniagua, G. Morales, J.A. Melero, D.P. Serrano CONVERSION OF FURFURAL INTO VALUABLE BIOPRODUCTS CATALYZED BY ZrO <sub>2</sub> -MODIFIED NANOCRYSTALLINE ZSM-5 ZEOLITE		
14:30	OP23	<u>K. Veselá</u> , J. Přech ZEOLITE-AMINE COMPLEX CATALYZES MEERWEIN-PONNDORF-VERLEY TYPE HYDROGEN TRANSFER REACTIONS		
14:45	OP24	<b><u>E. Martín</u></b> , P. Gabal, A. Lwazzani, J.H. Badia, J. Guilera ENHANCING MACROPOROSITY IN SHAPED ZEOLITES FOR HYDROCRACKING		
15:00	OP25	A. Erlebach, D. Willimetz, I. Saha, C. Lei, T. Benešová, C. Bornes, C.J. Heard, L. Grajciar PREDICTIVE DYNAMICAL MODELLING OF ZEOLITIC CATALYSTS VIA A FLEXIBLE REACTIVE MACHINE LEARNING FRAMEWORK		
15:15	OP26	M. Inés Ávila, M.M. Alonso-Doncel, J. Cueto, L. Briones, G. Gómez-Pozuelo, J.M. Escola, D.P. Serrano, A. Peral, J.A. Botas EFFECT OF ION-EXCHANGED H-USY ZEOLITES ON THE CATALYTIC UPGRADING OF PYROLYSIS LIGNIN-DERIVED BIO-OILS		
15:30	OP27	T. Nechvílová, L. Dolejšová Sekerová, E. Vyskočilová, I. Paterová EXPLORING THE BASICITY OF THERMOLABILE HYDROTALCITE CATALYSTS: THEIR ROLE IN ALDOL CONDENSATION OF CITRAL WITH PENTAN-2-ONE AND OPTIMIZATION OF ANTHRANILIC ACID SORPTION AS METHOD FOR BASICITY DETERMINATION		
15:45		Break		
	Chair:	Jan Veselý, Paolo Aprea		
16:15	OP28	A. Díaz, J. Cueto, D.P. Serrano, <u>I. Moreno</u> CATALYTIC HYDROPYROLYSIS OF CHLORELLA VULGARIS		
16:30	OP29	<u>A. Shafiq</u> , M. Pitinova, I. Danylo, M. Vesely HYDROGENATION OF CINNAMALDEHYDE BY PLATINUM SUPPORTED ON 2D AND 3D TRANSITION METAL SULFIDES		

16:45	OP30	L. Amodio, J. Cueto, A. Souza, J. López, H. Hernando, <u>P. Pizarro</u> , D.P. Serrano DEHALOGENATION OF WEEE PLASTICS VIA LOW-PRESSURE HYDROPYROLYSIS OVER PD-SUPPORTED CATALYSTS	
17:00	OP31	J. Moravčík, L. Kaluža METAL OXIDE CATALYSTS FOR CARBON-CARBON CONDENSATION REACTIONS OF BIOALCOHOLS	
17:15	OP32	<u><b>M. Linares</b></u> , A. Pérez, M. Orfila, R. Sanz, J. Marugán, R. Molina, J.A. Botas SYNTHESIS AND MACROSCOPIC SHAPING OF $La_{0.8}A'_{0.2}NiO_{3\pm\delta}$ (A' = AI, Ca AND Ba) PEROVSKITES FOR RENEWABLE H <sub>2</sub> PRODUCTION BY THERMOCHEMICAL WATER SPLITTING	
17:30	OP33	<u>J. Vysloužil</u> , P. Volfová PRAGOLAB AND ELECTRON MICROSCOPY	
17:45	OP34	<u>G. Morales</u> , F.J. Landazábal, M. Ventura, M. Paniagua, J.A. Melero SULFONIC ACID-MODIFIED SBA-15 SILICAS FOR THE PRODUCTION OF AVIATION FUEL PRECURSORS FROM ACETOIN	
18:00	OP35	<u>R. Kendra</u> , L. Grajciar FREE ENERGY CALCULATIONS IN ZEOLITE SYSTEMS USING OPTIMAL GRID REFINED (OGRE) UMBRELLA SAMPLING	
19:	:30	Farewell Dinner	
12. 6.	2025		
12. 6.	2025 Chair:	Roman Bulánek, Manuel Moliner	
12. 6. 9:00	2025 <i>Chair:</i> PL3	Roman Bulánek, Manuel Moliner         Girolamo Giordano       BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTS	
12. 6. 9:00 9:45	2025 Chair: PL3 OP36	Bio-Alcohols conversion: THE ROLE OF ZEOLITIC CATALYSTS         J. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. Orcajo         NEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND         VALORIZATION	
12. 6. 9:00 9:45 10:00	2025 Chair: PL3 OP36 OP37	Roman Bulánek, Manuel MolinerGirolamo GiordanoBIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTSJ. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. OrcajoNEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND VALORIZATIONP. Topka, K. Soukup, J. Kupčík, J. Balabánová, O. Šolcová ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITY	
12. 6. 9:00 9:45 10:00	2025 Chair: PL3 OP36 OP37 OP38	Roman Bulánek, Manuel MolinerGirolamo Giordano BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTSJ. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. Orcajo NEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND VALORIZATIONP. Topka, K. Soukup, J. Kupčík, J. Balabánová, O. Šolcová ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITYJ.V.C. Carmo, A.C. Oliveira, C. Cardoso, E. Rodríguez-Castellón, J. Jimenez-Jimenez Cu-CONTAINING YTRIUM ALUMINUM GARNET FOR ETHYLBENZENE OXIDATION: EFFECTS OF CU CONTENTS ON THE SELECTIVITY TO ACETOPHENONE	
12. 6. 9:00 9:45 10:00 10:15	2025 Chair: PL3 OP36 OP37 OP38 :30	Roman Bulánek, Manuel MolinerGirolamo Giordano BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTSJ. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. Orcajo NEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND VALORIZATIONP. Topka, K. Soukup, J. Kupčík, J. Balabánová, O. Šolcová ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITYJ.V.C. Carmo, A.C. Oliveira, C. Cardoso, E. Rodríguez-Castellón, J. Jimenez-Jimenez Cu-CONTAINING YTRIUM ALUMINUM GARNET FOR ETHYLBENZENE OXIDATION: EFFECTS OF CU CONTENTS ON THE SELECTIVITY TO ACETOPHENONEBreak	
12. 6. 9:00 9:45 10:00 10:15 10:50	2025 Chair: PL3 OP36 OP37 OP38 :30 KL2	Roman Bulánek, Manuel MolinerGirolamo Giordano BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTSJ. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. Orcajo NEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND VALORIZATIONP. Topka, K. Soukup, J. Kupčík, J. Balabánová, O. Šolcová ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITYJ.V.C. Carmo, A.C. Oliveira, C. Cardoso, E. Rodríguez-Castellón, J. Jimenez-Jimenez Cu-CONTAINING YTRIUM ALUMINUM GARNET FOR ETHYLBENZENE OXIDATION: EFFECTS OF Cu CONTENTS ON THE SELECTIVITY TO ACETOPHENONEBreakJoaquín Pérez-Pariente ON THE RECOVERY OF FORGOTTEN KNOWLEDGE AND ITS APPLICATION IN MODERN CATALYSIS. A PERSONAL VIEW	
12. 6. 9:00 9:45 10:00 10:15 10:50	2025 Chair: PL3 OP36 OP37 OP37 OP38 :30 KL2 :20	Roman Bulánek, Manuel MolinerGirolamo Giordano BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTSJ. Tapiador, P. Leo, D. Choquesillo-Lazarte, G. Orcajo NEW MANGANESE-BASED MOF MATERIAL FOR CO2 ADSORPTION AND VALORIZATIONP. Topka, K. Soukup, J. Kupčík, J. Balabánová, O. Šolcová ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITYJ.V.C. Carmo, A.C. Oliveira, C. Cardoso, E. Rodríguez-Castellón, J. Jimenez-Jimenez Cu-CONTAINING YTRIUM ALUMINUM GARNET FOR ETHYLBENZENE OXIDATION: EFFECTS OF Cu CONTENTS ON THE SELECTIVITY TO ACETOPHENONEBreakJoaquín Pérez-Pariente ON THE RECOVERY OF FORGOTTEN KNOWLEDGE AND ITS APPLICATION IN MODERN CATALYSIS. A PERSONAL VIEWClosing	

POSTERS			
Po01	<u>N. Benmebirouk-Pareja</u> , A. Plá-Hernández, A.E. Palomares REDUCTION OF CHLORATES IN THE AQUEUS PHASE BY SUPPORTED PLATINUM CATALYST		
Po02	P. Lafuente, <u>R. M. Blanco</u> , M. Sánchez-Sánchez, E. Sastre NEW AND EFFEICENT IN-SITU SUPPORT OF ENZYMES BASED ON THE AMORPHOUS PRECURSOR OF A SUSTAINABLE ZIF-8		
Po03	F. Rosso, A. Airi, H. Tabatabaeizadeh, M. Signorile, S. Galliano, S. Bordiga, V. Crocellà, <u>F. Bonino</u> DESIGN OF EXPERIMENTS APPROACH APPLIED TO THE STUDY OF THE HYDROTHERMAL SYNTHESIS OF METAL-SUBSTITUTED ZEOLITES		
Po04	M. Cavallo, M. Dosa, R. Nakazato, N. G. Porcaro, M. Signorile, M. Quintelier, J. Hadermann, N. C. Rosero-Navaro, K. Tadanaga, S. Bordiga, V. Crocellà, <u>F. Bonino</u> ATR-IR STUDY OF LAYERED DOUBLED HYDROXIDE AS ELECTROCATALYSTS FOR CO2RR		
Po05	M. Roldán-Matilla, <u>A. Cerpa-Naranjo</u> , M. L. Rojas-Cervantes, I. Lado-Touriño, M. Fuencisla-Gilsanz, J. Pérez-Piñeiro METAL NANOCLUSTERS ON PEGYLATED GRAPHENE OXIDE FOR CATALYTIC APPLICATIONS		
Po06	<u>M. Franc</u> , J. Veselý ASYMMETRIC SYTHESIS OF SPIROPYRROLIDINES USING SYNERGISTIC CATALYSIS		
Po07	R. de la Serna, J. Jurado-Sánchez, J. Pérez-Pariente, <u>L. Gómez-Hortigüela</u> HOST-GUEST TRANSFER OF CHIRALITY DURING ASYMMETRIC CATLYSIS IN GTM CHIRAL ZEOLITE MATERIALS		
Po08	J. Jurado-Sánchez, R. de la Serna, C. Márquez-Álvarez, J. Pérez-Pariente, L. Gómez-Hortigüela SYSTEMATIC STUDY OF THE SYNTHESIS OF THE CHIRAL GERMANOSILICATE GTM-4 AT DIFFERENT GE CONTENTS		
Po09	<b>F. Krakl</b> , Ch. J. Heard, P. Eliášová, M. <i>Mazur</i> ALUMINIUM CONTENT IN MFI ZEOLITES AS A FACTOR INFLUENCING THE THERMAL STABILITY OF Pd AND Pt NANOPARTICLES		
Po10	L. Leonova, G. Pampararo, V. Vykoukal, L. Simonikova, F. Devred, P. Eloy, A. Styskalik, D. P. Debecker ETHANOL DEHYDRATION WITH AEROSOL-MADE MESOPOROUS ALUMINOSILICATES FEATURING DISPERSED ACTIVE SITES		
Po11	<u>N. Lusiani</u> , O. Sedláček CATIONIC RING-OPENING POLYMERIZATION-INDUCED SELF-ASSEMBLY (CROPISA) OF 2-OXAZOLINES: FROM BLOCK COPOLYMERS TO ONE-STEP GRADIENT COPOLYMER NANOPARTICLES		
Po12	M. Mariyaselvakumar, A. Kurbanova, M. M. Álvarez Izaguirre, S. Kurucová, J. Přech SELECTIVE TRANSITION METAL-BASED HYDROGENATION CATALYSTS VIA REDUCTIVE DEMETALLATION OF ZEOLITES		
Po13	V. Calvino-Casilda, I. Sobczak, M. Ziolek, <u><b>R. Martin-Aranda</b></u> GREEN SYNTHESIS AND MESOPOROUS CELLULAR FOAMS.EFFECT OF GOLD DOPANT		

Po14	M. Moliner, B. Bohigues, I. Millet, P. Concepción, A. Corma, P. Serna HIGHLY STABLE SUBNANOMETRIC PT CLUSTERS IN ALL SILICA KDOPED ZEOLITES: IMPLICATIONS FOR THE CO OXIDATION REACTION
Po15	Elena García-Rojas, Jesús Tapiador, Pedro Leo, Carmen Martos, <u>Gisela Orcajo</u> TUNABLE UIO-66-TYPE MOFs FOR EFFICIENT GLYCEROL VALORIZATION VIA ACETALIZATION REACTION
Po16	<u>Reisel Millán</u> , Mercedes Boronat MOBILITY OF SOLVATED CU CATIONS IN CU-CHA PREDICTED BY MACHINE LEARNING ACCELERATED MOLECULAR DYNAMICS
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#### DESIGNING ZEOLITE-BASED CATALYSTS FOR INDUSTRIALLY RELEVANT CHEMICAL PROCESSES

#### Cristina Martínez

Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València -Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, Valencia 46022, Spain.

Climate change and, in particular, global warming due to the anthropogenic emission of greenhouse gases (GHGs), is one of the main problems of nowadays society. In order to avoid irreversible environmental effects that will unavoidable impact life as we know it today, drastic changes on the energy sources employed by industry and transportation have to be applied in order to minimize the overall carbon footprint, mainly generated by carbon dioxide (CO2) emissions.<sup>1</sup>

Facing these different challenges related to climate change, pollution and sustainable energy involves a common factor, which is the use of innovative catalytic technologies, an area where heterogeneous catalysts stand out as the core of effective cost-basis solutions leading to a sustainable future thanks to their recyclable nature.<sup>2</sup> Among heterogeneous catalysts, zeolite-type microporous crystalline materials may present high activity and selectivity for catalyzing a specific reaction by means of the proper combination of topology and active sites. They are widely applied as catalysts in a large number of processes because of their particular structure, formed by channels and cavities of molecular dimensions, of their compositional flexibility and of their thermal and hydrothermal stability. <sup>3–5</sup>

Here I will present a general overview of new trends in the development of zeolitebased catalysts for industrial applications and, in particular, of the most recent contributions of our group to this field. Processes such as CO2 hydrogenation, light olefin oligomerization or on-purpose propene production will be considered.

#### **References:**

- <sup>1</sup> Lanzafame, P.; Abate, S.; Ampelli, C.; Genovese, C.; Passalacqua, R.; Centi, G.; Perathoner, S. ChemSusChem 2017, 10, 4409–4419.
- <sup>2</sup> Hu, X.; Yip, A. C. K. Frontiers Catal. 2021, 1, 667675.
- <sup>3</sup> Martínez, C.; Corma, A. Coord. Chem. Rev. 2011, 255, 1558–1580.
- <sup>4</sup> Moliner, M.; Martínez, C.; Corma, A. Multipore Zeolites: Angew. Chemie Int. Ed. 2015, 54, 3560–3579.
- <sup>5</sup> Del Campo, P.; Martínez, C.; Corma, A. Chem. Soc. Rev. 2021, 50, 8511–8595.

#### **2D-CHEMISTRY OF FLUOROGRAPHENE TOWARD FUNCTIONAL GRAPHENE DERIVATIVES FOR CATALYTIC APPLICATIONS**

#### Michal Otyepka

Czech Advanced Technology and Research Institute (CATRIN), Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc, Šlechtitelů 27, Olomouc, 77900 Czech Republic; VSB – Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic, e-mail: michal.otyepka@upol.cz

Covalent functionalization significantly modifies graphene's electronic, magnetic, and surface properties, yet direct covalent modification remains challenging due to graphene's inherently low chemical reactivity, typically requiring harsh reaction conditions. To overcome these limitations, we developed a novel synthetic route utilizing fluorographene chemistry. Fluorographene (FG), a stoichiometric graphene derivative with an approximate composition of C<sub>1</sub>F<sub>1</sub>, is conveniently prepared through the chemical delamination of graphite fluoride, which is commercially available material. Importantly, FG is reactive under mild and well controllable conditions, allowing access to an extensive range of graphene derivatives.<sup>1</sup> The chemistry of FG facilitates the synthesis of graphene-based materials suitable for various applications, including electrode materials for supercapacitors,<sup>2,3</sup> Li-ion,<sup>4</sup> and Li-sulfur batteries,<sup>5</sup> as well as sensing<sup>6,7</sup> and catalysis.<sup>8</sup> For instance, graphene acid,<sup>9</sup> a prototypical derivative obtained from FG, exhibits excellent performance as a metal-free catalyst for alcohol oxidation reactions.<sup>10</sup> Additionally, cyanographene, a derivative bearing nitrile functional groups, efficiently anchors single-atom copper species in mixed valence states, demonstrating remarkable catalytic activity in key dioxygen-mediated processes such as oxidative amine coupling and selective oxidation of benzylic C-H bonds, essential for synthesizing valuable pharmaceutical intermediates.<sup>11</sup> Furthermore, the covalent attachment of the natural amino acid taurine to graphene via FG chemistry yields an effective catalytic material for glycerol conversion into solketal.<sup>12</sup> Overall, the utilization of FG chemistry presents a robust and versatile strategy to overcome graphene's chemical inertness, significantly broadening its applicability in catalytic, electronic, and energy-related technologies.

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#### **References:**

- 1. Chronopoulos D. et al. Appl. Mater. Today 2017, 9, 60.
- 2. Šedajová V. et al. Energy Env. Sci. 2022, 15, 740.
- 3. Hrubý V. et al. Power El. Dev. Comp. 2024, 7, 100058.
- 4. Obraztsov I. et al. Adv. Energy Mater. 2022, 12, 2103010.
- 5. Tantis I. et al. Adv. Funct. Mater. 2021, 31, 2101326.
- 6. Flauzino JMR. et al. Biosens. Bioelectr. 2022, 195, 113628.
- 7. Nalepa MA. et al. Biosens. Bioelectr. **2024**, 256, 116277.
- 8. Hrubý V. et al. Nanoscale **2022**, 14, 13490.
- 9. Bakandritsos A. et al. ACS Nano 2017, 11, 2982.
- 10. Blanco M. et al. Chem. Sci. 2019, 10, 9438.
- 11. Bakandritsos A. et al. Advanced Materials 2019, 31, 1900323.
- 12. Poulose AC. et al. Nat. Commun. 2023, 14, 1373.

#### **BIO-ALCOHOLS CONVERSION: THE ROLE OF ZEOLITIC CATALYSTS**

#### Girolamo Giordano

CECaSP Laboratory, University of Calabria, Via P. Bucci 42/A, 87036, Rende (CS), Italy

#### ggiordaunical@yahoo.it

Because of the increasing demand of de-fossilized resources, non-traditional carbonbased feedstocks could represent a strategic answer to global fuel and chemicals demand.

In this context, ethanol and methanol are relevant platform molecules as they can be derived from  $CO_2$  recycling processes, and the conversion of these simple alcohols into chemicals and fuel, such as ethers or light olefins, could play a significant role in the energy transition and sustainability strategies<sup>1</sup>.

In this concern, most work in literature is focused to the study of pure alcohols reaction and, on the contrary, the research in simultaneous alcohols conversion remains almost unexplored<sup>2</sup>.

In this presentation, after an outlook on worldwide energy demand, the main challenges of reactions involving lower alcohols/ethers are discussed, with particular focus on the role played by zeolites in both alcohols' synthesis and its conversions to ethers and olefins<sup>3</sup>.

Recent advances methanol and ethanol conversion towards olefins (e.g. ethylene/propylene) and ethers, (e.g. dimethyl ether/diethyl ether) will be presented, with particular emphasis on the role of catalyst features on product distribution and deactivation. In this regard, also the one-pot synthesis of olefins/oxygenates via alcohol-mediated routed will be presented and discussed on the basis of recent scientific literatures and patents.

Finally, recent results about the simultaneous alcohols conversion are also presented, as innovative strategy for long-chain intermediates synthesis from bio-alcohols.

#### **References:**

<sup>1</sup> Catizzone, E.; Freda, C.; Braccio, G.; Frusteri, F.; Bonura, G. J. Energy Chem. **2021**, 58, 55.

<sup>2</sup> Catizzone, E.; Ferrarelli, G.; Bruno, P.; Giordano, G.; Migliori, M. Catal. Today **2024**, 427, 114436.

<sup>3</sup> Zhong, J.; Han, J.; Wei, Y.; Liu, Z. J. Catal. **2021**, 396, 23.

#### FT-IR SPECTROSCOPY FOR CHARACTERIZATION OF SOLID CATALYSTS

#### Mariya V. Shamzhy

#### Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Infrared (IR) spectroscopy has long been a cornerstone technique for *in situ* characterization of functional materials, including but not limited to solid catalysts. The advancement of Fourier-transform infrared (FT-IR) spectroscopy and step-scan interferometry has dramatically improved temporal resolution, enabling real-time monitoring of chemical interactions at solid-gas and solid-liquid interfaces on the nanosecond scale. The integration of FT-IR spectroscopy with atomic force microscopy has further enhanced its spatial resolution to the nanometer scale, providing deeper insights into diffusion phenomena and host-guest interactions in heterogeneous catalytic systems.

In zeolite catalysis, *in situ* FT-IR spectroscopy plays a pivotal role in elucidating synthesis-property-performance relationships by offering detailed information on the nature and concentration of active sites and reaction intermediates, ultimately advancing the understanding of the mechanisms of catalytic reaction and catalyst deactivation.<sup>1-4</sup>

This lecture explores the capabilities of FT-IR spectroscopy in characterizing catalytic materials, with a focus on zeolite catalysts. The discussion covers the fundamental principles of FT-IR spectroscopy, advancements in instrumentation, and key experimental techniques, including transmission, attenuated total reflection, and diffuse reflectance infrared Fourier transform spectroscopy. It also addresses the role of quantitative FT-IR analysis in characterization of zeolite catalysts and showcases real-world applications of FT-IR spectroscopy in investigating zeolite-catalyzed reactions.

References:

<sup>1</sup>Shamzhy, M.; Přech, J.; Zhang, J.; Ruaux, V.; El-Siblani, H.; Mintova, S. Catal. Today, **2020**, 345, 80-87.

<sup>2</sup>Shamzhy, M.; Gil, B.; Opanasenko, M.; Roth, W.; Čejka, J. ACS Catal. **2021**, 11, 2366-2396.

<sup>3</sup>Gołąbek, K.; Shamzhy, M.; Kubů, M.; Soták, T.; Magyarová, Z.; Hronec, M.; Čejka, J. Appl. Mater. Today **2022**, 28, 101505.

<sup>4</sup>Zhou, Y.; Santos, S.O.; Shamzhy, M.; Marinova, M.; Blanchenet, A.-M.; Kolyagin, Y.; Simon, P.; Trentesaux, M.; Sharna, S.; Ersen, O.; Zholobenko, V. L.; Saeys, M.; Khodakov, A.Y.; Ordomsky, V.V. Nat. Commun. **2024**, 15, 2228

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## ON THE RECOVERY OF FORGOTTEN KNOWLEDGE AND ITS APPLICATION IN MODERN CATALYSIS. A PERSONAL VIEW

#### Joaquín Pérez-Pariente

#### Institute of Catalysis and Petroleum Chemistry ICP-CSIC (Marie Curie 2, 28049-Cantoblanco, Spain, jperez@icp.csic.es)

There is the dominant view in contemporary scientific establishment that knowledge advances in a linear and continuous progression. Old views are left behind, rapidly discarded as useless as new perspectives and facts provide better approaches to the comprehension of the functioning of nature. But we can wonder whether old achievements have always been integrated in the contemporary scientific discourse. Do materials and processes of the past have still something useful to offer for modern science, chemistry and catalysis in particular? I will discuss several examples, belonging to both distant past and closer times, of what can in a broad sense be called forgotten knowledge, that are worth being reexamined with new eyes. The first is a simple, two-liquid phases method reported in the eighteenth century to prepare colloidal gold solutions that a modern reproduction have revealed to contain Au nanoparticles, clusters and even isolated gold atoms<sup>1</sup>, which, after proper reworking, has been used to prepare active and selective oxidation catalysts.<sup>2</sup> The second example concerns the Gezeolites. Primarily due to their poor thermal stability and their facile hydrolysis when exposed to water, added to the high cost of Ge, they are in general considered not interesting for catalysis. But, opposite to that view, framework Ge has been found to catalyze a variety of reactions, endowed with a rich and at times surprising chemistry worth exploring.

Several lessons are to be learnt from these considerations. First, this concept of neglected knowledge not only affects century-old venerable achievements, but also concerns the way we nowadays approach scientific research. People of the past were not at all stupid, no more that we will be for those who within few years ahead will look back at us. Second, beware that scientific and technical knowledge (not the same thing!) are always framed in a given conceptual scheme, whose existence we often are unaware of, but which it is always there. The conceptual frameworks are nothing but a tool, useful for some purposes, but nothing more. This tool should never limit your thoughts, as you could make a new one if needed. Third, nature has an inexhaustible capacity of producing marvels, provided we are prepared to recognize them. Fourth, past achievements must be explored critically, as a source of inspiration for new research avenues, not for "copy-and-paste." Fifth, interdisciplinary cooperation between humanities and sciences is a must if we want to recover past knowledge. Better to build bridges than walls. Finally, an open question to think about: how do we know that something forgotten or neglected is worth of reexamination? Most of past knowledge is trivial, well-known, but how do we identify the one that it is not?

#### **References:**

<sup>1</sup> Mayoral, A., Agúndez, J., Pascual-Valderrama, I.-M., Pérez-Pariente, J. Gold Bull. **2014**, 47, 161-165.

<sup>2</sup> Delgado, R., Márquez-Álvarez, C., Mayoral, A., de la Serna, R., Agúndez, J., Pérez-Pariente, J. Chemistry **2023**, 5, 526-543.

#### HIERARCHICAL ZEOLITES FOR DIMETHYL ETHER DEHYDRATION INTO LIGHT OLEFINS

#### <u>Emanuele Giglio</u><sup>1</sup>, Giorgia Ferrarelli<sup>1</sup>, Fabio Salomone<sup>2</sup>, Elena Corrao<sup>2</sup>, Samir Bensaid<sup>2</sup>, Massimo Migliori<sup>1</sup>, Raffaele Pirone<sup>2</sup>, Girolamo Giordano<sup>1</sup>.

<sup>1</sup>University of Calabria, Via Pietro Bucci, 87036 Rende, Italy. <sup>2</sup>Polytechnic of Turin, Corso Duca degli Abruzzi 24, 10129 Turin, Italy.

Light olefins, such as ethylene and propylene, are key components of the petrochemical industry. They are conventionally produced via steam cracking of petroleum hydrocarbons; however, light olefins can be alternatively produced via dehydration according to the Dimethyl ether-to-Olefins (DTO) route<sup>1</sup>. Hierarchical zeolites have recently attracted interest due to lower deactivation rates compared to conventional ones. In this work, four different hierarchical zeolites have been synthesized, characterized, and tested to investigate catalytic activity, product distributions, and stability over time.

MFI zeolites with a nominal Si/Al ratio of 25 and 50 were synthesized via hydrothermal synthesis<sup>2</sup>. These zeolite samples were treated ("etching") with  $NH_4^+/HF$  solution under stirring<sup>3</sup>. The samples were named ETC-25 and ETC-50. Moreover, two hierarchical zeolites with a theoretical Si/Al ratio of 25 and 50 were directly prepared via hydrothermal synthesis<sup>4</sup>. The two samples were labeled HZ-25 and HZ-50. The samples were characterized via N<sub>2</sub> physisorption, X-ray diffraction (XRD), and infrared spectroscopy (FT-IR) to investigate textural properties, crystalline structure, and acidity. The samples were tested in a fixed bed reactor at a temperature range of 300-375 °C for about 14 hours to measure their catalytic performance. Thermogravimetric analysis (TGA) and mass spectrometry (GC-MS) were used to characterize the produced coke.

In all the time-on-stream catalytic tests the conversion increased at higher temperature. At 350 and 375 °C slight deactivation of the samples occurred. Propylene is the most abundant hydrocarbon produced, suggesting that the alkene cycle of the hydrocarbon pool mechanism seems to be the preferential route for olefins formation. Hierarchical zeolites presented improved stability if compared with conventional parent MFI, especially when the reference Si/Al ratio is 25 (i.e., more acid samples). This phenomenon can be partly ascribed to the different pore size distribution, allowing larger molecules to diffuse from the particle to the bulk of the gas without trapping them within the inner porosities. The acidity reduction of the zeolites improved the stability of the catalysts. Thus, combining a hierarchical structure and a milder acidity could enhance the efficiency of the DTO process.

#### **References:**

<sup>1</sup> Al-Dughaither, A. S.; de Lasa, H. Fuel **2014**, 138, 52-64.

<sup>2</sup> Giglio, E.; Ferrarelli, G.; Salomone, F.; Corrao, E.; Migliori, M.; Bensaid, S.; Pirone, R.; Giordano, G. Fuel **2024**, 362, 130559.

<sup>3</sup> Qin, Z.; Lakiss, L.; Gilson, J. P.; Thomas, K.; Goupil, J. M.; Fernandez, C.; Valtchev, V. Chem. Mater. **2013**, 25 (14), 2759-2766.

<sup>4</sup> Wen, C.; Jiang, J.; Chiliu, C.; Tian, Z.; Xu, X.; Wu, J.; Wang, C.; Ma, L. Energy Fuels **2020**, 34 (9), 11282-11289.

#### EXCEPTIONAL CATALYTIC ACTIVITY OF GERMANOSILICATE GTM-4 IN THE OXIDATION OF CYCLOHEXENE WITH MOLECULAR OXYGEN

#### <u>P. Sánchez-Morena</u>, J. Jurado-Sánchez, C. Márquez-Álvarez, L. Gomez-Hortigüela, J. Pérez-Pariente.

Instituto de Catálisis y Petroleoquímica (CSIC), Marie Curie, 2, 28049 Cantoblanco, Madrid, Spain; <u>p.sanchez@icp.csic.es</u>

From a catalytic perspective, germanosilicates have shown activity in catalytic cracking, acetalization, and ketone oxidation<sup>1–3</sup>. However, studies on their catalytic properties remain limited due to low hydrothermal stability and the high cost of Ge.

![](_page_20_Figure_5.jpeg)

**Figure 1**. **a**) Conversion vs. time for GTM-4 and BEC. **b**) Scheme of the catalytic reaction. **c**) Structure of the GTM-4 material highlighting a double four-membered ring position with interrupted sites.

This study explores a previously unreported reactivity of zeolitic germanosilicates in cyclohexene oxidation with molecular oxygen under mild conditions (Figure 1b). Our group recently discovered GTM-4 material<sup>4</sup>, tested as a catalyst for this reaction, showing high activity in cyclohexene oxidation with O<sub>2</sub>, unlike the BEC-structured germanosilicate (Figure 1a). Due to the small size of the reactants, the difference in catalytic activity between the two materials seems to be attributed to the presence of Ge in interrupted sites (Q3) (Figure 1c), which are the most favorable sites for this atom. These sites do not exist in the BEC structure, where all Ge atoms are connected to four other T atoms (Q4). Thus, the remarkable activity of Ge in the GTM-4 material, which even exceeds that of Ti in zeolites, is connected to the unique configuration of Ge in the structure provided by the interrupted site, making this special type of Ge an exceptional Lewis center. This study reveals a new catalytic functionality of Ge in zeolites, demonstrating its ability to activate molecular oxygen.

#### References

<sup>1</sup> Corma, A.; Díaz-Cabañas, M. J.; Jordá, J. L.; Martínez, C.; Moliner, M. Nature **2006**, 443 (7113), 842–845.

<sup>2</sup> Podolean, I.; Zhang, J.; Shamzhy, M.; Pârvulescu, V. I.; Čejka, J. Catal. Sci. Technol. **2020**, 10 (24), 8254–8264.

<sup>3</sup> Xu, H.; Jiang, J.; Yang, B.; Wu, H.; Wu, P. Catal. Commun. **2014**, 55, 83–86.

<sup>4</sup> de la Serna, R.; Jurado-Sánchez, J.; Márquez-Álvarez, C.; Pérez-Pariente, J.; Gómez-Hortigüela, L. Microporous Mesoporous Mater. **2024**, 371, 113083.

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#### XYLENE ISOMERIZATION OVER IWW ZEOLITE WITH A THREE-MODAL PORE STRUCTURE: THE EFFECT OF CRYSTAL MORPHOLOGY

#### Emad Shamma, Alica Seidlová, Jan Přech, Maksym Opanasenko, Mariya Shamzhy

#### Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Czech Republic

Xylene isomerization is a key zeolite-catalyzed petrochemical process targeted at producing p-xylene, a highly demanded commodity in polymer industry. MFI-type zeolites are commercially used for p-xylene production because their unimodal 10-ring pores suppress bimolecular disproportionation, which would otherwise decrease p-xylene selectivity. However, MFI catalysts also promote unwanted dealkylation, lowering the yield of the targeted aromatic. To address this issue, the bi-modal micropore EUO zeolite with medium 10-ring pores and larger 12-ring side pockets was developed and industrialized for selective isomerization of xylene under milder conditions.<sup>1</sup> Recent research has also increasingly focused on designing multi-modal pore systems in zeolite catalysts and using m-xylene isomerization as a benchmark test for evaluating newly synthesized zeolites or those with unconventional crystal morphologies.<sup>2</sup>

In this study, IWW zeolite catalysts with three-modal pore network of isolated 8- and 12ring pores intersected by 10-ring channels were hydrothermally synthesized as germanosilicates with platelet-like and needle-like shape of the crystals (Figure 1), functionalized by post-synthesis Ge-for-Al substitution and tested for m-xylene isomerization in a flow system with an online analysis of the products.

![](_page_21_Figure_6.jpeg)

Figure 1. The pore system and crystal morphology of the studied IWW zeolites.

Regardless of crystal morphology, Al-IWW zeolites showed higher m-xylene conversion  $(55 - 64 \% \text{ at WHSV} = 6 \text{ h}^{-1})$  than the reference MFI zeolite (47 %) with a similar concentration of acid sites. Notably, a 3-fold increase in WHSV had a marginal effect on the conversion of m-xylene for all Al-IWW catalysts (50 - 55 % at WHSV = 20 \text{ h}^{-1}), while the yield of p-xylene increased only for the Al-IWW catalyst with the needle-like crystals. These results were interpreted in terms of the multiple pore sizes within the IWW zeolite, where 10-ring channels aligned along the needle-like crystals, as validated by STEM, enable shape-selective formation of p-xylene, while the perpendicular 12-ring channels facilitate the diffusion of reacting molecules to and from the active sites.

#### **References:**

 <sup>1</sup> Gonçalves, J.C. and Rodrigues, A.E. Chem. Eng. Technol. **2013**, 36(10), 1658-1664.
 <sup>2</sup> Remperová, N.; Přech, J.; Kubů, M.; Gołąbek, K.; Miñambres, J. F.; Hsieh, M.-F.; Turrina, A.; Mazur, M. Catal. Today **2022**, 390-391, 78-91

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#### SYNTHESIS AND CATALYTIC PROPERTIES OF ZSM-11 ZEOLITES WITH CONTROLLED NANOARCHITECTURES

#### <u>A. López Albero<sup>1</sup></u>, D. de la Calle<sup>1</sup>, J. Cueto<sup>1</sup>, M. Alonso-Doncel<sup>1</sup> and D.P. Serrano<sup>1,2</sup> <sup>1</sup> Thermochemical Processes Unit, IMDEA Energy Institute, 28935, Madrid, Spain.

<sup>2</sup> Chemical and Environmental Engineering Group, Rey Juan Carlos University, 28933, Madrid, Spain. Several strategies have been developed in the past decades to overcome the diffusional restrictions of conventional microcrystalline zeolites. Recently, dendritic ZSM-5 zeolites with enhanced accessibility, attributed to its trimodal pore size distribution, was reported<sup>1</sup>. In this study, we propose extending this synthesis strategy to ZSM-11 zeolites, which shares structural similarities and micropore size with ZSM-5 but has a distinct channel architecture that may influence its catalytic and adsorption properties. For this, several ZSM-11 samples were synthesized. The effect of the addition of amphiphilic organosilane to a conventional liquid synthesis gel (LG) with a Si/Al ratio of 50 was examined. Both samples consisted of well-formed MEL structures but with distinct morphologies: the non-silanized sample formed globular nanocrystals aggregates, while the silanized sample (LG-50) displayed a cross-linked nanosheet structure (Fig. 1a) with improved accessibility. Moreover, the impact of modifying the LG procedure to follow a method via fast crystallization of a xerogel (XG) precursor<sup>2</sup> was studied for Si/Al ratios of 30 and 50. The XG-50 sample exhibited also cross-linked nanosheets (Fig. 1b) relatively similar to those formed in the liquid gel approach. However, increasing the aluminum content in the XG-30 sample led to a reduction in the whole nanocrystal size and resulted in dendritic nanostructures (Fig. 1c). The differences between the samples are also evident in their acid properties, with the samples derived from xerogel exhibiting a significantly higher proportion of Lewis acidity. The combination of the textural and physicochemical properties significantly influences their catalytic behavior in the aldol condensation of furfural (FFL) with cyclopentanone (CPO) (Fig.1d and e) to yield C10 and C15 adducts.

![](_page_22_Figure_4.jpeg)

Fig. 1. TEM images: (a) LG-50, (b) XG-50, and (c) XG-30. Aldol condensation of FFL and CPO: (d) time evolution of FFL conversion and (e) product yield at 6 h of reaction.

The xerogel-derived samples demonstrated superior performance compared to the LG one in this reaction, with the Si/Al = 30 sample showing the highest conversion. Additionally, it presented increased selectivity for the bulkier condensation adduct (C15), which is also a precursor for sustainable aviation fuels, due to the unique characteristics of the dendritic sample. On the other hand, xerogel-derived samples also exhibited greater selectivity for dihydrocarvone (DHC), a valuable compound in the synthesis of flavors, perfumes, and pharmaceuticals, in the 1,2-limonene epoxide isomerization reaction.

In summary, the XG route outperforms the LG method by achieving higher synthesis yields and significantly reducing crystallization time. This approach enables the production of ZSM-11 zeolites with tunable properties through the adjustment of organosilane and Al content, providing a more efficient and flexible synthesis process. **References** 

<sup>1</sup> M. Alonso-Doncel et al. Cryst. Growth Des. 23(8), (2023), 5658–5670.

<sup>2</sup> D.P. Serrano et al. Stud. Surf. Sci. Catal. 170 (2007), 282-28.

#### Acknowledgments

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#### ENHANCED ALDOL CONDENSATION OF BIOMASS-DERIVED LEVULINIC ACID AND FURFURAL USING METAL-MODIFIED ACID ZEOLITES FOR THE PRODUCTION OF AVIATION FUEL INTERMEDIATES

#### Natalia Uricochea<sup>1,2</sup>, Gabriel Morales<sup>1,2</sup>, <u>Marta Paniagua<sup>1</sup></u>, Juan A. Melero<sup>1,2</sup>

<sup>1</sup>Chemical and Environmental Engineering Group. <sup>2</sup>Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS). ESCET, Universidad Rey Juan Carlos. c/Tulipán s/n, Móstoles 28933, Spain

Lignocellulosic biomass can be processed through established methods to produce platform molecules such as levulinic acid (LA) and furfural (FAL)<sup>1</sup>. Through chemical valorization, these molecules can be converted into high value biochemicals and biofuels<sup>2</sup>. In particular, the synthesis of sustainable aviation fuels (SAFs) from lignocellulosic biomass represents a promising application for contributing to the decarbonization of air transport. In this context, the aldol condensation of FAL and LA leads to the formation of aldol products with 10 carbon atoms (C10) which can be converted in SAFs after a hydrodeoxygenation process<sup>3</sup>.

In this work, two types of zeolites, Beta and USY, were modified introducing Lewis acid-type functionality by metal (M) incorporation, wherein M stands for Zr, Hf or Ti. The procedure consists of a first dealumination step using different concentrations of nitric acid (partial, 2 M; total, 10 M) and temperatures (partial, RT; total, 100 °C), and a second step of metal incorporation. A total of 12 materials were synthesized and denoted as M-zeolite (Beta/USY)-dealumination degree (1-partial, 2-total). According to the characterization, metals were successfully introduced into the zeolite framework, mostly maintaining its integrity. Catalytic runs were performed to investigate the effect

of the synthesized zeolites on the aldol condensation of FAL and LA at 120 °C, a mass ratio FAL/catalyst of 5, and a molar ratio LA/FAL of 10. It is important to highlight the solventless nature of the reaction. According to the results (Figure 1), for the parent unmodified commercial zeolites the yield towards C10 adducts is almost negligible. The introduction of the metallic species with Lewis-type acidity does improve both conversion and yield. Among the tested metals, especially, Zr-modified Tiand, materials show a clear enhancement in the yield to the target products.

![](_page_23_Figure_7.jpeg)

Figure 1. Catalytic activity of the synthesized zeolites in terms of  $X_{FAL}$  and  $Y_{C10}$  (%).

#### **References:**

<sup>1</sup>Cousin E. et al., Sci. Total Environ. **2022**, 847,157599.

<sup>2</sup> Yan P.; Wang H.; Liao Y. Renew. Sustain. Energy Rev. **2023**, 178, 113219.

<sup>3</sup>Liang G.; Wang A.; Zhao X.; Lei N.; Zhan T. Green Chem. **2016**, 18, 3430–3438.

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#### ANCHORING Pd NANOPARTICLES TO ZEOLITE SURFACE SILANOLS TO DEVELOP HETEROGENEOUS TSUJI-TROST ALLYLATION CATALYSTS

#### Adéla Olšovská <sup>a</sup>, Martin Kamlar <sup>b</sup>, Jan Veselý <sup>b</sup>, Jiří Čejka <sup>a</sup>, and Michal Mazur <sup>a</sup>

#### <sup>a</sup> Department of Physical and Macromolecular Chemistry, Charles University, Prague, Czechia <sup>b</sup> Department of Organic Chemistry, Charles University, Prague, Czechia

Efficient catalysts are a keystone of modern industrial processes. While homogeneous catalysts ensure excellent contact with reactants and high catalytic activity, their separation from reaction mixtures is often challenging. Contrary, heterogeneous catalysts can be easily separated from the reaction mixture, what is more, they provide reusability offering both substantial economic and environmental benefits.

In our research, we aim to develop heterogeneous catalysts utilizing zeolites as supports. These crystalline microporous materials, primarily aluminosilicates, possess remarkable properties such as uniform microporosity, high surface area, and exceptional chemical and thermal stability. We utilize their surface defects, Si-OH groups (silanols), which have been shown to effectively stabilize metal nanoparticles (NPs), preventing deactivation processes like leaching or sintering.<sup>1</sup> To create a higher number of silanols, we apply acidic treatment, which causes dealumination of our support.

Herein, we synthesized our catalysts by impregnating USY, dealuminated USY, and layered MFI zeolites with a  $[Pd(NH_3)_4](NO_3)_2$  solution followed by calcination and reduction steps to obtain metallic Pd NPs. Employing the electron microscopy, we demonstrate how various zeolite supports impact the final NPs size and distribution. Specifically, Pd@USY exhibited the smallest NPs (~1.5 nm), Pd@deAl-USY had slightly larger ones (~2.5 nm), and Pd@lay-MFI featured NPs exceeding 10 nm. Our goal was to explore the correlation between nanoparticle size and catalytic performance while demonstrating that higher silanol concentrations enhance stability, allowing multiple reuse cycles without activity loss. To test these hypotheses, we used the Tsuji-Trost allylation, a key reaction in organic synthesis for forming C–C bonds, typically conducted in homogeneous systems. Specifically, we examined the reaction of diethylmalonate with allyl acetate, which yields both mono- and di-substituted products.

As expected, Pd@USY, which contained the smallest NPs (~1.5 nm), exhibited the highest catalytic activity, while Pd@lay-MFI showed no catalytic activity at all. Our results demonstrate that the materials with sufficiently small nanoparticles function as effective catalysts, with activity comparable to their homogeneous counterpart, Pd(dba)<sub>2</sub>. Both systems reach full conversion in five hours, but excess allyl acetate promotes di-substitution. Reducing its amount minimizes further reaction of the monosubstituted product. While this adjustment extends the reaction time to six hours, it ensures nearly 100% selectivity for the mono-substituted product. Furthermore, we confirmed the stability of our catalysts under reaction conditions against leaching by analyzing ICP-MS of our reaction mixtures and were able to isolate the final monosubstituted product with a separation yield exceeding 80 %. Future work will explore material reusability over multiple cycles and the rate of presumed activity decline.

#### **References:**

<sup>1</sup> Li A., et al., Angew. Chem. Int. Ed. **2023**, 62, e202213361.

<sup>2</sup> Kimura M., et al., J. Am. Chem. Soc. **2001**, 123 (42), 10401-10402.

#### OP6

#### SYNTHESIS AND CHARACTERIZATION OF -EWT ZEOLITE

#### M. Kubů, V. Přibyl and M. Shamzhy

Charles University, Department of Physical and Macromolecular Chemistry, Hlavova 8, 128 40, Prague, Czech Republic kubumar@natur.cuni.cz

Zeolites represent important group of porous crystalline materials. Owing to their unique microporosity, high thermal stability and large ion-exchange capacities, they are used in many industrial processes including adsorption, separation and catalysis. -EWT is a stable three-dimensional extra-large pore zeolite with regularly located defects in its framework. The size of pores (10.8 x 4.6 Å, 5.1 x 5.1 Å) and the presence of structural defects within the framework<sup>1</sup> allows one to incorporate catalytically active metal ions (e.g. Ti, Sn, Zr) to specific positions and tailor acidic properties thus affecting the catalytic performance, e.g. in transformation of bulky molecules.

Based on the literature, different structure-directing agents (SDAs) can be used for -EWT synthesis (**Fig. 1**)<sup>1,2,3</sup>. The polyquaternium ammonium SDA was used and the synthesis conditions in terms of the synthesis mixture composition (H<sub>2</sub>O/Si ratio), time (4 days), temperature (165 °C), and agitation were optimized. Also, a reliable way of SDA removal is crucial for further manipulation and modification of the structure.

![](_page_25_Figure_7.jpeg)

Fig. 1. SDAs used in -EWT synthesis<sup>1,2,3</sup>

It was shown, that the H<sub>2</sub>O/Si ratio and agitation are key parameters in the crystallization of the pure -EWT phase with Si/Al ratio in the range of 50-100. The removal of SDA was achieved by a harsh extraction using mineral acid and by the adjustment of calcination conditions under vacuum. The synthesis of pure silica -EWT and subsequent modification *via* metal ion incorporation will be investigated in the future as synthesis reliability and economy is crucial for potential industrial applicability.

#### **References:**

- 1. Willhammar, T. et al., J. Am. Chem. Soc. 2014, 136 (39), 13570–13573.
- 2. Mu, X. et al., Microporous Mesoporous Mater. 2019, 275, 87–94.
- 3. Method for synthesizing EMM-23 molecular sieve. CN112010325B, July 11, 2023.

#### SYNTHESIS OF ZSM-5 FROM NATURAL MORDENITE FROM SPAIN AND THE APPLICATION IN MTH PROCESS

#### <u>Itziar Arnaiz<sup>1</sup></u>, Leyre Perea<sup>1</sup>, Yaregal Awoke<sup>2</sup>, Manuel Sánchez-Sánchez<sup>1</sup>, Marisol Grande-Casas<sup>1</sup>, Isabel Diaz<sup>1</sup>, Carlos Márquez-Alvarez<sup>1</sup>, Enrique Sastre<sup>1</sup>

<sup>1</sup>Instituto de Catálisis y Petroleoquímica, ICP-CSIC, C/Marie Curie 2, 28049 Madrid, Spain <sup>2</sup>Chemistry department, Addis Ababa University, Arat Kilo Campus, Addis Ababa, Ethiopia

ZSM-5 zeolite is a key catalyst in petrochemicals, widely used in methanol-to-

hydrocarbons (MTH) reactions<sup>1</sup>. This study investigates converting natural mordenite from Spain<sup>2</sup> into ZSM-5 through direct inter-zeolite transformation and evaluates its application in MTH process.

By optimizing synthesis conditions, pure ZSM-5 was obtained from natural mordenite from Spain, without the need of previous treatments before crystallization. Two methods were employed to modify the Si/Al ratio: (i) acid treatment to remove aluminum and (ii) the addition of extra silica. NaOH or NH<sub>4</sub>OH have been used to control gel alkalinity, and a systematic study was conducted on the concentration of the structure-directing agent (TPAOH), as well as synthesis temperature and time<sup>3</sup>. This study led to the production of highly crystalline, pure ZSM-5 with Si/Al ratios around 20, with different sizes and crystal shapes, (Figure 1). The samples were characterized and, after ion exchange and calcination at 550°C, were tested in MTH conversion. The reaction was performed in a fixed bed reactor connected to a gas

![](_page_26_Picture_7.jpeg)

**Figure 1.** SEM images of both synthesized samples, A: using strategy (i) with NaOH, at 190°C, 48h and B: strategy (ii) with NH4OH, at 190°C, 48h.

chromatograph for product analysis. Temperatures between 400 and 500°C were studied to evaluate their influence on catalyst stability and product selectivity (olefins, paraffins, etc.). Preliminary experiments indicate that the synthesized zeolites exhibit initial activity and selectivity comparable to previously studied commercial zeolites<sup>4</sup>.

#### References

<sup>1</sup>Zhang, Q.; Yu, J.; Corma, A. Adv. Mater. **2020**, 32, 2002927.

<sup>2</sup> Presa, L.; Costafreda, J. L.; Martin, D. A.; Diaz, I. Molecules **2020**, 25, 1-13.

<sup>3</sup> Y. Awoke, M. Sánchez-Sánchez, I. Arnaiz, I. Diaz, Microporous Mesoporous Mater. **2025**, 385, 113463.

<sup>4</sup> García-Ruiz, M.; Solís-Casados, D. A.; Aguilar-Pliego, J.; Márquez-Álvarez, C.; Sastre, E. Catal. Lett. **2023**, 153, 2493-2503.

#### Aknowledgments

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#### SYNTHESIS OF ZEOLITE-SUPPORTED BIMETALLIC NANOPARTICLES FOR LIGNIN VALORISATION

#### Samuel Kolesár, Paul A. Diddams, and Michal Mazur

#### Department of Physical and Macromolecular Chemistry; Faculty of Science, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Lignin, a component of plant cell walls, is currently underutilized, primarily serving as combustion waste fuel. Its high aromatic content makes it a promising renewable source of aromatic compounds. By rational catalytic utilisation of metal nanoparticles (NPs) embedded onto zeolite supports and their advantageous properties, such as high surface to mass ratio due to the small size of metal species, valorisation of lignin-derived molecules takes on new dimensions from economic and ecological direction.

Herein, as a proof of concept, we utilized a degallated gallosilicate – MFI nanosponge, as a support for metal NPs. The support was obtained by degallation via concentrated nitric acid treatment of a hydrothermally synthesised gallosilicate. Its architecture comprises of an interconnected, disordered network of MFI nanolayers <sup>1</sup> with degallation-generated silanol nests <sup>2</sup> – surface hydroxyl groups crucial for anchoring and stabilising metal NPs. These silanol nests serve as key binding sites, significantly enhancing the material's capacity for metal NPs immobilization.

This work is focused on post-synthesis mechanochemical incorporation of metal NPs (Pd, Pt, Ru, Rh, Ni, and Cu) and bimetallic species (additional rare-earth metals (REE): La, Ce, and Y) onto prepared zeolite support. Catalysts were characterized using powder X-ray diffraction, nitrogen sorption, and scanning electron microscopy. Moreover, materials were analysed using scanning transmission electron microscopy and elemental mapping, focusing on metal particle size and dispersion. Simultaneous incorporation of REE elements as metallic promoters alongside metal species resulted in more sintering resistant and smaller NPs (maxima in range 1.0–1.5 nm) with a better dispersion in contrast to monometallic samples (1.5–2.0 nm).

The catalytic performance of the materials was evaluated for the selective hydrogenation and hydrodeoxygenation of eugenol (EUG), a lignin valorization <sup>3</sup> model molecule. The 6 h catalytic hydrogenation reaction was performed at the H<sub>2</sub> pressure of 25 bars at 150 °C. In the case of the monometallic Pt-impregnated sample, EUG conversion reached 53 % with observed 77 % selectivity towards the main observed product – 2-methoxy-4-propylphenol (MPPA) while the remaining 23 % corresponded to the minor product – isoeugenol (iEUG). Full EUG conversions were obtained when bimetallic Pt-REE-impregnated catalysts were used with a retained selectivity towards MPPA. However, when the monometallic Pd-impregnated catalyst was applied, complete conversion with 100 % selectivity towards MPPA was reached. In the case of Pd-REE-impregnated samples, 100 % EUG conversion was achieved with varying 83–93 % selectivity towards MPPA while yielding a variety of aromatic and cyclic aliphatic minor products with no iEUG formed.

#### **References:**

<sup>1</sup>C. Jo et al., Chem. Commun., 50, **2014**, 4175–4177

<sup>2</sup> A. Li et al., Angew. Chem. Int. Ed., 62, **2023**, e202213361

<sup>3</sup> A. Sreenavya et al., Ind. Eng. Chem. Res., 59, **2020**, 11979–11990

**OP10** 

#### INVERSION OF CHIRALITY IN GTM-4 ENANTIO-ENRICHED ZEOLITE DRIVEN BY A MINOR CHANGE OF THE STRUCTURE-DIRECTING AGENT

## <u>R. de la Serna</u>, I. Arnaiz, J. Jurado, C. Márquez-Álvarez, J. Pérez-Pariente and L. Gómez-Hortigüela

#### Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Calle Marie Curie, 2, 28049, Madrid. ramon.serna@csic.es

GTM-3, a germanosilicate zeolite with an -ITV framework, demonstrated outstanding asymmetric catalytic performance, achieving an enantiomeric excess (ee) of 50% in the ring-opening reaction of trans-stilbene oxide with 1-butanol<sup>1</sup>. However, its limited ee may result from incomplete chirality transfer from the catalyst to the reaction or the zeolitic structure being only partially enantiopure. Since chirality is induced by the

Table 1-Enantiomericexcesses when using catalystsprepared with both enantiomersof the indicated ADEs. The eecorrespond to the SN2 openingproducts of trans stilbene oxidewith 1-butanol.

	<i>ee</i> (%) unlike		
SDA	SS	RR	
EMPS	-51,1	+50,1	
BMPS	+44,0	-45,0	
o-MBMPS	+54,8	-53,9	

structure-directing agent (SDA) during crystallization, optimizing the chiral cation is essential.

To address this, benzyl- and o-methylbenzylsubstituted SDAs (BMPS and o-MBMPS) were employed, successfully crystallizing the -ITV framework. The resulting catalysts exhibited ee values similar to GTM-3, but unexpectedly, those enantiomer derived from the same of with different methylpseudoephedrine but substituents showed opposite ee signs <sup>2</sup>. This indicates that the same chiral precursor can direct the formation of either enantiomorphic polymorph, depending on whether it carries an ethyl (EMPS) or benzyl (BMPS, o-MBMPS) group, highlighting the

crucial role of cation packing within the zeolite structure. Furthermore, the catalyst with o-MBMPS showed enhanced enantioselectivity (ee = 55%), demonstrating that an ortho-methyl group improves this property.

These findings reveal that subtle modifications in the SDA can significantly influence chirality transfer, ultimately reversing the enantiomeric preference of the system and offering new insights into the rational design of chiral zeolites for asymmetric catalysis.

#### References

<sup>1</sup> R. de la Serna, D. Nieto, R. Sainz, B. Bernardo-Maestro, Á. Mayoral, C. Márquez-Álvarez, J.Pérez-Pariente and L. Gómez-Hortigüela, JACS, **2022**, 144, 7951-8400.
<sup>2</sup> R. de la Serna, I. Arnaiz, C. Márquez-Álvarez, J. Pérez-Pariente and Luis Gómez-Hortigüela, Chem. Commun. **2022**, 58, 13083-13086.

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#### BIOGAS VOC VALORIZATION: THE CASE OF ZEOLITE-CATALYZED D-LIMONENE ETHOXYLATION

#### Paolo Bruno<sup>1,2\*</sup>, Enrico Catizzone<sup>1</sup>, Francesco Pietramale<sup>1,3</sup>, Massimo Migliori<sup>1</sup>, Raffaella Mancuso<sup>4</sup>, Bartolo Gabriele<sup>4</sup>, Girolamo Giordano<sup>1</sup>

CECaSP Laboratory, University of Calabria, Via P. Bucci 42/A, 87036, Rende (CS), Italy
 Chibiofaram, University of Messina, Viale F. Stagno D'Alcontres 31, 98165, Messina, Italy
 SENEA, Trisaia Research Center, 75026, Rotondella (MT), Italy
 4 LISOC Laboratory, University of Calabria, Via P. Bucci 12/C, 87036, Rende (CS), Italy
 \*Presenting author email: paolo.bruno@unical.it

The anaerobic digestion of OFMSW is a mature and well-tested industrial practice that produces biogas (a mixture of methane and carbon dioxide) from waste materials, reducing at the same time the impact on landfills. The biogas produced through anaerobic digestion is usually rich in impurities which must be eliminated before proceeding with any upgrading or separation from the CO2 for subsequent introduction into the grid. These impurities include ammonia, hydrogen sulfide and volatile organic compounds (VOCs)<sup>1</sup>. Analyzing a mixture of VOCs coming from a local company (Calabria, Italy) revealed that this is mainly composed of D-Limonene, a monocyclic terpene bearing two double bonds with NBP 177 °C, p-Cymene, an aromatic compound with NBP 176 °C and numerous other compounds, present in traces. The main components of the VOC mixture cannot be separated by distillation due to the boiling points proximity, thus making the recovery of the pure components uneconomical. In this work, a possible solution to the separation problem is presented, which involves the chemical transformation of Limonene into a higher boiling component, with the aim of transforming waste into resource<sup>2</sup>. This work investigated the ethoxylation reaction of Limonene to  $\alpha$ -Terpinyl-Ethyl-Ether using BEA, MOR and MFI zeolites as acid catalysts. The liquid phase reaction was conducted in stainless steel batch reactors, using mixtures of 75-300 mmol L<sup>-1</sup> of Limonene in ethanolic solution. From an initial analysis of the activity of the catalysts it emerged that the reaction occurs only in the presence of a zeolitic structure capable of accommodating the bulky molecule produced, such as BEA and MOR. Beta zeolite was used for catalytic testing at different temperatures and reagent concentrations, showing good selectivity (up to 90%) and demonstrating that the conversion of Limonene is favored as the temperature increases,

but is not influenced by the initial reagent concentration. These data were subsequently used successfully in developing a kinetic model for the reaction. The effect of the acid sites' concentration was also evaluated, demonstrating the existence of an optimal point regarding the  $\alpha$ -Terpinyl-Ethyl-Ether yield which appears to be around 400  $\mu$ mol g<sup>-1</sup> (Figure 1).

![](_page_29_Figure_7.jpeg)

#### **References:**

<sup>1</sup> Zhao, R.; Novak, J. T.; Douglas Goldsmith, C., Waste Manag. **2013**, 33, 1207. <sup>2</sup> Stanciulescu, M.; Ikura, M., J. A. A. J. **2006**, 75, 217-225.

#### PALLADIUM/ZEOLITE NANOCLUSTERS IMPROVE SELECTIVITY FOR PARTIAL HYDROGENATION OF ALKYNES

#### Jun Xie, Jan Přech, Martin Kubů, Michal Mazur, Jiří Čejka

#### Department of Physical and Macromolecular Chemistry, Charles University, Prague, Czech Republic

Selective hydrogenation of alkynes to alkenes, is essential for preparation of polymergrade olefins and for fine chemicals production. Palladium (Pd) catalysts, particularly the Lindlar catalyst (Pd/CaCO<sub>3</sub>-Pb), are commonly used for this process to enhance selectivity by partially poisoning Pd sites with lead (Pb), which limits hydrogenation at the alkene stage to avoid over-hydrogenation to alkanes, but results in substantial Pd atoms waste and Pb toxicity concerns for future applications. Therefore, selective catalysts that maximize Pd atoms utilization without toxic components should be developed. Reducing metal nanoparticles (NPs) size to nanoclusters (NCs) and, ultimately, to single-atoms (SAs) level can improve atom use efficiency, but at the same time stability is challenged by high surface energy. Zeolites can enhance stability by confining the Pd species in their micropores. Recently, Bai et al. <sup>1</sup> reported PdC<sub>X</sub> subnanometric clusters encapsulated in silicalite-1 exhibited exceptionally high selectivity (99% at 99% conversion) for semihydrogenation of phenylacetylene. We aimed at simplifying the approach by creating Pd of various size on surface of 2D zeolites.

In this work, Pd-NCs were synthesized via ion exchange of aluminosilicate zeolites MCM-56, lamellar ZSM-5 and pure silica lamellar silicalite-1 (S-1) as supports, while Pd nanoparticle catalysts (Pd-NPs) were prepared by wet impregnation of the above supports. MCM-56 is composed of disordered MWW zeolite layers, while lamellar ZSM-5 and lamellar S-1 are composed from MFI nanosheets. The catalytic performance of the Pd-NCs and the Pd-NPs was evaluated in selective hydrogenation of 1-octyne (alkyne) in n-hexane at 5 bars of H<sub>2</sub> at 25°C. Commercial 2% Pd/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> and the Lindlar catalyst served as benchmarks. For all catalysts, the selectivity to 1-octene was compared at alkyne conversion of 92-99%. The 1-octene selectivity over Pd-NCs and Pd-NPs ranged from 76% to 92%, being more selective than 2% Pd/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> with a selectivity of 71% at 99% conversion. The Pd-NCs exhibited higher selectivity compared to Pd-NPs. For instance, Pd-NCs/MCM-56 achieved a selectivity 92% at 98% conversion, comparable to the Lindlar catalyst (selectivity 84% at 99% conversion) showing our catalysts give Lindlar like selectivity without Pb. Furthermore, Pd-NCs does not facilitate undesirable semihydrogenation-isomerization yielding 2-octene instead of 1-octene, while the Pd nanoparticles does. Notably, our Pd-NCs 1-octene selectivity values are comparable, e.g., with these for the  $PtC_x$  clusters in silicalite-1 (90% selectivity at 99% conversion <sup>1</sup>), thus highlighting competitiveness of 2D zeolite supported nanoclusters in semihydrogenation of alkynes.

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#### **References:**

<sup>1</sup> Bai, R.; He, G.; Li, L.; Zhang, T.; Li, J.; Wang, X.; Wang, X.; Zou, Y.; Mei, D.; Corma, A.; Yu, J. Angew. Chem. Int. Ed. **2023**, 62 (48), e202313101.

#### SYNTHESIS OF BIO-JET FUEL PRECURSORS BY ALDOL CONDENSATION OF FURFURAL AND CYCLOPENTANONE USING TITANIUM OXIDE-MODIFIED USY ZEOLITES

Daniel de la Calle<sup>1,2</sup>, Jennifer Cueto<sup>1</sup>, Rafael A. García-Muñoz<sup>2</sup>, David P. Serrano<sup>1, 2\*</sup>

<sup>1</sup>Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, E28935, Móstoles, Madrid, Spain

<sup>2</sup>Chemical and Environmental Group, Rey Juan Carlos University, c/ Tulipán, s/n, E28933, Móstoles, Madrid, Spain

The use of bio-jet fuels in the aviation industry is regarded as a sustainable approach to mitigating greenhouse gas emissions [1]. A significant focus has been placed on the aldol condensation of green aldehydes and ketones as a promising method for the production of sustainable aviation fuels (SAF). Thus, furfural (FFL) and cyclopentanone (CPO) are produced during (hemi)cellulosic biomass hydrolysis and can be converted to 10 and 15 carbons number bio-jet fuel precursors [2]. Zeolites have been identified as promising catalysts in this reaction due to their strong acidity and exceptional chemical and thermal stability. However, their use is limited by the restricted access of bulky molecules to their micropores [3]. This study aims to compare the catalytic activity of commercial Ultrastable Zeolite Y (USY), which possesses both

relatively large pores and cavities, with commercial nanocrystalline ZSM-5 zeolite (n-ZSM-5), used as a reference material. The also evaluates the impact study of incorporating TiO<sub>2</sub> (2.5, 5 y 10 wt%) to understand how acidity tuning influences catalytic performance. Catalytic tests were performed in a StarFish system at 100 °C and using toluene as solvent and 0.05 g of catalyst (90 wt%; 10:1 CPO:FFL molar ratio and 750 rpm). Samples were collected at 2, 4 and 6 h, then filtered and analysed by GC-FID. Figure

**1** shows that the USY zeolite exhibits significantly higher FFL conversion (60%) and C15 production

![](_page_31_Figure_9.jpeg)

Figure 1. FFL and CPO aldol condensation over the different catalysts at 6h.

(8%) compared to the n-ZSM-5 sample, which achieves only 12% and 1%, respectively, since in this case the reaction occurs just over the external surface of the zeolite nanocrystals [3]. In contrast, the larger micropores of USY zeolite, as well as the presence of a significant contribution of mesopores, provoke a better utilisation of its overall surface area (746 m<sup>2</sup>/g) and associated acid sites. Additionally, incorporating TiO<sub>2</sub> into the USY zeolite further enhances its catalytic activity by altering the total concentration of Brønsted and Lewis acid sites. Among the different TiO<sub>2</sub> loadings tested, the USY zeolite modified with 5 wt% TiO<sub>2</sub> exhibits the highest FFL conversion, reaching an impressive 85.7% and a C15 yield of 15% with a global C10+C15 global yield of 71%. This suggests that the presence of TiO<sub>2</sub> not only changes the number of active sites but also improves their catalytic effectiveness.

#### References:

<sup>1</sup>J. A. Muldoon, B. G. Harvey; *ChemSusChem* **2020**, 13, 5777-5807.

<sup>2</sup>J. Cueto, L. Faba, E. Díaz, and S. Ordóñez; *ChemCatChem.* **2017**, 9, 1765–1770.

<sup>3</sup>J. Cueto, D. de la Calle, M. M. Alonso-Doncel et al.; *Bioresour. Technol.* **2025**, 418, 131877.

#### Yuqi Zhang, Carlos Bornes, Jan Přech and Mariya Shamzhy

#### Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Zr-zeolite catalysts with Lewis acidity are active in biomass valorisation reactions.<sup>1</sup> Zr atoms can be bonded to the zeolite framework *via* four or three siloxane bonds, forming either 'closed' Zr(OSi)<sub>4</sub> or 'open' Zr(OH)(OSi)<sub>3</sub> acid sites. Notably, the ratio of 'open' to 'closed' acid sites significantly influences the catalytic behaviour of Zr-zeolites.<sup>2</sup> However, methods for distinguishing these acid centres remain limited, while their quantification presents a challenge. Specifically, *in situ* FTIR spectroscopy of adsorbed CO (IR-CO) has been proposed to differentiate between 'open' and 'closed' Zr sites, but it only provides semi-quantitative information.<sup>3</sup>

This study introduces carbonyl compounds, such as acetone and trimethylacetaldehyde as probe molecules for analyzing acid sites in Zr-BEA zeolites and proposes FTIR spectroscopic method for their quantification. We modulated the 'open' to 'closed' acid

![](_page_32_Figure_6.jpeg)

Figure 1. FTIR spectra of tri-methylacetaldehyde adsorbed on Zr-BEA zeolite.

site ratio of Zr-BEA by varying hydrothermal synthesis conditions, as semi-quantitatively validated by IR-CO spectroscopy. Dose-by-dose adsorption of tri-methylacetaldehyde monitored by FTIR spectroscopy, showed a progressive evolving of the absorption bands (Figure 1), attributed to different surface adducts: stronger 'open' sites (1683(4) cm<sup>-1</sup>), weaker 'closed' sites (1695(7) cm<sup>-1</sup>), H-bonded and physisorbed probe molecules (1708-1717 and 1719-1728 cm<sup>-1</sup>). The assignment of the absorption bands observed in FTIR spectra was verified by complimentary <sup>1</sup>H-<sup>13</sup>C CP MAS NMR studies.

Molar absorption coefficients for the characteristic absorption bands of trimethylacetaldehyde were determined, enabling the quantification of Zr Lewis acid sites using *in situ* FTIR spectroscopy. The results of this study are expected to facilitate the establishment of property-performance correlations for zeolite catalysts in reactions sensitive to the configuration of Zr Lewis acid sites.

#### **References:**

<sup>1</sup>Suib, S. L.; Prech, J.; Szaniawska, E.; Cejka, J. *Chem. Rev.* **2023**, *123* (3), 877-917. <sup>2</sup>Harris, J. W.; Cordon, M. J.; Di Iorio, J. R.; Vega-Vila, J. C.; Ribeiro, F. H.;

Gounder, R. J. Catal. 2016, 335, 141-154.

<sup>3</sup> Sushkevich, V. L.; Vimont, A.; Travert, A.; Ivanova, I. I. *J. Phys. Chem. C* **2015**, *119* (31), 17633-17639.

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#### CATALYTIC TRANSFORMATION OF DIALKYLUREAS INTO METHANE BY Ru-MOFs

#### Itziar Arnaiz<sup>1</sup>, Carlos Márquez-Álvarez<sup>1</sup>, Marcos Zubimendi<sup>1</sup>, M. Asunción Molina<sup>2,3</sup>, Andrew M. Beale<sup>2,3</sup>, Joaquín Pérez-Pariente<sup>1</sup> and Manuel Sánchez-Sánchez<sup>1</sup>

 <sup>1</sup> Instituto de Catálisis y Petroleoquímica (ICP), CSIC, Madrid, Spain
 <sup>2</sup> Department of Chemistry, University College London, London, UK
 <sup>3</sup> Research Complex at Harwell, Rutherford Appleton Laboratories, Harwell Science and Innovation Campus, Harwell, Didcot, UK

Direct  $CO_2$  hydrogenation is a key challenge for the catalytic community. However,  $CO_2$  is nowadays widely used for the synthesis of urea (or dialkylureas) by reacting with ammonia (or amines). Such (dialkyl)urea can therefore be considered as a solid (and easily manageable) source  $CO_2$ . Furthermore, Milstein et al. have shown that Ru or Mn complexes can catalyze the hydrogenation of dialkylureas to methanol, also giving the corresponding amine<sup>1,2</sup>, which could be recycled to react again with  $CO_2$ .

In this context, this work aims to find heterogeneous catalysts for such reaction. MOF materials were selected because of their nanoporosity, whereas Ru was chosen because of its hydrogenating power. Ru-HKUST-1, with the formula  $Ru^{II}_{1.5}Ru^{III}_{1.5}(BTC)_2Cl_{1.5}$ , and the new Ru-BTC MOF, homologous to the semiamorphous Fe-BTC, in which all Ru is as Ru(III), were prepared and catalytically tested. Figure 1 summarizes much of the results of this study. Using different characterization techniques, it was possible to identify the Ru environment in both Ru-MOFs, which were tested as catalysts in the hydrogenation of dimethylurea under relatively mild conditions (150 °C, 30 bar, 48 h). In the absence of catalyst there is no reaction, whereas Ru-BTC converted 67% of dimethylurea under these conditions with a selectivity to methane of 96%.

![](_page_33_Figure_7.jpeg)

**Figure 1.** Schematic representation of the results of this work, including the characterization techniques used to establish the metallic environments and oxidation states of the two Ru MOFs, as well as the most relevant catalytic results in the methanation of dimethylurea.

<sup>1</sup> Balaraman, E.; Ben-David, Y.; Milstein, D. Angew. Chem. Int. Ed. 2011, 50 11702-11705.

<sup>2</sup> Das, U.K.; Kumar, A.; Ben-David, Y.; Iron, M.A.; Milstein, D. J. Am. Chem. Soc. 2019, 141,12962-6.

Acknowledgements: MCIN/AEI/10.13039/501100011033 and UE for projects TED2021-131143B-I00 and PID2022-1363210B-C21. M.A.M. thanks Laurelin project (101022507) for PDRA contract at UCL.

#### SYNTHESIS OF SPIROCYCLIC ISOXAZOLONES USING ENANTIOSELECTIVE CONIA-ENE TYPE REACTION

#### Martin Kamlar, Salil Putatunda, Jan Veselý

#### Charles University, Department of Organic Chemistry, Hlavova 2030/8, Prague, 128 00, Czech Republic

Complex three-dimensional molecules with quaternary carbon centers containing heteroaromatic units often exhibit remarkable biological properties due to their conformational rigidity. The presence of heteroaromatic units as bioactive frameworks makes them particularly valuable in natural product synthesis and medicinal chemistry. As a result, developing stereoselective methods for these complex molecules presents a significant challenge in modern synthetic organic chemistry.<sup>1</sup> Among other strategies, synergistic catalysis when a combination of chiral organocatalysis together with transition metal catalysis is employed, offers an elegant solution in this field.<sup>2</sup>

Building on our previous research in this area, we have explored a stereoselective strategy for the synthesis of spirocyclic isoxazolones. This method utilizes a Michael/Conia-ene cascade reaction sequence, catalyzed cooperatively by a chiral secondary amine organocatalyst with palladium (0) catalyst (Scheme 1). Under these conditions, the reaction yields a broad range of corresponding spirocyclic molecules containing isoxazolone moiety, with excellent yields and with good to high levels of diastereo- and high levels of enantiomeric control. Moreover, the prepared molecules are compatible with various subsequent synthetic transformations, highlighting the versatility of this protocol.

![](_page_34_Figure_7.jpeg)

**Scheme 1**: Synergistic Catalysis-Driven Enantioselective Michael/Conia-Ene Reaction for the Synthesis of Spiro Isoxazolone Derivatives.

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#### **References:**

<sup>1</sup> Wang, J.; He, F.; Yang, X. Nat. Commun. 2021, 6700.

<sup>2</sup> Del Vecchio, A.; Sinibaldi, A.; Nori, V.; Giorgianni, G.; Di Carmine, G.; Pesciaioli, F. *Chem. Eur. J.* **2022**, *28*, e202200818.

#### STYRENE HYDROFORMYLATION CATALYZED BY RHODIUM SUPPORTED ON 3D AND 2D TRANSITION METAL DICHALCOGENIDES

#### <u>Martina Pitínová</u>, Alica Krnáčová, Ayesha Shafiq, Iryna Danylo, Lukáš Koláčný, Jan Luxa, Martin Veselý

#### University of Chemistry and Technology, Prague, Technická 5, Prague, Czech Republic

The hydroformylation is a key industrial process which involves the addition of syngas (carbon monoxide and hydrogen) to an olefin to produce aldehydes. This reaction is of great importance, as the aldehydes serve as key precursors in the production of alcohols, carboxylic acids, and other valuable compounds used in the manufacturing of bulk or special chemicals. Despite the fact, that the most of modern industrial processes are catalyzed by the heterogeneous catalysts, hydroformylations are still nowadays catalyzed homogeneously. Therefore, an effort for replacing homogeneous catalysts by the heterogeneous counterparts is significant.

The aim of the presented research was focused on the preparation of heterogeneous Rh catalysts utilizing transition-metal dichalcogenides (TMDs) as the supports, their deep characterization and testing their catalytic activity in hydroformylation reaction. Different supports from TMDs family, namely MoS<sub>2</sub>, WS<sub>2</sub>, Mo<sub>x</sub>W<sub>y</sub>S<sub>2</sub> composites and their exfoliated 2D nanosheets, as well as different preparation methods (incipient wetness impregnation, microwave-assisted synthesis) and different Rh loadings (0.5 – 10 wt.%) were investigated. Styrene was selected as the model reactant and its hydroformylation was performed in the batch autoclave reactor at 100 °C and 3 MPa (CO/H<sub>2</sub> 1:1) for 6 h. The successful deposition of Rh on 3D and 2D analogues of TMDs was confirmed using range of characterization methods (XRF, SEM/EDS, TEM, XRD).

The prepared catalysts were successfully tested in styrene hydroformylation and predominantly desired aldehydes were formed. Hydrogenation of styrene to ethylbenzene was the only competitive undesired reaction. High aldehyde selectivity over 80 % was achieved with the most of the catalysts with Rh loading in the 1.5–6 wt.% range. The n/iso aldehyde ratio remained stable (0.7) across the most tested catalysts. Catalysts supported on MoS<sub>2</sub> mostly outperformed WS<sub>2</sub> and Mo<sub>x</sub>W<sub>y</sub>S<sub>2</sub> composites, as well as their 2D analogues, with higher achieved conversions, and slightly higher aldehyde selectivity. Calcination of the prepared catalysts generally slightly increased conversion but had negligible effect on aldehyde selectivity. The best performing catalysts was Rh<sub>5%</sub>/MoS<sub>2</sub>-3D with 50 % of styrene conversion and over 80 % aldehyde selectivity.

![](_page_35_Figure_8.jpeg)

Scheme 1: Styrene hydroformylation

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# Assessment of zeolite efficiency in heavy metal removal from MSWI fly ash leachates

<u>Maura Mancinelli</u>,<sup>a</sup> Costanza Bonadiman, <sup>a</sup> Renzo Tassinari, <sup>a</sup> Bernasconi Davide, <sup>b</sup> Destefanis Enrico, <sup>b</sup> Caviglia Caterina, <sup>b</sup> Alessandro Pavese, <sup>b</sup> Annalisa Martucci <sup>a</sup>

<sup>a</sup> Earth Science and Physics Department, 44122 Ferrara, Italy

<sup>b</sup> Earth Sciences Department, University of Turin, 10125 Turin, Italy

maura.mancinelli@unife.it

This study investigates the performance of both natural and synthetic zeolites (specifically 5A, 13X, Y720, and CHA) in capturing heavy metals from leachates produced during steam cleaning of Municipal Solid Waste Incineration (MSWI) fly ash [1–2]. A series of batch adsorption tests was conducted to evaluate and compare the effectiveness of each zeolite in removing elements such as Pb, Zn, Cd, Cu, Mn, and Fe. Among the tested materials, zeolite 13X showed the highest efficiency, especially for Pb, Zn, and Cu, which is attributed to its generous pore volume and advantageous structural configuration. Zeolite 5A also showed strong affinity for Zn and Pb, while Y720 displayed selectivity for Mn and Fe, likely due to its high Si/Al ratio that promotes specific cation uptake. CHA-type zeolite exhibited intermediate removal capacities for Pb and Zn, although its performance was reduced by competition from other ions like Ca, K, and Mg. The findings underscore the importance of key structural parameters such as pore architecture, cation exchange potential, and framework composition in determining metal retention efficiency. The results support the strategic use of tailored zeolites for environmentally sustainable remediation of hazardous leachates.

#### References

[1] Destefanis, M., et al. (2020). Steam washing for incinerator residue treatment: Improving leaching efficiency and metal recovery. Waste Manag., 104, 1-8.

[2] Bernasconi, D., et al. (2025). Steam washing for MSWI-FA treatment. Waste Manag., 195, 10-21.

# ENHANCED OXIDATIVE STEAM REFORMING OF BIO-OIL AQUEOUS PHASE USING NOBLE METAL-DOPED Co/CeO<sub>2</sub>/SBA-15 CATALYSTS

# <u>Carlos A. Chirinos</u><sup>1</sup>, Pedro J. Megía<sup>1</sup>, Arturo J. Vizcaíno<sup>1</sup>, José A. Calles<sup>1,2</sup> and Alicia Carrero<sup>1,2</sup>

# <sup>1</sup>Chemical and Environmental Engineering Group, Universidad Rey Juan Carlos, Móstoles, Spain

<sup>2</sup> Institute of Sustainable Technologies, Universidad Rey Juan Carlos, Móstoles, Spain

Hydrogen plays a key role in several industrial sectors, including oil refining, petrochemicals, chemical manufacturing, metallurgy, as well as a future energy sector. Hence, sustainable hydrogen production has been a high-priority objective in recent years. A promising renewable approach is catalytic oxidative steam reforming of the aqueous phase of bio-oil<sup>1</sup>, where catalyst development with high catalytic performance and resistance to coke deposition is crucial for enhancing process efficiency.

This study focusses on developing of novel bimetallic Co-M/CeO<sub>2</sub>/SBA-15 catalysts (M: Pt, Rh and Ru). Catalysts chemical composition includes 10wt% of CeO<sub>2</sub>, 7w.% of Co and 1 wt.% of noble metal (M). All the samples were characterized by ICP-AES, XRD, H<sub>2</sub>-TPR, N<sub>2</sub> physisorption, and TGA. A simulated bio-oil aqueous phase mixture reported elsewhere<sup>2</sup> was used to carry out the oxidative steam reforming reactions in a fixed bed reactor at 550°C, WHSV = 60.2 and atmospheric pressure.

The catalytic performance in terms of hydrogen yield is shown in Fig. 1. As it can be observed, Co-Rh/CeO<sub>2</sub>/SBA-15 catalyst exhibited the best activity, achieving 90% conversion and hydrogen vield of 54% after 5 hours, next to the thermodynamic equilibrium. These results highlight that the presence of Rh in the catalyst significantly enhances the catalytic performance, increasing the conversion of the simulated bio-oil aqueous phase mixture by 29% and the hydrogen yield by 21%, compared to the Co/CeO<sub>2</sub>/SBA-15 catalyst, thus evidencing the role of Rh in promoting both activity and H<sub>2</sub> yield in the oxidative steam reforming reaction.



Fig. 1. Hydrogen yield in the OSR of simulated bio-oil aqueous phase using Co-M/CeO<sub>2</sub>/SBA15 (M: Pt, Rh and Ru).

#### **References:**

<sup>1</sup> Xu, X.; Zhou, Q.; Yu, D. Int J Hydrogen Energy **2022**, *47* (79), 33677–33698.
<sup>2</sup> Bergem, H.; Xu, R.; Brown, R. C.; Huber, G. W. Green Chem. **2017**, 19(14), 3252-6262.

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# THE ISSUE OF COPPER ENCAPSULATION IN MICROPOROUS MATERIALS

# Kateřina Knotková<sup>1</sup>, Safaa Essid<sup>1</sup>, Jakub Halamek<sup>1</sup>, Roman Bulanek<sup>1</sup>

# <sup>1</sup> Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic

Since the 1950s, copper-based catalysts have demonstrated significant activity in the non-oxidative dehydrogenation of ethanol. To prevent side reactions at acidic or basic sites, neutral SiO2 supports were employed to support the copper species. Characterization studies have attributed the high catalytic activity to the uniform dispersion of copper species.<sup>1, 2</sup> However, due to the very low Tammann temperature of copper, copper exhibits fast surface diffusion and sintering.

One approach to ensuring precise copper dispersion and preventing bulk formation is to encapsulate copper within the channels of purely siliceous zeolitic matrices. In our study, we focused on the synthesis of siliceous MFI, BEA, and FER, followed by the incorporation of copper through direct synthesis.

The preparation of purely siliceous forms of the mentioned zeolitic structures is not a critical point of the synthesis. Using generally known methods, MFI, BEA, and FER matrices were prepared. Depending on the ratio of starting materials, the use of crystallization centers, and the crystallization time, it is possible to obtain zeolite crystals of various sizes and external surfaces.

However, the incorporation/encapsulation of copper during synthesis encounters the issue that the presence of HF destabilizes Cu complexes, preventing Cu from being incorporated into the zeolite channels. Cu-Si-MFI zeolites were prepared using tetraethylenepentamine (TEPA) and ethylenediamine (EN), where the success of the synthesis depends on the presence of crystallization centers and the crystallization time. Using these methods, Cu-Si-MFI catalysts containing 0.2 to 1 wt. % copper were prepared.

However, the use of these methods is much more challenging in the case of BEA and FER, where the presence of HF in the mixture prevents copper from being incorporated and also hinders the formation of the correct crystalline structure. In these cases, some more complicated and laborious procedures, such as the OSDA-mismatch approach, must be chosen.

#### **References:**

1. Pang, J.; Zheng, M.; Wang, C.; Yang, X.; Liu, H.; Liu, X.; Sun, J.; Wang, Y.; Zhang, T., Hierarchical echinus-like Cu-MFI catalysts for ethanol dehydrogenation. *ACS Catalysis* **2020**, *10* (22), 13624-13629.

2. Pang, J.; Yin, M.; Wu, P.; Li, X.; Li, H.; Zheng, M.; Zhang, T., Advances in catalytic dehydrogenation of ethanol to acetaldehyde. *Green Chemistry* **2021**, *23* (20), 7902-7916.

## BIOFUEL SYNTHESIS FROM SHORT-CHAIN ALCOHOL CONDENSATION OVER CU/MGAL CATALYSTS

# Valdivieso-Vera Daniel A.<sup>1,2</sup>, Santos-López Iván A.<sup>1</sup>, Barroso-Martín Isabel<sup>3</sup>, Rodríguez-Castellón Enrique<sup>3</sup>, Flores-Escamilla Gerardo A<sup>1</sup>, Cano-Gómez José J.<sup>1</sup>, Guerrero-Pérez M. Olga<sup>2</sup>

<sup>1</sup>Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, 66455, San Nicolás de los Garza, N.L. México

<sup>2</sup>Departamento de Ingeniería Química, Universidad de Málaga, Campus Teatinos, 29071, Málaga, Spain

<sup>3</sup>Departamento de Química Inorgánica, Cristalografía y Mineralogía,, Facultad de Ciencias, Instituto Interuniversitario de Investigación en Biorrefinerías I3B, Universidad de Málaga, Campus Teatinos, 29071, Málaga, Spain

The catalytic conversion of (bio)methanol and (bio)ethanol to higher alcohols with properties like conventional fossil fuels has gained significant attention in recent years due to environmental concerns, such as the emission of greenhouse gases responsible for global warming. The Guerbet reaction is an essential process for enhancing the value of short-chain alcohols (MeOH and EtOH), which involves three main steps in transforming aliphatic alcohols: dehydrogenation, aldol condensation, and subsequent hydrogenation. Bifunctional hydrotalcite-derived mixed oxide catalysts are effective for the Guerbet reaction and the incorporation of Cu into the catalysts can enhance the dehydrogenation and hydrogenation properties [1]. In this study, Mg<sub>x</sub>Al<sub>y</sub>Oz oxides derived from hydrotalcite materials were synthesized by coprecipitation method. Copper incorporation was achieved by incipient wet impregnation. The physicochemical properties of the catalysts were characterized by XRD, N<sub>2</sub>-Physisorption, H<sub>2</sub>-TPR, TPD and XPS. CuMgAl catalysts were employed in the Guerbet reaction of methanol and ethanol.

The results showed that Cu<sub>10</sub>MgAl and Cu<sub>15</sub>MgAl catalysts exhibited typical diffraction patterns of MgO phase according to JCPDS No. 45-0946 [2]. The Cu<sup>o</sup> crystalline phase was also detected at  $2\theta = 50.4^{\circ}$  (200) [3]. Furthermore, Cu<sub>10</sub>MgAl and Cu<sub>15</sub>MgAl catalysts displayed BET surface areas of 116 and 108 m<sup>2</sup>/g, respectively. The H<sub>2</sub>-TPR profiles revealed a peak at 275 °C, which was assigned to reducing Cu<sup>2+</sup> species to Cu<sup>o</sup> [4]. The catalytic performance results indicated that CuMgAl catalysts are active for the synthesis of three higher alcohols: isobutanol, *n*-butanol, and 1-propanol, in a continuous system at atmospheric pressure at 400 °C. In addition, catalysts with a higher Cu<sup>+</sup>/Cu<sup>0</sup> ratio (with Cu 10 wt.%) exhibited higher selectivity for iBuOH.

#### **References:**

[1] D.A. Valdivieso-Vera, I.A. Santos-López, J.J. Cano-Gómez, G.A. Flores-Escamilla, J.R. de la Rosa, E. Rodriguez-Castellón, I. Barroso-Martín, O. Guerrero-Pérez, App. Catal. A: Gen. 685 (2024) 119881

[2] D. Stošić, F. Hosoglu, S. Bennici, A. Travert, M. Capron, F. Dumeignil, J.L. Couturier, J.L. Dubois, A. Auroux, Catal Commun 89 (2017) 14–18.

[3] J. Guo, H. Yu, F. Dong, B. Zhu, W. Huang, S. Zhang, RSC Adv 7 (2017) 45420–45431.

[4]P. Benito, A. Vaccari, C. Antonetti, D. Licursi, N. Schiarioli, E. Rodriguez-Castellón, A.M. Raspolli Gallleti, T. Funaioli, Appl. Catal. A: General, 575 (2019) 111-119.

## CONVERSION OF FURFURAL INTO VALUABLE BIOPRODUCTS CATALYZED BY ZrO<sub>2</sub>-MODIFIED NANOCRYSTALLINE ZSM-5 ZEOLITE

# <u>Gemma Pérez-Martín</u><sup>1,2</sup>, Jennifer Cueto<sup>1</sup>, Marta Paniagua<sup>2</sup>, Gabriel Morales<sup>2</sup>, Juan A. Melero<sup>2</sup>, David P. Serrano<sup>1,2</sup>

<sup>1</sup>Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, E28935, Móstoles, Madrid, Spain <sup>2</sup>Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/Tulipán, s/n, E28933, Móstoles, Madrid, Spain

The transformation of hemicellulose-derived sugars into valuable chemicals has garnered significant attention due to its economic and environmental advantages<sup>1</sup>. One prominent example is the dehydration of xylose, obtained from hemicellulose hydrolysis, which yields furfural (FFL) a crucial platform molecule for synthesizing  $\gamma$ -valerolactone (GVL),  $\alpha/\beta$ -angelica lactone ( $\alpha/\beta$ -ANG), and isopropyl levulinate (IPL). These compounds serve diverse applications, including use as green solvents, biofuel additives, and precursors for biodegradable polymers<sup>2</sup>. The Meerwein-Ponndorf-Verley (MPV) reduction of FFL has been extensively investigated, employing 2-propanol as a hydrogen donor and zeolite supports as catalysts, with particular attention given to BETA zeolite<sup>3</sup>. This work studied this reaction using a nanocrystalline ZSM-5 zeolite (n-ZSM-5, Si/Al=45, Clariant), modified with ZrO<sub>2</sub>, as catalyst. The influence of operation parameters, such as ZrO<sub>2</sub> loading, temperature, and reaction time, on FFL conversion and yields to the desired products (GVL,  $\alpha/\beta$ -ANG, and IPL) was analyzed (Figure 1). A positive effect is observed in both parameters by increasing the temperature and reaction time, but excessively high values (200 °C and 24 h) can lead to undesirable byproducts like humins. While higher ZrO2 loadings do not always enhance conversion, an optimal balance is achieved using 5 wt% ZrO<sub>2</sub>, maximizing the yield and selectivity towards GVL,  $\alpha/\beta$ -ANG, and IPL. The ZrO<sub>2</sub> modification of the zeolite complements its acidic properties by generating a new population of highly accessible Lewis acid sites.



Figure 1. Influence of (a) different ZrO<sub>2</sub> loading at 180 °C and 6 h, (b) temperature with 10 wt% ZrO<sub>2</sub>/n-ZSM-5 and 6 h, and (c) time with 10 wt% ZrO<sub>2</sub>/n-ZSM-5 at 180 °C. 0.1 g catalyst, 10 g·L<sup>-1</sup> as [FFL]<sub>0</sub>.

#### **References:**

<sup>1</sup>Banu, J.; R., Kavitha, S.; Tyagi, V. K.; et al. Fuel. **2021**, 302, 121086.

<sup>2</sup> Yan, P.; Wang, H.; Liao, Y.; et al. Renew. Sust. Energ. Rev. **2023**, 178, 113219.

<sup>3</sup> Melero, J. A.; Morales, G.; Iglesias, J.; et al. Ind. Eng. Chem. Res. **2018**, 57(34), 11592-11599.

# ZEOLITE-AMINE COMPLEX CATALYZES MEERWEIN-PONNDORF-VERLEY TYPE HYDROGEN TRANSFER REACTIONS

# <u>Klára Veselá</u>, Jan Přech

### Department of Physical and Macromolecular Chemistry, Charles University, Prague, Czechia

The Meerwein-Ponndorf-Verley (MPV) reduction is a selective hydrogen transfer reaction allowing transformation of carbonyl compounds (ketones or aldehydes) to corresponding alcohols under mild conditions. Compared to traditional hydrogenation methods, the MPV reduction offers a safer alternative as it avoids use of molecular hydrogen. Over the last decade, Zr- and Sn-substituted zeolites were disclosed to be promising catalysts for this reaction, while the respective heteroatoms incorporated into the zeolite framework act as Lewis acid sites.<sup>1</sup>

MPV reduction of citronellal (representative biomass-derived carbonyl compound) with 2-propanol catalyzed by Zr- or Sn-beta can provide not only citronellol (the MPV reduction product), but also side products formed through parallel competing pathways, including en-al cyclization to isopulegol and acetalization to citronellal diisopropylacetal. We aim to control the citronellal MPV reduction selectivity to citronellol by using small organic bases, such as pyridine or N-methylpiperidine, through a selective site modification approach. Our experiments showed that the addition of pyridine, in a 1:10 ratio to substrate, significantly improved the selectivity towards citronellol. Without pyridine, the reaction over Zr-beta gave 36% yield of citronellol and 62% yield of isopulegol, while with pyridine the yield increased to 90% of citronellol and 10% of isopulegol after 6 hours of reaction. Comparison of the citronellol yield curves for the reactions with and without pyridine indicates that the pyridine accelerated the rate of citronellol formation. This confirms selective modification of the catalytic centers, ruling out a (selective) poisoning mechanism usually observed for the interaction of base molecules with aluminosilicate zeolite acid sites.

To further investigate the nitrogen base's role on the reaction mechanism, we performed a kinetic study over a temperature range of 40-80°C. Using Zr-beta catalyst prepared by hydrothermal synthesis, we determined the apparent activation energies for reactions leading to individual products. The formation of citronellol was evaluated using kinetic model developed for MPV reduction by Román-Leshkov et al.<sup>2</sup>, while isopulegol formation was described by pseudo-second-order kinetics. Acetal was neglected from the kinetic analysis as it is a minor product (<3% yield) over the Zr-beta and is not formed when the base is present. For the base-free reaction over the Zr-beta, the apparent activation energy was determined to be 57 kJ/mol for the isopulegol formation and 62 kJ/mol for the citronellol formation. In the presence of, e.g., pyridine, the apparent activation energy for the isopulegol production remained nearly unchanged (58 kJ/mol). However, a decrease was observed for the citronellol formation to 53 kJ/mol. Notably, reaction selectivity remained constant over the entire temperature range, favoring citronellol in the presence of the base. These results indicate the base modifies the reaction environment on or close to the active sites, where the cited reaction takes place, effectively enhancing the MPV product selectivity and offers significant potential for broader applications in Lewis acid-catalyzed reactions, particularly those involving zirconosilicate zeolite-based systems.

# **References:**

<sup>1</sup> Suib, S. L., Přech, J., Szaniawska, E. & Čejka, J. Chem. Rev. **2023**, 123, 877–917

<sup>2</sup> Johnson, B. A.; Di Iorio, J. R.; Román-Leshkov, Y. J. Catal. **2021**, 404, 607–619

## ENHANCING MACROPOROSITY IN SHAPED ZEOLITES FOR HYDROCRACKING

# Elena Martín<sup>1</sup>, Paula Gabal<sup>1</sup>, Amine Lwazzani<sup>1</sup>, Jordi H. Badia<sup>2</sup>, Jordi Guilera<sup>1,2</sup>

## <sup>1</sup>Catalonia Institute for Energy Research (IREC), Sant Adrià de Besòs, 08930, Spain <sup>2</sup>Facultat de Química, Universitat de Barcelona (UB), Barcelona 08028, Spain

Hydrocracking, a key process in petroleum refining, often relies on bifunctional zeolitebased catalysts to convert heavy hydrocarbons into valuable fuels through hydrogenation-dehydrogenation and acid cracking mechanisms<sup>1</sup>. While catalyst formulation is often explored at the powder level, transitioning to industrially relevant pellets is crucial for practical applications, addressing agglomeration, pressure drop, mechanical stability, and heat/mass transfer challenges. However, pelletization, typically achieved by mixing powders with binders, can alter porosity and chemical composition. For instance, the use of natural clays like bentonite and attapulgite reduced strong acid sites in ZSM-5 zeolites<sup>2</sup>, and silica/boehmite binders induced aluminum migration which created additional acid sites<sup>3</sup>. Maximizing hydrocracking performance requires pellet designs that ensure accessible, strong acid sites while balancing stability, diffusion, and efficiency.

In this study, Y-type zeolite (CBV760, Zeolyst) was shaped into extrudates using boehmite as a binder, **Y-bh** (8:2 zeolite/binder ratio), and peptized with diluted acetic acid. Peptization with acetic acid significantly enhanced mechanical strength compared to water (crush strength increased from 1 N to 12 N) by improving boehmite dispersion. To enhance macroporosity, **Y-bh-pmma** supports were fabricated by addition of poly(methyl methacrylate) (PMMA, dp = 1  $\mu$ m) as a pore former. Peptization also induced dealumination<sup>4</sup>, increasing mesoporosity, as confirmed by N<sub>2</sub>-physisorption and Hg-porosimetry. Y-bh-pmma showed greater macropore volumes and larger pore entries, while Y-bh retained a higher proportion of mesopores despite comparable total pore volumes. SEM analysis revealed rough surfaces and macropores in both samples.

Ni impregnation (5 wt.%) resulted in higher metallic surface areas for pelletized catalysts (0.57 and 0.42 m<sup>2</sup> Ni/g<sub>cat</sub> for Ni/Y-bh and Ni/Y-bh-pmma, respectively) compared to powdered zeolite (0.09 m<sup>2</sup> Ni/g<sub>cat</sub>), due to increased mesoporosity. However, the greater macroporosity in Y-bh-pmma did not improve Ni dispersion. XRD, H<sub>2</sub>-TPR, and ICP characterization supported these findings, highlighting the potential of the developed zeolite-based catalysts for hydrocracking. Future work will assess the impact of enhanced macroporosity on mass transfer and product selectivity to optimize catalytic performance in industrial hydrocracking applications.

#### **References:**

<sup>1</sup> Weitkamp, J. ChemCatChem. **2012**, 4, 3, 292. <sup>2</sup> Hernando, H.; Ochoa-Hernández, C.; Shamzhy, M.; Moreno, I.; Fermoso, J.; Pizarro, P.; Coronado, J. M.; Čejka, J.; Serrano, D. Catal. Sci. Technol. **2019**, 9, 789. <sup>3</sup> Velthoen, M. E. Z.; Paioni, A. L; Teune, I. E.; Baldus, M.; Weckhuysen, B. M. Chem. Eur.J. **2020**, 26, 11995. <sup>4</sup> Whiting, G.; Chung, S-H.; Stosic, D.; Chowdhury, A. D.; van der Wal, L. I.; Fu, D.; Zecevic, J.; Travert, A.; Houben, K.; Baldus, M.; Weckhuysen, B. M. ACS Catal. **2019**, 9, 4792.

# PREDICTIVE DYNAMICAL MODELLING OF ZEOLITIC CATALYSTS VIA A FLEXIBLE REACTIVE MACHINE LEARNING FRAMEWORK

# Andreas Erlebach, Daniel Willimetz, Indranil Saha, Chen Lei, Tereza Benešová, Carlos Bornes, Christopher J. Heard, <u>Lukáš Grajciar</u>

# Charles University, Prague, Czechia

Zeolites are microporous aluminosilicates that are crucial in various industries. Many of the desirable properties of zeolite catalysts derive from behaviours that are dynamical in nature, from the character and location of the catalytic active sites<sup>1</sup> to (reactive) interaction with the solvent present in the reaction mixtures under operating conditions. In addition, the characterization of zeolite also requires attention to the dynamics of guest species within the zeolite pore, including the diffusion of solvent molecules through the pore system, and the migration of cations, for example during collection of NMR or INS data. To accurately capture these dynamical effects, one must move beyond a static view of zeolites as rigid frameworks. However, it is computationally prohibitive to do such calculations at the ab initio level. Machine learning (ML) methods offer a way to massively accelerate the modelling while maintaining the desired ab initio accuracy.

In this contribution, we outline the development and several recent applications of transferrable reactive neural network interatomic potentials (NNIP) for a range of siliceous, H- and Na-exchanged zeolitic bulk/surface structures (e.g., CHA, MFI, FAU, ...) in reactive interaction with water, and silica-supported platinum clusters. Also we briefly outline various ways to use these baseline potentials as a stepping stone for improvements and extensions, including: i) data-efficient improvement of NNIPs to a higher reference level (e.g., hybrid DFT);<sup>1</sup> ii) re-use of the parts of the baseline NNIPs to generate the ML-based collective variables to enhance reaction sampling;<sup>1</sup> and, iii) use of NNIPs with other ML-based models (LASSO regression, kernel ridge regression, etc.) for prediction of other properties of interest than energies/forces, e.g., NMR chemical shifts.<sup>2,3</sup> In particular, we will demonstrate the value of this approach with examples drawn from dynamical modelling of: i) diffusion of water (clusters) inside the pores of realistic, defective protonic aluminosilicate zeolites such as H-FAU, ii) <sup>1</sup>H/<sup>23</sup>Na/<sup>27</sup>Al/<sup>29</sup>Si solid state NMR spectra, towards identification of Al and cation siting/distributions as well as nature of defects,<sup>2,3</sup> and iii) Pt cluster diffusion and agglomeration in (defective) siliceous zeolites and on their surfaces.<sup>4</sup>

In summary, our work exemplifies how to leverage machine learning for large-scale simulation of complex (zeolitic) catalysts in a comprehensive, bias-free fashion with a tunable accuracy, under at operating conditions.

# **References:**

<sup>1</sup> Erlebach, A.; Šípka, M.; Saha, I.; Nachtigall, P.; Heard, C. J.; Grajciar, L. et al. Nat. Commun. **2024**, 15, 4215.

<sup>2</sup> Lei, C.; Bornes, C.; Bengtsson, O.; Erlebach, A.; Slater, B.; Grajciar, L.; Heard, C.J. Faraday Discuss. **2025**, 255, 46-71.

<sup>3</sup> Willimetz, D.; Erlebach, A.; Heard, C. J.; Grajciar, L. Digit. Discov. **2025**, doi: 10.1039/D4DD00306C.

<sup>4</sup> Heard, C. J.; Erlebach, A.; Grajciar, L. Nanoscale **2024**, 16, 8108-8118.

# EFFECT OF ION-EXCHANGED H-USY ZEOLITES ON THE CATALYTIC UPGRADING OF PYROLYSIS LIGNIN-DERIVED BIO-OILS

# M. Inés Ávila<sup>1\*</sup>, M.M. Alonso-Doncel<sup>2</sup>, J. Cueto<sup>2</sup>, L. Briones<sup>1</sup>, G. Gómez-Pozuelo<sup>1</sup>, J.M. Escola<sup>1,3</sup>, D.P. Serrano<sup>1,2</sup>, A. Peral<sup>1</sup>, J.A. Botas<sup>1,3</sup>

<sup>1</sup>Chemical and Environmental Engineering Group, Rey Juan Carlos University <sup>2</sup>IMDEA Energy Institute, Av. Ramón de la Sagra, 28935, Móstoles (Spain) <sup>3</sup>Instituto de Investigación de Tecnologías para la Sostenibilidad, Rey Juan Carlos University, c/Tulipán s/n, 28933, Móstoles (Madrid), Spain. \*ines.avila@urjc.es

Lignin is a renewable and carbon-neutral resource with a relevant potential to produce high-added value products such as phenolic compounds. Catalytic pyrolysis is especially notable for its ability to enhance selectivity and deoxygenation. It has been demonstrated that alkali and alkaline earth ion-exchanged nanocrystalline zeolites, such as ZSM-5 and Beta, improve bio-oil quality by optimizing Lewis/Brønsted acidity, boosting the proportion of phenolic compounds in the bio-oil<sup>1</sup>. In this context, this study investigates the catalytic behaviour of a commercial USY zeolite in lignin pyrolysis, including its alkali and alkaline-earth ion-exchanged forms (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>). The experiments were carried out in a fixed-bed reactor operating at 550 °C for thermal lignin decomposition and 450 °C for catalytic vapour upgrading, and two different catalyst/lignin mass ratios (C/L = 0.2 and 0.4) were tested. The resulting char, bio-oil\* (water-free basis), water, permanent gases, and coke (the latter just for catalytic tests) were analysed using different techniques to assess conversion efficiency and products selectivity. In comparison to the non-catalytic test (N-C), employing commercial and ion-exchanged USY zeolite (H-USY and MeH-USY, respectively) reduces the bio-oil\* yield from 37 to 20-28 wt.%, increasing water and coke production (Figure 1.a). Figure 1.b shows the concentration of oxygenated aromatics (O-AR), carboxylic acids (CA), light oxygenates (LO), furans (FUR) and aromatics (AR) in the bio-oil\*. Related to the non-catalytic test, H-USY enhances the concentration of LO, AR and O-AR, due to its strong acidity which promotes lignin oligomers conversion. MeH-USY zeolites, with lower acid strength and higher proportion of Lewis acid sites, increase the concentration of O-AR due to the ketonisation and deoxygenation reactions. Notably, KH-USY and NaH-USY exhibit the highest concentration of O-AR which have numerous industrial applications.



Figure 1. Catalytic pyrolysis of lignin with H-USY and MeH-USY zeolites (C/L=0.2 and 0.4): a) fractions yield; b) detected concentration of compounds families in bio-oil<sup>\*</sup>.

#### **References:**

(1) M.I. Ávila et al. Catal. Today, 2024, 427, 114419

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### EXPLORING THE BASICITY OF THERMOLABILE HYDROTALCITE CATALYSTS: THEIR ROLE IN ALDOL CONDENSATION OF CITRAL WITH PENTAN-2-ONE AND OPTIMIZATION OF ANTHRANILIC ACID SORPTION AS METHOD FOR BASICITY DETERMINATION

## Tereza Nechvílová<sup>1</sup>, Lada Dolejšová Sekerová<sup>1</sup>, Eliška Vyskočilová<sup>1</sup>, Iva Paterová<sup>1</sup>

# <sup>1</sup>University of Chemistry and Technology, Prague, Technicka 5, Prague, Czech Republic; iva.paterova@vscht.cz

Hydrotalcites are materials suitable for a wide range of applications due to their unique properties such as compositional variability, anion exchange capacity and surface modifiability. This study investigated the influence of hydrotalcite composition on their basic properties. Mg/Al and Zn-Mg/Al hydrotalcites modified with Sn or Fe showing different acid-base properties were studied. The acid-base properties of the studied materials were assessed using common by TPD-CO<sub>2</sub><sup>1-3</sup> and TPD-pyridine of mixed oxides derived from hydrotalcites by calcination.

Hydrotalcites containing Brønsted basic sites demonstrate potential as heterogeneous base catalysts for reactions such as aldol condensations. However, the commonly used TPD-CO<sub>2</sub> method is limited to studying basic sites in mixed oxides with Lewis basicity due to their thermal stability. Rehydrated hydrotalcites, containing Brønsted basic sites, react with  $CO_2$  to form hydroxycarbonates, requiring alternative methods for their basicity determination. To address this, catalytic tests using a model reaction (aldol condensation of citral with pentan-2-one to form pseudoionone) were performed.

The basicity determined by TPD-CO<sub>2</sub> for the prepared (Sn)Zn-Al mixed oxides was up to 10 times lower than that of (Sn/Fe)Mg-Al, resulting in very low activity of the rehydrated (Sn)Zn-Al hydrotalcites in the model reaction. However, incorporating Mg into the (Sn)Zn-Al hydrotalcite structure significantly enhanced the basicity, increasing it 6 times in MgZn-Al and 7 times in SnMgZn-Al mixed oxides. This improvement was reflected in catalytic performance, with citral conversion reaching 69 % and 94 % after 4 hours of reaction, respectively. The study confirms a strong correlation between the basicity of Brønsted base sites-containing hydrotalcites and catalytic test results, as well as Lewis basicity determinations of the mixed oxides.

Additionally, a novel method for basicity determination by anthranilic acid sorption<sup>4</sup> was developed and optimized for thermally labile hydrotalcite samples. The findings underline the significance of optimizing hydrotalcite composition for specific catalytic applications and highlight the utility of advanced methods for characterizing their acid-base properties.

# **References:**

<sup>1</sup> Di Cosimo., J.I.; Díez, V.K.; Xu, M.; Iglesia, E.; Apesteguía, C.R., J. Catal. **1998**, 178(2) 499-510.

<sup>2</sup> Paterova, I.; Slana, M.; Gorlova, O. Catal. Today **2024**, 427, 114405.

<sup>3</sup> Gorlova, O.; Pálková, S.; Kocík , J.; Tišler, Z.; Paterová, I., Appl. Catal. A, **2024**, 671, 119573.

<sup>4</sup> Dolejsova Sekerova, L.; Paterova, I.; Vrbkova, E.; Vyskocilova, E. Microchem. J. **2024**, 200, 110353.

#### CATALYTIC HYDROPYROLYSIS OF CHLORELLA VULGARIS

#### Ainhoa Díaz<sup>a</sup>, Jennifer Cueto<sup>a</sup>, David P. Serrano<sup>a,b</sup>, <u>Inés Moreno<sup>a,b</sup></u>

<sup>a</sup>Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Móstoles, 28935 Madrid, Spain; <sup>b</sup>Chemical and Environmental Engineering Group, Rey Juan Carlos University, c/Tulipán s/n, Móstoles, 28933 Madrid, Spain

This work investigates the valorisation of the microalgae Chlorella Vulgaris (CV) via catalytic hydropyrolysis using a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst using an ex-situ fixed bed reactor. This study reports on the optimisation of operating conditions, including catalytic bed temperature, pressure (< 10 bar),  $H_2$  partial pressure and [catalyst/CV] mass ratio. As an example, Figure 1 compares the mass yields of the different pyrolysis fractions obtained from thermal pyrolysis and thermal and catalytic hydropyrolysis tests performed at pressures of 1 and 6 bar. As observed, the incorporation of hydrogen during the pyrolysis of CV increased the bio-oil\* yield (water-free basis) by reducing the production of biochar, gases and water. The use of 6 bar pressure reduced the biooil\* production due to the hindered volatilisation of the pyrolysis vapours and their longer residence time in the reactor, which promoted their cracking and, consequently, the generation of gaseous products. Catalyst incorporation also decreased the bio-oil\* yield, due to the catalytic cracking of the pyrolysis vapours and coke deposition on the catalyst surface. However, this bio-oil\* showed a higher share of the GC-MS detected fraction, indicating that it was formed by lighter components. Although the oxygen content of the bio-oil\* (9-14 wt%) was in all cases lower than that typical of lignocellulosic pyrolytic oil, it has a significant proportion of nitrogen (~12 wt%), resulting from the degradation of proteins, which limits its further application as a fuel. However, the chemical composition of this bio-oil\* is of potential interest as a pool of valuable chemicals, including aromatic and long-chain aliphatic hydrocarbons ( $C_{12}$ - $C_{20}$ ) and a variety of nitrogenated compounds, such as amines, pyrrolyes and indoles, which are a widely used in the pharmaceuticals, pesticides and dyes precursors.



**Figure 1.** A) Product distribution in terms of fractions and B) component family yields, determined by GC-MS analyses, obtained in the CV thermal pyrolysis and thermal and catalytic hydropyrolysis at pressures of 1 and 6 bar. Operation conditions:  $T_{THERMAL.CATALYTIC}$ =500-350 °C, N<sub>2</sub>/H<sub>2</sub>=50:50 mL, [catalyst/CV]<sub>mass</sub>=0.2. (WSC: Water soluble compounds)

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# HYDROGENATION OF CINNAMALDEHYDE BY PLATINUM SUPPORTED ON 2D AND 3D TRANSITION METAL SULFIDES

# Ayesha Shafiq, Martina Pitinova, Iryna Danylo, Martin Vesely

# University of Chemistry and Technology, Prague, Technicka 5, Prague, Czech Republic

The hydrogenation of cinnamaldehyde (CAL) has attracted significant interest as a model reaction for the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes. Moreover, its resulting products, cinnamyl alcohol (COL) and hydrocinnamaldehyde (HCAL), are valuable as intermediates in production of chemical specialties. Selective CAL hydrogenation involves the reduction of two distinct functional groups: the carbonyl group (C=O) and the carbon–carbon double bond (C=C), leading to the formation of COL and HCAL, respectively (Scheme 1).

Current research focused on the preparation of heterogenous catalytic systems where Pt was supported on selected transition-metals dichalcogenides (TMDs) as  $MoS_2$ ,  $WS_2$ , and  $Mo_{0.25}W_{0.75}S_2$  composite. Their 2D and 3D forms were tested as supports for Pt deposition by varying preparation approaches such as microwave-assisted and wet impregnation. Prepared catalysts were deeply characterized using XRF, SEM-EDS, XRD and N<sub>2</sub> physisorption techniques. The hydrogenation experiments were performed in the batch autoclave reactor at 80 °C and hydrogen pressure 1MPa.

The obtained results demonstrated that utilization of the 2D nanosheets of TMDs as the supports led to the enhanced activities as the higher CAL conversions were achieved. Pt supported on Mo-W-S composite surpassed Pt/MoS<sub>2</sub> and Pt/WS<sub>2</sub> in the hydrogenation performance. Higher CAL conversions were attributed to the presence of more finely dispersed Pt nanoparticles on composite material. On the other hand, the preparation method had only minor effect on hydrogenation products were not significantly influenced by the used support or the preparation methods. COL was the main formed hydrogenation product with selectivity up 90% using all tested catalysts. The best tested catalyst was Pt/2D-Mo<sub>0.25</sub>W<sub>0.75</sub>S<sub>2</sub> prepared through microwave-assisted impregnation with CAL conversion 74.9 % (within 360 min), COL, HCAL and HCOL selectivities being 90 %, 6 % and 4 %, respectively.



Scheme 1: Hydrogenation of Cinnamaldehyde

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#### DEHALOGENATION OF WEEE PLASTICS VIA LOW-PRESSURE HYDROPYROLYSIS OVER PD-SUPPORTED CATALYSTS

# Lidia Amodio<sup>1,2</sup>, Jennifer Cueto<sup>1</sup>, Adriana Souza<sup>1</sup>, Julio López<sup>1,2</sup>, Héctor Hernando<sup>1</sup>, <u>Patricia Pizarro</u><sup>1,2</sup>, David P. Serrano<sup>1,2</sup>

 <sup>1</sup> Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, 28935, Móstoles, Madrid, Spain
<sup>2</sup> Chemical and Environmental Group, Rey Juan Carlos University, c/ Tulipán, s/n, 28933, Móstoles, Madrid, Spain

The digital transformation is increasing the demand for interconnected electronic devices, resulting in a rise in Waste from Electrical and Electronic Equipment (WEEE) with plastics corresponding to 15-30 wt.%<sup>1</sup>. Traditional recycling methods are not suitable when dealing with degraded materials or mixed waste streams, whereas chemical recycling via pyrolysis offers a promising solution in these cases. However, halogens in WEEE plastics complicate the process by generating harmful byproducts<sup>2</sup>. Hydropyrolysis, a variant incorporating hydrogen, combined with palladium as an effective catalyst for halogen removal, can significantly improve the process. This study explores the role of Pd-supported catalysts in the production of dehalogenated oil from WEEE plastics by low-pressure (6 bar) hydropyrolysis. Three supports (Al<sub>2</sub>O<sub>3</sub>, n-ZSM-5 and SiO<sub>2</sub>) were impregnated with 2.5 wt.% Pd. Catalytic tests employed a real WEEE plastic containing a mix of polymers (ABS, PS, PP, PA, PMMA, EVA, PC), heteroatoms (N, O, Cl, Br) and inorganics. Operating conditions were optimized in a previous study<sup>3</sup>. Results shown in Fig. 1A indicate that over 65 wt.% is converted into oil with char as second major product (20 wt.%). Notably, while Pd/n-ZSM-5 enhances cracking and produces higher mono-aromatics (Fig. 1B), Pd/SiO<sub>2</sub> achieves superior dehalogenation yielding a Br-free oil and reducing Cl levels below 10 ppm (Fig.1C).



Figure 1. Products mass yield of hydropyrolysis tests (A), yields by family groups and GC-MS total detected and non-detected fractions of the oils (B) and halogen content in the oil (C).

#### **References:**

<sup>1</sup> Wagner, F., Peeters, J. R., De Keyzer, J., Janssens, K., Duflou, J. R., & Dewulf, W. Waste Manag., **2019**, 100, 269–277.

<sup>2</sup> Kusenberg, M., Eschenbacher, A., Djokic, M. R., Zayoud, A., Ragaert, K., De Meester, S., & Van Geem, K. M. (2022). Waste Manag., **2021**, 138, 83–115.

<sup>3</sup> Amodio, L., López, J., Souza, A., Cueto, J., Hernando, H., Pizarro, P., & Serrano, D.P., J. Hazard. Mater., 2024, 465(December 2023), 133357.

#### METAL OXIDE CATALYSTS FOR CARBON-CARBON CONDENSATION REACTIONS OF BIOALCOHOLS

#### Jan Moravčík and Luděk Kaluža

#### Institute of Chemical Process Fundamentals of the CAS, Rozvojová 135/1, CZ-16500 Prague 6, Czech Republic, moravcik@icpf.cas.cz

Heteroatoms N, O, S, or Cl bound in hydrocarbons represent a barrier in the chemical processing of fossil and renewable feeds. They are removed by various decomposition reactions. For example, hydrodeoxygenation (HDO) is used to eliminate oxygen in biomass-based feeds such as triglycerides containing long hydrocarbon chains. HDO, however, is not convenient for feedstocks reach in oxygen such as saccharides or bioalcohols because it consumes unacceptable amount of H<sub>2</sub>. Dehydration of such feeds to produce olefins appears more attractive despite the need of subsequent oligomerization. Dehydration of bioalcohols, however, can be accompanied with carbon-carbon condensation reactions to yield high-value hydrocarbon derivatives. Low activity of solid catalysts in C-C condensation limits large-scale industrial implication. The C-C condensation includes the Guerbet coupling, direct coupling and formation of 2n-1 and 2n ketones. We investigated Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, Ce, Sm, Eu, Co, Ni, and Cu oxides supported on activated carbon (0.6 mmol  $g^{-1}$ ) in the reaction of 1-butanol in a fixed-bed tube reactor at 400 °C and atm. pressure. We found that Li and Mg exhibited the highest C-C condensation activities within the studied alkaline and alkaline earth metal oxides, respectively, possessing pseudo-first-order rate constant, k<sub>C-C</sub>, of the formation of condensed C<sub>7</sub>+C<sub>8</sub> hydrocarbons and hydrocarbon derivatives 200 and 160 mg  $g^{-1}h^{-1}$ . Moreover, La and Sm oxides led to the highest activity within all studied oxides possessing  $k_{C-C}$  420 and 470 mg g<sup>-1</sup>h<sup>-1</sup>, respectively. In contrast, only toluene and methane were found over Co and Ni oxides despite total conversion of 1-butanol. The supported Mg species were most selective to Guerbet coupling (2n pathway) and to the formation of C<sub>8</sub> derivatives. The ratio of pseudo-first-order rate constants  $k_{C8}$  (the formation of all  $C_8$ , the 2n pathways) to  $k_{C7}$ (the formation of all C<sub>7</sub>, the 2n-1 pathway, mostly 4-heptanone) was 1.9. In contrast, the high activity of the Li, La, and Sm counterparts was accompanied with high selectivity to  $C_7$  providing the  $k_{C8}/k_{C7}$  ratio 0.9, 0.4, and 0.4, respectively. The most active Mg, La, and Sm catalysts were also investigated at the 2.5-40.0 wt.% oxide loading range. The increasing activity  $k_{C-C}$  was observed with the increasing loading up to about 10 wt.% for the MgO and 25 wt.% for the La<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>. Then, the k<sub>C-C</sub> leveled off at the values about 210 and 1000 mg  $g^{-1}h^{-1}$ , respectively. The selectivity index k<sub>C8</sub>/k<sub>C7</sub> was hardly influenced by the studied loadings. The investigation into prolonged (5 days continuously) reaction of ethanol over 30 wt.% MgO, La<sub>2</sub>O<sub>3</sub> and  $Sm_2O_3$  catalysts showed that the yields of butanols (2n pathways) were 6.3, 5.8 and 5.0 wt.% while the yields of acetone and isopropanol (2n-1) pathway) were 0.9, 3.5 and 5.5 wt.% respectively, at the conversions of ethanol 20, 25, and 30 %, respectively. We concluded that the C-C condensation reaction of 1-butanol and ethanol over the studied catalysts proceeded by the similar way. The high activity in total C-C condensation is accompanied with high selectivity to 2n-1 pathway, i.e. to the formation of symmetrical ketones. Low yields of the coupled 2n alcohols or aldehydes are caused by subsequent C-C coupling or dehydration reactions. The studied bioalcohol reactions provide a promising and sustainable alternative to conventional petroleum processing.

#### SYNTHESIS AND MACROSCOPIC SHAPING OF La<sub>0.8</sub>A'<sub>0.2</sub>NiO<sub>3±δ</sub> (A' = Al, Ca AND Ba) PEROVSKITES FOR RENEWABLE H<sub>2</sub> PRODUCTION BY THERMOCHEMICAL WATER SPLITTING

# <u>M. Linares<sup>1\*</sup></u>, A. Pérez<sup>1</sup>, M. Orfila<sup>1</sup>, R. Sanz<sup>1,2</sup>, J. Marugán<sup>1,2</sup>, R. Molina<sup>1,2</sup>, J.A. Botas<sup>1,2</sup>

<sup>1</sup>Chemical an Environmental Engineering Group, Universidad Rey Juan Carlos <sup>2</sup>Instituto de Investigación de Tecnologías para la Sostenibilidad, c/Tulipán s/n, 28933 Móstoles, Spain maria.linares@urjc.es

In recent years, renewable hydrogen (H<sub>2</sub>) has gained importance as a solution to the economic and environmental problems caused by fossil fuels. It can be produced via thermochemical water splitting using thermosolar energy, which involves thermal reduction of metal oxides and their reoxidation with water to generate H<sub>2</sub><sup>1</sup>. The selection of the metal oxide is a key factor for the development of the process due to the high energy requirements of the reduction step (usually higher than 1300 °C). Non-stoichiometric oxides such as perovskites (ABO<sub>3±δ</sub>) have been proposed for this application as their properties can be tailored to promote its thermal reduction at lower temperatures<sup>2</sup>. Additionally, it is necessary to shape these metal oxides into macroporous structures capable of being used in current solar reactor configurations. This work focuses on the synthesis and macroscopic shaping, as pellets, reticulated porous structures (RPC), and ceramic monoliths with ordered channels, of perovskites type La0.8A'0.2NiO<sub>3±δ</sub> (A' = Al, Ca, and Ba) for H<sub>2</sub> production by thermochemical water splitting. The perovskites were

synthesized by optimization of a reactive grinding method, and characterized by ICP-AES, XRD, and SEM. Then the powder materials were shaped into the different macroporous structures as described elsewhere<sup>2</sup>. In all the cases, H<sub>2</sub> production was evaluated in five consecutive cycles working isothermally at 800 °C, using a tubular high temperature furnace coupled to a gas analysis system. Figure 1 shows the results of the average H<sub>2</sub> production obtained with the different materials and structures. As can be seen, the H<sub>2</sub> production obtained with the structures  $(13.5-14.7 \pm 0.02 \text{ cm}^3\text{STP}/\text{g}_{material}\cdot\text{cycle})$  is much higher than that obtained with the powdered materials (4.5-5.3  $\pm$ 0.03 cm<sup>3</sup>STP/gmaterial·cycle). Macroporous and openchannel structures enhance solid-gas contact, improving mass and energy transfer. Efficient H<sub>2</sub> production at 800 °C matches or exceeds reference materials, operating isothermally within solar concentration technology ranges<sup>2</sup>. **References:** 



**Figure 1.**  $H_2$  production obtained with  $La_{0.8}A'_{0.2}NiO_{3\pm\delta}$  (A' = Al, Ca and Ba) powder and macroscopic structures as pellets (PEL), reticulated porous structures (RPC), and ceramic monoliths (MC).

<sup>1</sup> Dincer I., Int. J. Hydrogen Energy, **2023**, 48, 16143-16147.

<sup>2</sup> Pérez A. et al., Catal. Today, **2024**, 442, 114919.

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## PRAGOLAB AND ELECTRON MICROSCOPY

#### Jan Vysloužil, Petra Volfová

### Pragolab s.r.o. Nad Krocínkou 285/55, Praha

Pragolab is a leading distributor of high-end analytical instruments and laboratory equipment for scientific, research, and industrial applications. The company specializes in the supply and service of equipment for chromatography, mass spectrometry, microscopy, spectroscopy, and other analytical techniques. With years of experience and partnerships with renowned manufacturers, Pragolab provides comprehensive solutions, expert consulting, and technical support to customers in academia, pharmaceuticals, the chemical and food industries, and other sectors.

In the field of electron microscopy, Pragolab collaborates with **Delong Instruments** and **Semplor**.

<sup>1</sup>**Delong Instruments** is a Czech company specializing in the development and production of transmission electron microscopes (TEM) with a low-voltage emission cathode. Their technology enables high-resolution imaging at lower accelerating voltages. Delong Instruments microscopes are primarily used in academic research, biological sciences, nanotechnology, and material analysis. Thanks to their compact design, which allows for TEM, SEM, STEM, ED, and EDS modes, and their user-friendly operation, they are also suitable for laboratories that cannot accommodate traditional TEM instruments due to high space and infrastructure requirements.

<sup>2</sup>Semplor specializes in manufacturing innovative scanning electron microscopes (SEM) that emphasize compact design, ease of use, fast analysis, and EDS integration. Their microscopes are designed for a wide range of users, from industrial laboratories to university research centers. With optimized user interfaces and efficient automation, Semplor microscopes are ideal for applications in materials science, biotechnology, and industrial inspection.

Both manufacturers bring innovative approaches to electron microscopy, and their products are widely applied in scientific and industrial fields.

References: <u>https://www.delong.cz/</u>

<sup>2</sup>https://semplor.com/

# SULFONIC ACID-MODIFIED SBA-15 SILICAS FOR THE PRODUCTION OF AVIATION FUEL PRECURSORS FROM ACETOIN

# <u>G. Morales<sup>1,2</sup></u>, F.J. Landazábal<sup>1,2</sup>, M. Ventura<sup>1,2</sup>, M. Paniagua<sup>1</sup>, J.A. Melero<sup>1,2</sup>

<sup>1</sup>Chemical and Environmental Engineering Group. <sup>2</sup>Instituto de Investigación de Tecnologías para la Sostenibilidad (ITPS). ESCET, Universidad Rey Juan Carlos. c/Tulipán s/n, Móstoles 28933, Spain

Air transport remains as a challenging sector to achieve the global decarbonization objectives. Therefore, the EU is promoting the development of sustainable aviation fuels (SAFs) [1]. There are different routes for the synthesis of SAFs, being one of them the valorization of organic waste through biotechnological and catalytic processes. In this context, acetoin, a C<sub>4</sub> molecule obtained from the ABE fermentation, is a promising platform molecule to produce hydrocarbons in the range of jet-fuel (C<sub>9</sub>-C<sub>14</sub>) [2].

This work presents the solvent-free hydroxyalkylation/alkylation (HAA) of acetoin and 2-methyfuran (2-MF) over different sulfonic acid-modified SBA-15 catalysts, aiming at a selective and efficient production of jet-fuel precursors, particularly the di-condensed C<sub>14</sub> adduct (AcMF<sub>2</sub>). These materials show enhanced stability as compared to the equivalent commercial resin (Amberlyst-15). As shown in Figure 1, while A15 undergoes a progressive deactivation in repeated uses, the propyl-SO<sub>3</sub>H-functionalized SBA-15 silica exhibits an outstanding stability, attributed to an adequate balance of SO<sub>3</sub>H concentration upon a silica surface, allowing to achieve the adequate hydrophilic/hydrophobic balance. Additional studies are being carried out to identify the optimal catalyst (type and concentration of sulfonic groups) as well as to optimize the HAA reaction conditions.



Figure 1. Reusability of Amberlys-15 and Pr-SO<sub>3</sub>H-SBA-15 catalysts on the HAA of acetoin and 2-methyfuran. Reaction conditions: 60°C, 2 h, cat. 10 wt.%, acetoin/2-MF 2.5 (mol).

#### Acknowledgements

The authors acknowledge the financial support of BIOCTANE project with Grant 101084336, funded by the European Union.

#### **References:**

<sup>1</sup> Ahmad, S.; Ouenniche, J. et al., Int. J. Prod. Econom. **2021**, 238, 108156. <sup>2</sup> Zhu, C.; Shen, T.; Liu, D.; Wu, J. et al. Green Chem. **2016**, 18, 2165-2174.

# FREE ENERGY CALCULATIONS IN ZEOLITE SYSTEMS USING OPTIMAL GRID REFINED (OGRE) UMBRELLA SAMPLING

# RICHARD KENDRA<sup>1</sup>, LUKÁŠ GRAJCIAR<sup>1</sup>

# <sup>1</sup> Department of Physical and Macromolecular Chemistry, Faculty of Sciences, Charles University, Hlavova 8, Prague 2, 128 43, Czech Republic

Numerous physical or chemical processes that occur within zeolite systems have high activation energy that makes ergodic sampling of such transitions computationally inaccessible in reasonable time using equilibrium molecular dynamics (EMD). To tackle this problem, enhanced sampling methods utilize artificial biases added to the natural potential of the system.

Umbrella sampling (US) is one of such biased MD methods that is used to obtain potential of mean force (PMF) profile along some collective variable (CV) space, i.e., a projection of free energy on this CV, for processes with high activation energy barrier. Umbrella sampling consists of multiple biased MD simulations restrained with harmonic potentials centered on different places along CV space, from which the PMF is constructed. However, the convergence of the umbrella sampling algorithm is highly dependent on multiple hyperparameters, such as the appropriate number of biased simulations, their centers and strength constants of harmonic restraint bias.

Optimal Grid Refinement (OGRe) procedure proposed by Borgmans et al.<sup>1</sup> for finding optimal harmonic restraint centers and strength constants was reimplemented in this work with minor modifications. Our implementation of OGRe method was tested on 2 zeolitic systems: diffusion of platinum dimer through chabazite 8-membered ring and proton hop in chabazite. Molecular dynamics simulations in this work were performed using pretrained Neural Network Potentials (NNP) with DFT accuracy<sup>2,3</sup>.

Our OGRe implementation was successful in obtaining reasonably accurate PMF surfaces for our test systems. However, temperature and simulation length also have strong influence on ergodicity of biased MD simulations, but these parameters were used as predefined constants in our work. Reasonable manipulation of these parameters within the OGRe process can lead to even more effective computation of PMF profile.

#### **References:**

<sup>1</sup> Borgmans, S.; Rogge, S. M. J.; Vanduyfhuys, L.; Van Speybroeck, V. J. Chem. *Theory Comput.* **2023**, *19*, 9032–9048.

<sup>2</sup> Erlebach, A.; Šípka, M.; Saha, I.; Nachtigall, P.; Heard, C. J.; Grajciar, L. *Nat Commun* **2024**, *15*, 4215.

<sup>3</sup> J. Heard, C.; Grajciar, L.; Erlebach, A. *Nanoscale* **2024**, *16*, 8108–8118.

# NEW MANGANESE-BASED MOF MATERIAL FOR CO<sub>2</sub> ADSORPTION AND VALORIZATION

# Jesús Tapiador<sup>1</sup>, Pedro Leo<sup>1</sup>, Duane Choquesillo-Lazarte<sup>2</sup> and Gisela Orcajo<sup>1</sup>

<sup>1</sup>Chemical and Environmental Engineering Group. ESCET, Universidad Rey Juan Carlos. c/Tulipán s/n 28933 Móstoles, Spain. <sup>2</sup>Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain.

Global CO<sub>2</sub> emissions are rising exponentially as a result of anthropogenic activities, leading to significant environmental concerns related to air quality<sup>1</sup>. Various strategies are available to mitigate CO<sub>2</sub> emissions and counteract global warming, with carbon dioxide capture and valorization emerging as a key opportunity to address this issue because carbon dioxide is a non-toxic, low-cost, abundant, and renewable source of C1<sup>2</sup>. One of the possible applications of CO<sub>2</sub> is the formation of five-membered cyclic carbonates from epoxides via cycloaddition reactions<sup>3</sup>. Unfortunately, most of the heterogeneous catalysts used in this reaction require high pressures and temperatures to achieve good yields.

Therefore, a new Mn-based metal-organic framework (MOF) material has been designed to be employed as a heterogeneous catalyst in the cycloaddition reaction between  $CO_2$ and epoxides. Mn-URJC-13 is a novel MOF material incorporating two organic linkers: 4,4'-biphenyldicarboxylic acid and isonicotinic acid. This material demonstrates remarkable properties as both  $CO_2$  adsorbent and heterogeneous catalyst, displaying stability over at least five consecutive reaction cycles, with reaction yields ranging from 77 to 87%. Therefore, this novel MOF material demonstrates significant potential as heterogeneous catalyst for  $CO_2$  cycloaddition.



Figure 1. Cycloaddition reaction between epoxides and CO<sub>2</sub> using the Mn-URJC-13 catalyst.

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#### **References:**

<sup>1</sup> K.-T. Liu, J.-Y. Chuang, R.-J. Jeng, and M. Leung, ACS Omega, 6, 2021, 27279.

<sup>2</sup> A. J. Hunt, E. H. K. Sin, R. Marriott and J. H. Clark, ChemSusChem, 3, 2010, 306–322.

<sup>3</sup> Zhang, Z. et al. New Journal of Chemistry, 44, 2020, 19037–19045.

<sup>4</sup> Babu, R., Kathalikkattil, A.C., Roshan, R., Tharun, J., Kim, D.-W., Park, D.-W, Green Chem. 18, 2016, 232-242.

# ELECTROSPUN NANOFIBER MATS: PERSPECTIVE CATALYST SUPPORTS WITH HIGH POROSITY

# Pavel Topka, Karel Soukup, Jaroslav Kupčík, Jana Balabánová, Olga Šolcová

### Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 135, 160 00 Praha 6, Czech Republic

Structured catalysts with high porosity are particularly suitable for industrial processes carried out at high space velocities. One of these processes is catalytic oxidation of volatile organic compounds, which is economically feasible and environmentally friendly way of emission abatement. Designing catalysts with low amount of active phase is important for industrial applications<sup>1</sup>. In this work, Pt nanoparticles were deposited on electrospun polybenzimidazole mat. By tuning the preparation conditions, catalysts with different Pt loading and particle size were obtained. The Pt active sites were deposited on the surface of nanofibers (Fig. 1) and due to high porosity of the catalyst (80%) were readily accessible to the reactants. The catalyst containing only 0.08 wt.% of Pt was able to reach a high conversion (90%) of model VOCs (ethanol, acetone, toluene) at moderate temperatures (229 °C, 271 °C, and 334 °C, respectively).



Fig. 1. STEM image of Pt nanoparticles supported on polybenzimidazole nanofiber mat.

Furthermore, we have shown that the TOF depends on the size and type of Pt nanoparticles. The catalysts with Pt particle sizes 1.5 nm and 26 nm exhibited lower catalytic activity than that with Pt particle size of 12 nm. The catalysts with Pt particle size 1.5 nm and 12 nm were prepared by equilibrium adsorption and the higher catalytic activity of the latter catalyst can be explained by the decrease of the Pt–O bond strength with the enlargement of the Pt particle size, which led to more reactive adsorbed oxygen on Pt sites. On the other hand, the catalyst with Pt particle size 26 nm was prepared by solvent evaporation method and contained polycrystalline platinum. Thus, although the Pt particle size determined by TEM was 26 nm, the size of single coherent domains was lower, which correlated with the lower catalytic activity of this catalyst.

# **References:**

<sup>1</sup> Dvořáková, M.; Perekrestov, R.; Kšírová, P.; Balabánová, J.; Jirátová, K.; Maixner, J.; Topka, P.; Rathouský, J.; Koštejn, M.; Čada, M.; et al., Catal. Today **2019**, 334, 13-23.

## Cu-containing Ytrium Aluminum Garnet for Ethylbenzene Oxidation: Effects of Cu Contents on the Selectivity to Acetophenone

José Vitor C. Carmo<sup>1</sup>, Alcineia C. Oliveira<sup>1</sup>, Caio Cardoso<sup>1</sup>, <u>Enrique Rodríguez-Castellón<sup>2\*</sup></u>, José Jimenez<sup>2</sup>

<sup>1</sup>Universidade Federal do Ceará, Departamento de Quimica Analitica e Físcco-Quimica, 60455-760, Fortaleza, Ceará, Brazil.

<sup>2</sup>Universidad de Málaga, Departamento de Química Inorgánica, 29071 Málaga, Spain castellon@uma.es 29071 Málaga, Spain <u>castellon@uma.es</u>

Yttrium aluminum garnet ceramics (YAG) have a vast potential for applications in several technologies, and are said to be used as solid state lasers in medicine and industry<sup>1,2</sup>. Apart from optical properties, a variety of metals e.g. Cu, Ce, Nd, Pt, and Pd can be included in the YAG structure, resulting in a stable Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> phase with good thermodynamic and mechanical properties<sup>1-3</sup>. However, the overall efficiency of YAG as catalysts is very limited to ethylene polymerization, dry reforming, ether- and esterification reactions, among other reactions<sup>4,5</sup>. Much effort has been made to improve the catalytic properties, such as doping with rare earth elements or substitution with transition metal elements in the structure, but other phases are obtained. In this work, the effects of Cu substitution on the catalytic properties of YAG in the ethylbenzene oxidation to obtain valuable acetophenone, benzaldehyde and phenylethanol derivatives were investigated. The samples were synthesized by sol-gel assisted combustion method using citric acid as a chelating agent. After calcination, YAG garnets were obtained possessing a composition of  $Y_{3-x}Cu_xAl_5O_{12}$ , where x represents the content of Cu for x values of 0.0, 0.02, 0.04, 0.06 and 0.1. The solids were characterized by XRD, SEM-EDS, chemical analyses, XPS, EPR, FTIR, Raman measurements. Catalytic evaluation on the oxidation of ethylbenzene in the presence of H<sub>2</sub>O<sub>2</sub> was conducted using a batch glass reactor system, using 50 mg of the solids with a 1:1 ethylbenzene to hydrogen peroxide ratio in the presence of acetone. Distinct reaction conditions such as changing ethylbenzene by other substrates such as styrene or benzaldehyde, temperature and recyclability studies are carried out. The spent catalyst was subsequently recovered by filtration and washed with ethanol and dried for further characterizations. Substitution of Cu in YAG with very low contents resulted in the formation of the crystalline Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> garnet phase, whereas high contents produce perovskite and other phases. Particle size control of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> nanoparticles was achieved by reducing the calcination temperature of the solids. Cu<sup>2+</sup> and Cu<sup>+</sup> ions in YAG were identified by XPS with monovalent copper as a stable entity in the garnet. The Cu-substituted YAG catalysts were all actives in the oxidation of ethylbenzene with high copper contents playing a major role in the activity. On the contrary, product selectivity was detrimental at copper contents above 6 wt.% due to leaching of active Cu sites. Acetophenone selectivity increased by adjusting the ethylbenzene to hydrogen peroxide molar ratio and temperature, and the catalyst was recyclable more than threefolds.

<sup>1.</sup> Kostic et al. Mater. Resear. Bull. 2015,63,80–87.

<sup>2.</sup> Huang et al. Solid. State Chem.. 2012, 14, 1327-1332

<sup>3.</sup> Ma et al. Ceram, Int... 2019, 45, 4817-4823

<sup>4.</sup> Fritsh et al. Cheme Ingenier Technick 2022, 94, 1727-1738

<sup>5.</sup> K.Zhang et al. Renew.Sustain.Energy Rev.2017,77, 899-915

#### REDUCTION OF CHLORATES IN THE AQUEUS PHASE BY SUPPORTED PLATINUM CATALYST

#### N. Benmebirouk-Pareja<sup>1</sup>, A. Plá-Hernández<sup>1</sup>, A.E. Palomares<sup>1</sup>

<sup>1</sup> Instituto de Tecnología Química, Universidad Politècnica de València – Consejo Superior de Investigaciones Científicas (UPV-CSIC)

Water is an essential resource for life and its availability and quality must be ensured. One emerging contaminant that compromises water purity is the chlorate ion. Chlorates are byproducts generated during the disinfection of natural water with oxidizing agents such as chlorine dioxide or ozone. They are formed when the chloride ion present in natural water is oxidized in the disinfection plant. These compounds may can cause hemolytic anemia, interfere with iodine absorption, and affect sperm quality. For this reason, the WHO has set a provisional limit of 0.7 mg/L in drinking water.

Then, sustainable methods for their removal must be developed. Catalytic hydrogenation is a promising alternative, as it enables the reduction of chlorates to chlorides through this reaction:

# $CIO_3^+H_2 \rightarrow CI^+H_2O$

This study presents the results obtained with Pt-supported catalysts on different materials such as  $Al_2O_3$ ,  $TiO_2$  and different zeolites and analyzes their activity in the above reaction.

The catalysts were prepared by the wetness impregnation method, employing aqueous solutions of PtCl<sub>4</sub> as the platinum precursor. Subsequently, they were calcined at 350 °C and reduced at 200 °C to obtain the active phase [1]. The chlorate hydrogenation reaction was carried out in a batch reactor at room temperature and atmospheric pressure, with stirring 900 rpm. A solution containing 50 ppm of ClO<sub>3</sub><sup>-</sup> in 600 mL of water was used with a continuous addition of H<sub>2</sub> [2].



Figure 1. Conversion with different catalysts

Figure 2. XRD of different catalysts

The results are shown in **Figure 1**, observing that the most active catalyst are that supported on  $TiO_2$ , followed by the catalyst supported on a FAU zeolite with a Si/Al ratio of 6.3 (CBV712) The highest activity of the catalysts supported on  $TiO_2$  could be related to the photochemical and acidic properties of this support. Zeolite catalyst shows an intermediate activity between alumina and titania, observing that there is a high influence of the presence of acid sites in the catalyst behavior as they favor the chlorate adsorption. The catalysts were characterized by XRD (**Figure 2**), revealing that after the addition of platinum, no new peaks associated with the noble metal appear, indicating a high dispersion of Pt- species on the supports. The possibility of introducing a second metal in the Pt -catalyst, specifically vanadium, was evaluated observing that it increases the catalysts activity due to a synergistic effect between Pt and V.

#### **References:**

<sup>1</sup> Plá-Hernández, A.; Cerrillo, J. L.; Rey, F.; Palomares, A. E. Catal Today 2023, 424.

<sup>2</sup> Plá-Hernández, A.; Rey, F.; Palomares, A. E. *Catal Today* **2024**, 429.

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#### Paloma Lafuente, Rosa M. Blanco, Manuel Sánchez-Sánchez, Enrique Sastre

#### Instituto de Catálisis y Petroleoquímica (ICP), CSIC, Madrid, Spain

MOFs (Metal-Organic Frameworks) have multiple applications, including as supports of enzymes. In situ immobilization of enzymes, where the MOF support is formed in the presence of the enzyme, is the most efficient one but requires MOFs that can be prepared in mild conditions compatible with enzymatic activity: in water, at room temperature and moderate pH. ZIF-8, a zinc 2-methylimidazolate, is one of the most widely used MOFs to this end, but its synthesis involves the use of a large excess of the organic ligand (2-methylimidazole, 2mIm), at least a Zn/2mIm molar ratio of 40. Recently, ZIF-8 has been described under sustainable conditions, starting from a Zn/2mIm molar ratio of 2, which matches the stoichiometry of the ZIF-8 material, in the presence of triethylamine (TEA) In this work two related MOFs were prepared in two hours at room temperature and in water: (i) a conventional ZIF-8 (ZIF-8-Conv) starting from a Zn/2mIm molar ratio of 40, and (ii) a ZIF-8 precursor in the presence of TEA (Pr-ZIF-8-TEA) starting from a Zn/2mIm molar ratio of 2. Both supports have been tested for the in-situ immobilization of two enzymes: alcohol dehydrogenase (ADH) and laccase (Lac), , all of them capable of retaining 100% of the enzyme present in the synthesis medium.

Figure 1A shows X-ray diffraction patterns. While conventional ZIF-8 is completely formed within two hours, the sample prepared in the presence of TEA is a Zn-2-methylimidazolate (precursor of ZIF-8) almost completely amorphous with only traces of ZIF-8. However, the enzymatic activity of the Lac@Pr-ZIF-8-TEA sample is more than one order of magnitude higher than that of the Lac@ZIF-8-Conv sample (Figure 1B). This difference is even greater between the ADH@Pr-ZIF-8-TEA and ADH@ZIF-8-Conv biocatalysts, this last one being inactive (Figure 1C). This study opens the doors to amorphous precursor of ZIF-8 MOF as an efficient universal enzyme support.



Figure 1. (A) Normalized XRD patterns of Lac@Pr-ZIF-8-TEA and Lac@ZIF-8-Conv. Catalytic activity of Lac@Pr-ZIF-8-TEA and Lac@ZIF-8-Conv in ABTS oxidation (B) and of ADH@Pr-ZIF-8-TEA and ADH@ZIF-8-Conv in the oxidation of ethanol to acetaldehyde (C).

<sup>1</sup> Molina, M.A; Rodríguez-Campa, J.; Flores-Borrell, R.; Blanco, R.M.; Sánchez-Sánchez, M. Nanomaterials **2024**, 14, 348.

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# DESIGN OF EXPERIMENTS APPROACH APPLIED TO THE STUDY OF THE HYDROTHERMAL SYNTHESIS OF METAL-SUBSTITUTED ZEOLITES

# Francesca Rosso,<sup>1</sup> Alessia Airi,<sup>1,2</sup> Hedieh Tabatabaeizadeh,<sup>1</sup> Matteo Signorile,<sup>1</sup> Simone Galliano,<sup>1</sup> Silvia Bordiga,<sup>1</sup> Valentina Crocellà<sup>1</sup> and <u>Francesca Bonino<sup>1</sup></u>

1 Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino, Via G. Quarello 15, 10135 and Via P. Giuria 7, 10125, Torino, Italy. 2 Present address: INRiM Istituto Nazionale di Ricerca Metrologica, Strada delle cacce 91, I-10135, Turin, Italy.

The Design of Experiments (DoE) approach (Fig. 1) is a way to plan and conduct experiments that exploit the MultiVariate data Analysis (MVA) to extract the maximum amount of information from the collected data.<sup>1</sup> The isomorphous substitution of small amounts of transition metals in all-silica zeolites is a particularly challenging topic, due to the possible co-precipitation of metal-oxide phases or formation of metal sites with coordination higher respect to perfect isomorphous substitution. Here, the optimization of titanium



**Fig. 1.** DoE approach applied to TS-1 and FeS-1 synthesis.

silicalite-1 (TS-1) synthesis and a preliminary study of Fe insertion is MFI framework (iron silicalite-1, FeS-1), using the DoE approach, are reported.

The TS-1<sup>2</sup> synthesis was optimized with 3 successive DoEs, in which, each time, the information obtained from the previous DoE was implemented. First, the effect of heating and length of the synthesis steps preceding the hydrothermal one were ruled out.<sup>3</sup> Then, attention was focused on the conditions of hydrothermal crystallization, the choice of the reagents and the atmosphere used during the synthesis, to avoid acidification due to CO<sub>2</sub>. Finally, the correlation between the Ti loading, the crystallization temperature and the dilution of the synthesis gel was understood, finding an optimal point. The obtained TS-1 sample contained a high amount of Ti inserted exclusively in an isomorphous way, without co-precipitation of any fraction of titanium oxide phase. The synthesis of FeS-1 was studied from the point of view of the composition of the synthesis gel. This choice derives from the peculiarity of  $Fe^{3+}$  to provide an extra negative charge to the framework, requiring a counter-cation for balancing. In this case, the DoE was performed varying the composition of the synthesis gel, obtaining very interesting results regarding the crystallinity of the material, Fe<sup>3+</sup> loading and speciation. This work demonstrates that using consecutive DoEs is a wonderful strategy to identify the best conditions for metals insertion in zeolite catalysts. Parallelly, a rational understanding of the insertion process can be drawn, thanks to the statistical distribution of experiments in the experimental domain.

# **References:**

<sup>1</sup> Leardi, R. Anal. Chim. Acta, **2009**, 652, 161-172.

<sup>2</sup> Taramasso, M.; Perego, G.; Notari, B. US Patent 4410501, **1983**.

<sup>3</sup> Rosso, F; Rizzetto, A.; Airi, A.; Khoma, K.; Signorile, M.; Crocellà, V.; Bordiga, S.; Galliano, S.; Barolo, C.; Alladio, E.; Bonino, F.; Inorg. Chem. Front., 2022, 9, 3372-3383.

# ATR-IR STUDY OF LAYERED DOUBLED HYDROXIDE AS ELECTROCATALYSTS FOR CO2RR

# Margherita Cavallo,<sup>1</sup> Melodj Dosa,<sup>1</sup> Ryosuke Nakazato,<sup>2</sup> Natale Gabriele Porcaro,<sup>1</sup> Matteo Signorile,<sup>1</sup> Matthias Quintelier,<sup>3</sup> Joke Hadermann,<sup>3</sup> Nataly Carolina Rosero-Navaro,<sup>2,4</sup> Kiyoharu Tadanaga,<sup>2</sup> Silvia Bordiga,<sup>1</sup> Valentina Crocellà<sup>1</sup> and <u>Francesca Bonino</u><sup>1</sup>

1 Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino,
Via G. Quarello 15, 10135 and Via P. Giuria 7, 10125, Torino, Italy.
2 Division of
Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628,
Hokkaido, Japan
3 EMAT, Department of Physics, University of Antwerp, 2020
Antwerp, Belgium
4 Instituto de Cerámica y Vidrio, CSIC, Madrid 28049, Spain

Electrochemical reduction of CO<sub>2</sub> (CO2RR) is expected to play a key role among the various strategies to diminush global warming.<sup>1</sup> Zn-Al Layered Double Hydroxides (LDH) at three different molar ratios were studied as possible candidates for CO2RR to CO by means of a custom-made three -compartment cell, showing an increase in CO selectivity by decreasing the  $Zn^{2+}/Al^{3+}$  ratio.

After fundamental characterizations by means of different techniques (XRD, STEM-EDX and HR-TEM) and the analyses of the dried transmission IR spectra of the LDHs



**Fig. 1.** Scheme of in-situ ATR-IR experiments.

materials, the interaction with  $CO_2$  was studied by means of *in-situ* and *operando* ATR-IR setup depicted in Fig. 1.<sup>2,3</sup> The samples showed a different evolution in the vibrational region of the carbonatelike species (1800 - 1200 cm<sup>-1</sup>).

A careful assignment of the main IR bands of the carbonate was carried out by comparing these results with the existing literature and, interestingly, in the case of Zn-Al 1:2 LDH, the most efficient electrocatalyst for CO2RR, a higher monodentate to total bidentate carbonates ratio is observed, suggesting the presence of a higher content of low coordination

oxygen anions with stronger basic character influencing very probably the electrocatalytic activity.

# **References:**

1 Leonzio, G.; Hankin, A.; Shah, N. Chem. Eng. Res. Des. 2024, 208, 934–955.

<sup>2</sup> Nakazato, R.; Matsumoto, K.; Yamaguchi, N.; Cavallo, M.; Crocellà, V.; Bonino, F.; Quintelier, M.; Hadermann, J.; Rosero-Navarro, N. C.; Miura, A.; Tadanaga, K. Electrochemistry **2023** 91 (9), 097003.

2 Cavallo, M.; Dosa, M.; Nakazato, R.; Porcaro, N. G.; Signorile, M.; Quintelier, M.; Hadermann, J.; Bordiga, S.; Rosero-Navarro, N. C.; Tadanaga, K.; Crocellà, V.; Bonino, F. J. CO2 Util. **2024**, 83, 102804.

# METAL NANOCLUSTERS ON PEGYLATED GRAPHENE OXIDE FOR CATALYTIC APPLICATIONS

# Miriam Roldán-Matilla<sup>1</sup>, <u>Arisbel Cerpa-Naranjo<sup>2</sup></u>, María Luisa Rojas-Cervantes<sup>3</sup>, Isabel Lado-Touriño<sup>2</sup>, María Fuencisla-Gilsanz<sup>4</sup>, Javier Pérez-Piñeiro<sup>4</sup>,

<sup>1</sup>Professional Formation Centre. European University of Madrid, <sup>2,4</sup>School of Architecture, Engineering, Science and Computing. European University of Madrid, <sup>3</sup>Department of Inorganic and Technical Chemistry, Science Faculty. UNED

Graphene and graphene oxide (GO) are increasingly utilised in catalytic applications, energy and healthcare sectors [1], [2]. Silver (Ag) and copper (Cu) nanomaterials, including their nanoclusters, are pivotal for advanced antimicrobial therapies and enhancing materials for energy and biomedical applications [3]. However, achieving uniform dispersion and stability in both hydrophobic and hydrophilic environments remain a challenge [4]. This study addresses these challenges by synthesising and characterising PEGylated  $GO_{10}$  (10% GO oxidised, PEG: polyethylene glycol) functionalised with Ag and Cu nanoclusters through amide bond formation. For structural characterization, different techniques were used, such as: TEM, SEM, TGA, FTIR and UV-Visible spectroscopy.

Using molecular dynamics (MD) simulations, we identified optimal strategies for stable nanostructures, focusing on radial distribution function (RDF) and mean squared displacement (MSD) analyses. The oxidation and subsequent PEGylation of graphene significantly enhance the interaction energy of Ag nanoclusters by 239.47 kcal/mol and Cu nanoclusters by 259.98 kcal/mol. This functionalisation also substantially reduces nanocluster mobility, with MSD values of 20-30 Å<sup>2</sup> at 500 ps, compared to 150-175 Å<sup>2</sup> for non-functionalised clusters. RDF analysis reveals improved nanocluster dispersion on the PEGylated GO surface, supporting the formation of stable nanostructures. SEM and TEM analyses corroborate these findings, showing that PEGylation enhances nanoparticle dispersion and reduces aggregation on GO sheets. UV-Visible spectroscopy indicates that PEGylated Ag nanoparticles exhibit a stable plasmonic response between 400-450 nm, which is crucial for their antimicrobial activity.

The enhanced dispersion and stability of Ag and Cu nanoclusters on PEGylated GO expand their catalytic applications in biomedicine. Ag nanoclusters act as nano catalysts for bacterial biofilm degradation via ROS (radical oxygen species) generation, while Cu nanoclusters function as nanozymes, mimicking peroxidase- and oxidase-like activity to modulate oxidative stress and enhance drug activation. These materials also serve as platforms for biosensing and biocatalysis, enabling precise biomolecular detection and catalytic transformations in diagnostics and therapeutics.

#### **References:**

<sup>1</sup>Szabó, T.; Szeri, A.; Dékány, I. Carbon N Y. **2005**, 43, 87–94.

<sup>2</sup>Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. B. T.; Ruoff, R. S.; Nature. **2006**, 442, 282–286.

<sup>3</sup>Khan, I.; Saeed, K.; Khan, I. Arabian Journal of Chemistry. **2019**, 12, 908–931.

<sup>4</sup>Yang, K.; Wang, J.; Chen, B. J Mater Chem A Mater. **2014**, 2, 18219–18224

#### ASYMMETRIC SYTHESIS OF SPIROPYRROLIDINES USING SYNERGISTIC CATALYSIS

#### Michael Franc, Jan Veselý

#### Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, Prague, 128 00, Czech Republic

The pyrrolidine motif is a key structural component of numerous natural compounds and pharmaceuticals.<sup>1</sup> Consequently, developing synthetic methods for the efficient synthesis of substituted pyrrolidines remains an important objective in organic chemistry. Similarly, the spirocyclic motif can be found in many natural substances and synthetic drugs, demonstrating their biological activity.<sup>2</sup> Therefore, we are focused on developing methods providing chiral spiropyrrolidines, which can also be biologically active.<sup>3</sup>

As part of our continued efforts, we have designed an enantioselective synthesis of spiropyrrolidine compounds through a synergistic strategy. The developed transformation, involving the reaction of vinylcyclopropane derivatives (1) with aldimines (2), enables the one-step formation of enantiomerically enriched spiropyrrolidines (3) bearing three stereogenic centers. A detailed discussion of reaction optimization and stereocontrol will be provided.



**Scheme 1**: Synergistic Catalysis Using for the Synthesis of Synthesis of Chiral Spiropyrrolidines Combination of Chiral Phosphoric Acid and Achiral Palladium Complex.

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#### **References:**

<sup>1</sup> a) Li Petri, G.; Raimondi, M. V.; Spanò, V.; Holl, R.; Barraja, P.; Montalbano, A. *Top. Curr. Chem.* **2021**, *379*, 34; b) Jeelan Basha, N., Basavarajaiah, S.M. & Shyamsunder, K. Mol Divers 2022, 26, 2915.

<sup>2</sup> a) Singh, G.S.; Desta, Z. Y. Chem. Rev. 2012, 112, 6104; b) Cui, C.B.; Kakeya, H.; Osada, H. *Tetrahedron* **1997**, *53*, 59; c) Cui, C.B.; Kakeya, H.; Osada, H. *J. Antibiot.* **1996**, *49*, 832.

<sup>3</sup> a) Saraswat, P.; Jeyabalan, G.; Hassan, M. Z.; Rahman, M. U.; Nyola, N. K. *Synth. Commun.* **2016**, *46*, 1643; b) Chalyk, B. A.; Butko, M. V; Yanshyna, O. O.; Gavrilenko, K. S.; Druzhenko, T. V; Mykhailiuk, P. K. *Chem. Eur. J.* **2017**, *23*, 16782; c) Carreira, E. M.; Fessard, T. C. *Chem. Rev.* **2014**, *114*, 8257.

#### HOST-GUEST TRANSFER OF CHIRALITY DURING ASYMMETRIC CATLYSIS IN GTM CHIRAL ZEOLITE MATERIALS

## Ramón de la Serna, Jaime Jurado-Sánchez, Joaquín Pérez-Pariente and <u>Luis</u> <u>Gómez-Hortigüela</u>\*

Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas (ICP-CSIC), c/ Marie Curie 2, 28049 Madrid, Spain; email: <u>lhortiguela@icp.csic.es</u>

We have recently discovered a new class of extra-large pore chiral zeolite asymmetric catalysts based on the -ITV germanosilicate framework (GTM) that are able to perform enantioselective operations during catalytic processes.<sup>1,2</sup> Their unique combination of extra-large pores, chiral confinement and ease of preparation using natural alkaloids as chiral precursors makes them very attractive catalytic materials to be used in industrial processes involving chiral molecules. Because of their novelty, understanding the molecular mechanism whereby these microporous materials transfer their chirality from the asymmetric framework into molecular guest entities during a catalytic reaction is crucial in order to spread the scope for the catalytic enantioselective production of chiral compounds of interest.



Figure 1. Asymmetric catalytic reactions studied in this work; only the *RR*-case is shown for TSO.

So far, we have found two catalytic reactions where GTM asymmetric catalysts perform enantioselectively (Figure 1): the ring-opening of racemic trans-stilbene oxide (TSO) with alcohols, giving mainly the unlike 2alkoxy-1,2-diphenyl-ethanol products with (R,S) and (S,R)configurations, and the ringopening of the achiral cisstilbene oxide (meso form) (CSO), yielding mainly the

*like* products with (R,R) and (S,S) configurations. In both cases, enantiomeric excesses up to 60 % are reached when proper host-guest chiral size matches are met (1-butanol as nucleophile for TSO and 1-propanol for CSO). DFT computational calculations allowed to understand the mechanism whereby enantioselectivity arises in these asymmetric reactions, which is directly linked to the particular orientation adopted by stilbene oxide molecules confined within the asymmetric space of -ITV and coordinated with Ge active sites, in a similar way as how enzyme biocatalysts induce their enantioselectivity.

#### **References:**

<sup>1</sup> R. de la Serna, D. Nieto, R. Sainz, B. Bernardo-Maestro, Á. Mayoral, C. Márquez-Álvarez, J. Pérez-Pariente, L. Gómez-Hortigüela, J. Am. Chem. Soc. **2022**, 144, 8249-8256.

<sup>2</sup> R. de la Serna, J. Jurado-Sánchez, J. Li, C. Márquez-Álvarez, J. Pérez-Pariente, L. Gómez-Hortigüela, ACS App. Mater. Inter. **2024**, 40, 54067-54080.

# SYSTEMATIC STUDY OF THE SYNTHESIS OF THE CHIRAL GERMANOSILICATE GTM-4 AT DIFFERENT GE CONTENTS

# <u>Jaime Jurado-Sánchez<sup>1</sup></u>, Ramón de la Serna<sup>1</sup>, Carlos Márquez-Álvarez<sup>1</sup>, Joaquín Pérez-Pariente<sup>1</sup>, Luis Gómez-Hortigüela<sup>1</sup>.

#### 1 Instituto de Catálisis y Petroleoquímica (ICP-CSIC), Calle Marie Curie, 2, 28049, Madrid, Madrid. <u>jaime.jurado@csic.es</u>

The development of chiral heterogeneous catalysts that favour the synthesis of an enantiomer over its mirror image represents one of the most difficult and exciting challenges in scientific research today. One of the most suitable candidates for this task are zeolites. Zeolites are crystalline materials with a perfectly ordered three-dimensional

structure, with channels and cavities of molecular dimensions, which provide very interesting confinement properties for use as heterogeneous catalysts. At present, there are several chiral zeolitic structures, which are formed by helical channels (BEA, STW, CZP...etc.) but in most cases they crystallise in a racemic form. For the materials to be enriched in one of the two polymorphs, the use of chiral structure-directing agents is necessary. With characteristics. only these five enantiomerically enriched chiral zeolitic materials have been reported, including GTM-3 and GTM-4 prepared using derivatives of the chiral precursors ephedrine and pseudoephedrine, on which this study is based.<sup>1</sup>



**Figure 1.** Polymorphs composing the -ITV type

of GTM-3 and GTM-4.

In the synthesis of any type of zeolitic material, it is advisable to look for synthesis or post-synthesis treatment methods

capable of modifying the lattice composition of the material. This is particularly important in the case of zeolitic germanosilicates, as the Ge content determines both the stability of the material and fundamentally its catalytic properties, with these Ge sites being the active centres of the material.

For this reason, this work will analyse the synthesis and modification of the material GTM-4, which is a chiral germanosilicate highly enriched in one of the two enantiomeric polymorphs depending on the enantiomer of the structure-directing agent



**Figure 2.** Incorporation of atoms (Si in blue, Ge in red) of the obtained GTM-4 materials as a function of the yield in crystallisation product.

used in the synthesis, as already seen in previous studies.<sup>3</sup>

Figure 2 shows different versions of the GTM-4 material where, despite being the same structure, materials with a higher or lower Ge content are obtained depending on the preparation conditions of the material. Thus, materials with variable Ge content have been obtained, which will determine not only their hydrothermal stability but also their catalytic activity and enantioselective properties.

#### **References:**

<sup>1</sup> R. de la Serna, D. Nieto, et al. J. Am. Chem. Soc. **2022**, 144, 8249–8256.

<sup>2</sup> R. de la Serna, I. Arnaiz, et al. Chem. Comm. **2022**, 58, 13083–13086.

<sup>3</sup> R. de la Serna, J. Jurado-Sánchez, et al. Microporous Mesoporous Mater. **2024**, 370, 113083.

# ALUMINIUM CONTENT IN MFI ZEOLITES AS A FACTOR INFLUENCING THE THERMAL STABILITY OF Pd AND Pt NANOPARTICLES

## František Krakl, Christopher J. Heard, Pavla Eliášová, and Michal Mazur

## Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 43, Prague, Czech Republic

Supported metal nanoparticles (NPs) are a point of interest in catalysis, but thermal sintering poses a challenge in preparing sustainable catalyst. Aluminosilicate zeolites, due to their properties, are promising supports for sintering-resistant catalysts. However, the interactions between metal NPs and zeolite supports remain a challenge. Knowledge of these interactions could help design sintering-resistant catalysts.<sup>1,2</sup>

This work focuses on investigating how the Al content in reaction mixture (Si/Al ratios ranging from 20 to  $\infty$ ) influences the formation of encapsulated subnanometric particles during hydrothermal synthesis. The materials were characterized using PXRD, ICP-MS, argon sorption, SEM, and STEM-EDS.

Pt and Pd nanoparticles were encapsulated in MFI zeolites with varying Si/Al ratios. The fraction of sub-2 nm Pt NPs depended on the Al content in reaction mixture. The largest fraction was present in sample with Si/Al of 28. Whereas the Pd NPs PSD was independent on MFI composition.



Figure 1:PSD diagrams and STEM images of Pt@MFI as-synthesised, after heating to 400 °C and 700 °C

The effect of Al content in reaction mixture on the size and thermal stability of Pt and Pd NPs was studied using in-situ heating STEM imaging. We tracked NP size distribution based on imaging during stepwise heating from room temperature  $(\mathbf{RT})$ to 400 °C, 700 °C. and respectively (figure 1).

In the as-synthesized sample (RT) majority of Pt NPs were smaller than 1 nm. After heating to 400 °C, sintered Pt NPs are visible. However, the well confined NPs are still present even after 2 h at 700 °C, which confirms the stabilization effect of zeolite support. The results were supported by DFT and MD calculations. NNP simulated annealing indicated the preferred location for  $Pt_6$  is sinusoid channel. Larger clusters,  $Pt_{13}$  and  $Pt_{24}$ are preferentially located in the intersections of channels. DFT calculations of encapsulated Pt clusters in MFI with 0, 1, or 2 Al per unit cell revealed distinct cluster configurations based on the Si/Al ratio.

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# **References:**

<sup>1</sup> Zhang, Q.; Gao, S.; Yu, J Chem. Rev. **2023**, 123 (9), 6039–6106.

<sup>2</sup> Dai, Y.; Lu, P.; Cao, Z.; Campbell, C. T.; Xia, Y. Chem. Soc. Rev. **2018**,47 (12)

# ETHANOL DEHYDRATION WITH AEROSOL-MADE MESOPOROUS ALUMINOSILICATES FEATURING DISPERSED ACTIVE SITES

# <u>Lucie Leonova</u><sup>a</sup>, Giovanni Pampararo<sup>b</sup>, Vit Vykoukal<sup>c</sup>, Lucie Simonikova<sup>a</sup>, François Devred<sup>b</sup>, Pierre Eloy<sup>b</sup>, Ales Styskalik<sup>\*a</sup>, Damien P. Debecker<sup>\*b</sup>

<sup>a</sup>Masaryk University, Department of Chemistry, Kotlarska 2, CZ-61137 Brno, Czech Republic

<sup>b</sup>Institute of Condensed Matter and Nanoscience (IMCN), UCLouvain, Place Louis Pasteur 1, 1348 Louvain-La-Neuve, Belgium

<sup>c</sup>Thermo Fisher Scientific, 627 00, Brno, Czech Republic

damien.debecker@uclouvain.be, styskalik@chemi.muni.cz

Amorphous aluminosilicates are known for their excellent performance in (bio)ethanol dehydration for ethylene production. Several studies showed that the homogeneous dispersion of Al in amorphous aluminosilicates is the key to obtain active and stable catalysts.<sup>1</sup> However, ensuring a high dispersion of Al in the aluminosilicate matrix remains a complicated task. Here, the aerosol-assisted sol-gel (AASG) process is presented as a facile one-step and continuous production method towards highly homogeneous aluminosilicates.

We systematically examined the effect of the aluminum loading (1–9 wt.% Al) in silica matrix incorporated via AASG technique on the catalytic activity during ethanol dehydration. Aluminum dispersion, chemical structure, textural properties, and acidic behavior were investigated by SEM-EDS, MAS NMR, XPS, nitrogen porosimetry, and infrared spectroscopy combined with pyridine adsorption. Aluminum content is shown to influence textural properties and acidity, and therefore strongly modifies catalytic activity. The most active AASG-prepared aluminosilicate catalysts exhibited higher activity and on-stream stability if compared to commercial silica-alumina. It reached a similar performance to other amorphous aluminosilicates with a highly homogeneous Al dispersion prepared via peculiar protocols.

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# **References:**

<sup>1</sup>A. Styskalik, et al., *Appl. Catal. B Environ.*, 2020, 271, 118926.

## CATIONIC RING-OPENING POLYMERIZATION-INDUCED SELF-ASSEMBLY (CROPISA) OF 2-OXAZOLINES: FROM BLOCK COPOLYMERS TO ONE-STEP GRADIENT COPOLYMER NANOPARTICLES

# NICCOLO LUSIANI<sup>1</sup>, ONDREJ SEDLACEK<sup>1</sup>

## <sup>1</sup>Dept. of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, 128 40 Prague 2 (Czech Republic) – Email: lusianin@natur.cuni.cz

Polymerization-induced self-assembly (PISA) has become a powerful strategy for synthesizing polymer nanoparticles at high concentrations. In this work,<sup>1</sup> we present the synthesis of poly(2-oxazoline) nanoparticles via dispersion cationic ring-opening polymerization-induced self-assembly (CROPISA) in *n*-dodecane. By employing an *n*-dodecane-soluble aliphatic poly(2-(3-ethylheptyl)-2-oxazoline) (PEHOx) macroinitiator, we successfully chain-extended it with poly(2-phenyl-2-oxazoline) (PPhOx). Although the PhOx monomer is soluble in *n*-dodecane, its polymerization leads to the formation of *n*-dodecane-insoluble PPhOx, driving the in situ self-assembly of PEHOx-b-PPhOx copolymers.

We systematically investigated the polymerization kinetics and morphological evolution of the nanoparticles during the formation of the second block. By varying the block lengths and polymerization conditions, we tailored distinct nanoparticle morphologies.

Finally, we explored the functional versatility of the resulting nanoparticles, by employing them as stabilizers for Pickering emulsions. Notably, distinct nanoparticle morphologies resulted in varying emulsifying efficiencies. Therefore, future studies will focus on their potential for catalytic applications, where emulsion-stabilized systems can facilitate heterogeneous catalysis by providing enhanced reaction interfaces. We gratefully acknowledge the financial support from the Czech Science Foundation (grant Nr. 25-16818X).

# **References:**

<sup>1</sup>Lusiani, N.; Pavlova, E.; Hoogenboom, R.; Sedlacek, O. Cationic Ring-Opening Polymerization-Induced Self-Assembly (CROPISA) of 2-Oxazolines: From Block Copolymers to One-Step Gradient Copolymer Nanoparticles. Angew. Chem. Int. Ed. 2024, e202416106.

# SELECTIVE TRANSITION METAL-BASED HYDROGENATION CATALYSTS VIA REDUCTIVE DEMETALLATION OF ZEOLITES

# <u>Mariyamuthu Mariyaselvakumar</u>, Anastasia Kurbanova, Marino M. Álvarez Izaguirre, Svetlana Kurucová, Jan Přech\*

# Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 43 Prague 2, Czech Republic

Abstract: Developing cost-effective and selective hydrogenation catalysts is crucial for fine chemical synthesis and sustainability of industrial processes. Among these, alkyne semihydrogenation and selective C=C hydrogenation besides C=O groups represent a selectivity challenge. Pd-based catalysts are widely used for these reactions, but still suffer from high costs, toxic additives, insufficient selectivity. Lindlar catalyst (Pd/CaCO<sub>3</sub>-Pb) is effective for alkyne semihydrogenation but poses environmental risks, while PdAg/Al<sub>2</sub>O<sub>3</sub> improves selectivity but lacks stability. Despite advancements, Pd catalysts remain expensive and environmentally costly. Thus, developing non-noble metal systems could offer viable solutions for the selective hydrogenations. In this work, we demonstrate that bimetallic CuFe@zeolite catalyst, synthesized via reductive demetallation, can represent an alternative to the above Pd based selective hydrogenation catalysts. In our CuFe@zeolite catalysts, copper was introduced by ion exchange of a ferrisilicate zeolite, and reduced to form nanoparticles together with the Fe initially present in the zeolite framework. Their synergy creates new active phase, which is more stable but the single metals. The zeolite support provides high surface area and encapsulation within zeolite micropores ensures high dispersion and prevents sintering, thus enhancing catalyst stability. Characterization confirmed Janus type CuFe nanoparticles having 1-6 nm in size<sup>[1,2]</sup>.

The catalytic properties were evaluated using cinnamaldehyde and 3-ethynylanisole as model substrates from area of fine chemistry for the respective hydrogenation reactions. In 3-ethynylanisole hydrogenation, selectivity for 3-vinylanisole was 93% at 97% ethynylanisol conversion, which is comparable to the Lindlar catalyst (85% at 99% conversion). In contrast, pure Pd/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> gave only 55% 3-vinylanisole selectivity (at 99% conversion). In cinnamaldehyde hydrogenation, CuFe@MFI unselectively hydrogenated both C=C and C=O groups. Nevertheless, comparison with conventionally prepared co-impregnated CuFe/MFI (of the same metal content) and single metal catalysts showed an advancement in terms of activity. The reductively demetallated CuFe@MFI provided 98 % conversion in 70 h while the reference only 45% cinnamaldehyde conversion. Overall, the bimetallic CuFe@MFI catalysts prepared by reductive demetallation demonstrate high selectivity in semihydrogenation of alkynes reactions compared to conventional noble metal catalysts, highlighting their potential as a sustainable alternative.

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic through the ERC\_CZ project LL 2104.

#### **References:**

<sup>1</sup>Iida, T.; Zanchet, D.; Ohara, K.; Wakihara, T.; Román-Leshkov, Y. Angew. Chem., Int. Ed. **2018**, 57, 6454-6458.

<sup>2</sup>Kurbanova, A.; Zakutná, D.; Gołąbek, K.; Mazur, M.; Přech, J. Catal. Today. **2022**, 390-391, 306-315.

#### GREEN SYNTHESIS AND MESOPOROUS CELLULAR FOAMS.EFFECT OF

#### **GOLD DOPANT**

#### Vanesa Calvino-Casilda<sup>1</sup>, Izabela Sobczak<sup>2</sup>, Maria Ziolek<sup>2</sup>, Rosa Martin-Aranda<sup>3</sup>

<sup>1</sup>Departamento de Ingeniería Eléctrica, Electrónica, Control, Telemática y Química Aplicada a la Ingeniería, ETS de Ingenieros Industriales, UNED, Juan del Rosal 12, E-28040 Madrid, Spain

<sup>2</sup>Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland

<sup>3</sup>Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, UNED, Avenida de Esparta s/n. E-28232 Las Rozas, Madrid, Spain

The influence of dopants (Cu and Au) added to modified mesoporous cellular foams (MCF and Nb/MCF) on the catalytic activity are analyzed in this work. All the materials were characterized and tested in the probe reaction of Knoevenagel condensation between ethyl cyanoacetate and benzaldehyde or 2,4-dichlorobenzaldehyde. The Knoevenagel condensation with chlorine-substituted benzaldehyde can be challenging due to the deactivation of the aldehyde group.

We demonstrate that the activity of mesoporous cellular foams (MCF and Nb/MCF) modified with 3-aminopropyl-trimethoxysilane (AP) as a source of basicity can be enhanced for this reaction by the anchoring of Au species. Gold species were loaded onto amine-modified materials to create Au/AP-MCF and Au/AP-Nb/MCF. Additionally, Cu was used as another dopant in the preparation of the sample AuCu/AP/MCF. The mesoporous cellular foams were characterized by different techniques (N<sub>2</sub> adsorption isotherms, TEM, UV-Vis, TG/DTA, XPS, and DFT calculations). The interaction between Nb species and AP increases the stability of the basic modifier. However, this interaction is weak when Au and Cu are introduced. The existence of Au cations and negatively charged Au nanoparticles simultaneously is crucial for the activation of 2,4-dichlorobenzaldehyde. The reaction between benzaldehyde and ethyl cyanoacetate is not significantly influenced by Au dopants.

Mesostructured cellular foam (MCF) is a type of mesoporous silica with a continuous 3D pore system and a large pore size. It is hydrothermally robust and stable at high temperatures and pressures, making it ideal for applications in fine chemistry. Its large porous network also provides better stability compared to SBA-15 or MCM-41. These characteristics make MCF an attractive option for green chemistry technologies, which prioritize environmental protection. The production of fine chemicals traditionally involves homogeneous processes. Alternative heterogeneous catalysis, on the other hand, requires significant research to develop new catalysts. The target of the present study is estimating the basicity of different mesoporous cellular foams on the preparation of fine chemicals under green synthesis.

#### **References:**

Sobczak, I; Calvino-Casilda, V; Wolski, L; Siodla, T; Martín-Aranda, R.M.; Ziolek, M: Catal. Today, **2019**, 325, 81-88

# M. Moliner, B. Bohigues, I. Millet, P. Concepción, A. Corma, P. Serna

# Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 València, Spain

Supported Pt catalysts have been intensively studied for elemental steps in industriallyrelevant applications, such as CO oxidation to  $CO_2$  and water-gas-shift reactions. Pt clusters and small nanoparticles are highly active species for the CO oxidation reaction due to the effective activation of both CO and  $O_2$  at moderate temperatures.<sup>1</sup>

Typical non-reducible supports interact with Pt clusters too weakly to stabilize the dispersed species when the reaction conditions are harsh (e.g. high temperature in presence of reducing or oxidizing gases), contributing to a deactivation by Oswaldt-ripening sintering.<sup>2</sup> Nevertheless, certain non-reducible supports, such as zeolites, are highly tunable to modify the chemical environment of metals inside their micropores following rules that can be rationalized.<sup>2,3</sup>

In this work, we have rationalized the preparation of highly active/highly stable CO oxidation catalysts using K-MFI zeolites.<sup>4</sup> The incorporation of K as a counter cation of highly defective, pure silica MFI allows to support and retain Pt clusters smaller than 1 nm under harsh reaction conditions. These highly dispersed species resist, on the one hand, oxidative fragmentation in excess of O2 (including O2-rich CO oxidation conditions), which causes state-of-the-art Pt/CeO2 catalysts to deactivate; on the other hand, they also resist Ostwald-ripening sintering when exposed to severe redox stress at high temperature, in contrast to other supported catalysts based on non-reducible supports, thus, avoiding deactivation by agglomeration into low surface area metal particles. In addition to outstanding stability, a key to the high activity is the effective electron promotion of these small Pt species by K inside the MFI pores, leading to improved electron-rich metal clusters. Electronic promotion allows to compensate particle sizes effects, by which the smallest Pt clusters in some of these catalysts (< 0.9 nm) would not be so active if charge donation from the support was not substantial, as demonstrated by a combination of microscopy, FTIR and kinetic experiments. K in our sample plays, therefore, a dual role in K-Pt@MFI samples, as a metal-electron density modifier and as a stabilization agent, resulting in an outstanding catalytic performance for the CO oxidation.

# **References:**

- <sup>1</sup> Ding, K. et al. Science. **2015**, 350, 189-192.
- <sup>2</sup> Moliner, M. et al., J. Am. Chem. Soc., **2016**, 138, 15743-15750.
- <sup>3</sup> Liu, L. et al., Nat. Mater., **2019**, 18, 866-873.
- <sup>4</sup> Bohigues, B., et al., ACS Catal., **2025**, 15, 608-615.

# TUNABLE UIO-66-TYPE MOFs FOR EFFICIENT GLYCEROL VALORIZATION VIA ACETALIZATION REACTION

# Elena García-Rojas, Jesús Tapiador, Pedro Leo, Carmen Martos, Gisela Orcajo

# Chemical and Environmental Engineering Group, ESCET, Rey Juan Carlos University, C/Tulipán s/n 28933 Móstoles, Spain.

The increasing global demand for sustainable energy sources has led to the widespread production of biofuels, such as biodiesel. However, this process generates a significant amount of glycerol as a by-product, representing approximately 10-12% of the total biodiesel yield<sup>1</sup>. Although refined glycerol has applications in various industries, such as pharmaceuticals, cosmetics, and food, it does not provide a sufficient outlet to address this surplus. Consequently, there is a strong interest in developing alternative strategies for the valorization of crude glycerol into high-value products.

A promising approach is the acetalization of glycerol with aldehydes to produce highvalue automotive bio-additives that can improve the cold-flow properties of biodiesel and reducing particulate emissions, thus contributing to a circular economy<sup>3</sup>. This reaction can be efficiently conducted by heterogeneous catalysts, avoiding the drawbacks of traditional homogeneous acid catalysts. In this context, Metal-Organic Frameworks (MOFs) have emerged as highly attractive materials as catalysts due to their high porosity, tunable structure, and the presence of metal nodes coordinated by functionalized organic linkers<sup>2</sup>.

This work investigates the direct valorization of glycerol through acetalization with benzaldehyde, employing UiO-66-type materials as heterogeneous catalysts, due to their structural versatility, allowing modifications of both the metal center and the organic linker while maintaining the crystalline framework. Specifically, zirconium and hafnium were explored as metal centers, combined with terephthalic acid functionalized with various groups (-(OH)<sub>2</sub>, -NO<sub>2</sub>, -F<sub>4</sub>, -(COOH)<sub>2</sub>) to evaluate their influence on benzaldehyde conversion and product selectivity. The best catalytic performance was achieved using a hafnium-based UiO-66 functionalized with nitro (-NO<sub>2</sub>) groups.

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#### **References:**

<sup>1</sup>Moreira, M.N., Corrêa, I., Ribeiro, A.M., Rodrigues, A.E., Faria, R.P.V. Ind Eng Chem Res. **2020**, 59, 2805-2816.

<sup>2</sup>Guo, J., Qin, Y., Zhu, Y., Zhang, X., Long, C., Zhao, M., Tang, Z. Chem Soc Rev. **2021**, *50*, 5366-5396.

<sup>3</sup>Silva, P.H.R., Gonçalves, V.L.C., Mota, C.J.A. Bioresour Technol. **2010**, 101, 6225-6229.
#### MOBILITY OF SOLVATED CU CATIONS IN CU-CHA PREDICTED BY MACHINE LEARNING ACCELERATED MOLECULAR DYNAMICS

#### Reisel Millán<sup>1</sup>, Mercedes Boronat<sup>1</sup>

#### <sup>1</sup> Institute of Chemical Technology, Universitat Politècnica de València, 46022, Valencia, Spain

Cu-exchanged zeolites play a crucial role in the chemical industry as redox catalysts, for instance, in the abatement of NOx emissions with the selective catalytic reduction (SCR) using NH<sub>3</sub> as reductant.[1] These materials rely on mobile solvated Cu<sup>+</sup> cations for their catalytic activity, but the effect of the framework composition (e.g Si/Al ratio) and the nature of the ligands (NH<sub>3</sub>, H<sub>2</sub>O, etc) in diffusion is not fully understood. [2-4] Ab initio molecular dynamics simulations can provide quantitative atomistic insight but are too computationally expensive to explore large length and time scales or diverse compositions. We report a machine-learning interatomic potential that accurately reproduces ab initio results allowing multinanosecond simulations and diverse chemical compositions.

The training of Neural Network potentials (NNP) was based on the PaiNN architecture which uses equivariant message-passing for the ground truth prediction. The acquisition of training data was performed using active learning (AL) with a query-by-committee approach with an ensemble of four potentials. The final dataset contains 70k geometries with Si/Al ratios ranging from 5 to 50 for CHA framework and different Cu cationic species. The trained NNP is capable of prediction energies and forces with a mean absolute error of 1 kcal/mol.

Simulations at several temperatures in the NVT ensemble show that while two ammonia molecules are sufficient to mobilize  $Cu^+$ , a higher water concentration is needed to fully detach  $Cu_+$  from the framework. Aluminum pairs in 8R windows lower the free energy barrier for diffusion and stabilize the product configuration with two [ $Cu(NH_3)_2$ ]<sup>+</sup> cations in the same cage. The mobility of [ $Cu(NH_3)_2$ ]<sup>+</sup> is increased by  $NH_3$  up to 3 molecules per cavity while the mobility of  $Cu^+$  and  $Cu^{2+}$  complexes increase with water content. In general, the mobility of  $Cu^{2+}$  species is lower compared with  $Cu^+$ . Regular MD simulations show that Cu complexes can diffuse as far as ~30 Å in the nanosecond scale. Our results demonstrate the power of combining high-throughput DFT calculations, machine learning, and molecular dynamics simulations for simulating transport in nanoporous catalysts.

#### **References:**

- 1. Peden, C. Journal of Catalysis 2019, 373, 384-389.
- 2. R. Millan, R.; Bello-Jurado, E.; Moliner, M.; Boronat, M.; Gomez-Bombarelli, R. ACS Central Science **2023**, 9, 2040-2056.
- 3. Signorile, M. et al. Chem. Sci. 2022 13, 10238.
- 4. Paolucci, C. et al. Science 2017 357, 898.

#### Surface-Sensitivity of the Mesoporous Carbon Supported Iron Catalysts for Carbides Phases during Fischer–Tropsch Synthesis

João P. Nascimento<sup>1</sup>, Alcineia C. Oliveira<sup>1</sup>, <u>Enrique Rodríguez-Castellón<sup>2\*</sup></u>, Olga Guerrero Pérez<sup>3</sup>, Juan Pedro Holgado<sup>4</sup>, Alfonso Caballero<sup>4</sup>

<sup>1</sup>Universidade Federal do Ceará, Departamento de Quimica Analitica e Físcco-Quimica, 60455-760, Fortaleza, Ceará, Brazil.

<sup>2</sup>Universidad de Málaga, Departamento de Química Inorgánica, 29071 Málaga, Spain castellon@uma.es 29071 Málaga, Spain <u>castellon@uma.es</u>

<sup>3</sup>Universidad de Málaga, Departamento de Ingeniería Química, 29071 Málaga, 29071 Málaga, Spain <u>castellon@uma.es</u>

<sup>4</sup>Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla-CSIC, 41092 Sevilla, Spain

Iron based-oxides have been reported as well-established catalysts for the commercial Fischer-Tropsch Synthesis (FTS) process, aiming the conversion of syngas into liquid fuels and valuable chemicals products<sup>1</sup>. The iron-based catalysts in FTS are active only after reducing the precursor into a mixture of iron carbides, iron oxides and metallic iron with adequate reduction gas composition (H<sub>2</sub>, CO, or H<sub>2</sub>/CO), temperature and pressure, which in turn, exert profound influences on the stability, activity and selectivity of the catalysts<sup>2</sup>. Nevertheless, the FTS activity and selectivity with the extent of the Fe<sub>3</sub>O<sub>4</sub> catalysts transformation into iron carbides still remain a controversial issue. A previous work revealed that the Fe-based catalysts supported on polystyrene mesoporous carbons are stable in FTS reation<sup>2</sup>. Therefore, surface-sensitive investigation of the temperature, pressure and gas feed composition on the FTS performance mesoporous carbon supported iron catalysts represents a useful and valuable tool to control their properties in FTS. Herein, a systematic investigation of the surface properties of the supported mesoporous iron catalysts were studied by the in situ XPS analyses to understand the chemical evolution of the catalysts to improve their performance in the FTS reaction. Besides, the structural properties of mesoporous Fe-based oxides were deeply studied by Raman and Mössbauer spectroscopy measurements. Two distinct Fe-based oxides samples were synthesized, according to the methods previously described<sup>2</sup>. The FTS synthesis on the mesoporous iron catalysts were carried out varying the pressure from 20 and 25 atm in a temperature range of 240-250 °C, using a CO to H<sub>2</sub> ratio of The in situ surface XPS analyses were conducted under quite similar conditions. 1. Mössbauer and Raman measurements evidenced that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with rhombohedral structure was converted into Fe<sub>3</sub>O<sub>4</sub> well dispersed on the mesoporous carbon support, which is accessible to CO<sub>2</sub> and H<sub>2</sub> and responsible for the catalytic performance in FTS reaction. Results in FTS synthesis revealed that the solids were actives with 38-45% of CO conversion and a rate of  $1x10^{-5}$  mol<sub>CO</sub>.g<sup>-1</sup>.s<sup>-1</sup>, depending on the pressure and temperature conditions applied. The products selectivity analysis illustrated the formation of  $C_1$ - $C_4$  and  $C_5^+$ products, indicating that the solid structure marginally affects the type of product obtained. The surface-structure relashionship demonstrated that the Fe<sup>3+</sup> to Fe<sup>2+</sup> ions in Fe<sub>3</sub>O<sub>4</sub> phase is reduced to metallic iron during the FTS reaction. Further, in situ XPS investigations using a pressure of 10 atm at ~240-270 °C, with a CO to H<sub>2</sub> ratio of 1 for 1h showed the evolution of the Fe 2p, O 1s and C 1s core levels spectra with increasing the temperature up to 255 °C suggested the surface carburization forming various iron carbides phases, mainly Hägg carbide ( $\gamma$ -Fe<sub>5</sub>C<sub>2</sub>), along with Fe<sub>3</sub>O<sub>4</sub>, FeOOH, and tentatively, metallic iron phase. The mesoporous marbon supported ion catalyst having carbide  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> is active and stable in the FTS synthesis.

- 1 H. Hayakawa et al. Catal. Sci. Technol., 2022,12, 4217-4227
- 2 M.G.A. Cruz et al. Catal. Today 2017,282,174–18.
- 3 M. Shipilin et al. ChemCatChem. 2024, 16, e202400726

#### MONTMORILLONITES IMPREGNATED WITH Co(II) AND/OR Fe(II) AS ACTIVATORS OF PEROXYMONOSULFATE FOR THE DEGRADATION OF DYES

#### Niurka Barrios-Bermúdez<sup>1,2</sup>; Arisbel Cerpa-Naranjo<sup>3</sup>; Rosa María Martín-Aranda<sup>1</sup>; <u>María Luisa Rojas-Cervantes</u><sup>1</sup>

<sup>1</sup>Dpto. de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Madrid, Spain; <sup>2</sup>Dpto. de Ciencias, Escuela de Ingeniería, Arquitectura y Diseño, UEM, Villaviciosa de Odón (Madrid), Spain; <sup>3</sup>Dpto. de Ingeniería Industrial, Escuela de Ingeniería, Arquitectura y Diseño, UEM, Villaviciosa de Odón (Madrid), Spain.

Synthetic dyes, characterized by being colour organic compounds, often contaminate and colorize effluent water discharged from industries like textile, leather, food processing, paper and dye manufacturing [1]. Due to the complexity of their aromatic structures, advanced oxidation processes are required for their removal. Within this category, those utilizing peroxymonosulfate (PMS) have garnered special attention [2], primarily owing to the elevated redox potential and extended shelf-life of sulfate radicals in comparison to OH radicals [3]. Furthermore, peroxymonosulfate shows a higher selectivity for unsaturated bonds and aromatic constituents.

Montmorillonites, being abundant and cost-effective natural aluminosilicates, possess distinctive attributes like high expansion capacity, significant specific surface area, and elevated cation exchange capacity. These qualities render them excellent candidates for deployment as promising adsorbents or supports for heterogeneous catalysts in environmental remediation efforts [4]. In this work we present some impregnated Co(II) or Co(II)-Fe(II) montmorillonites as activators of PMS for the degradation of different dyes. Orange II, an anionic azo dye, and Rhodamine B, a cationic dye, were studied. Two commercial montmorillonites, namely montmorillonite K10 (MK10) and montmorillonite pillared with aluminium (MPil) were used as supports. Various characterization techniques, including ICP-MS, XRD, SEM and TEM with EDX, and physisorption, confirmed the successful impregnation process of the  $N_2$ montmorillonites with the metallic acetates. Adsorption experiments of the dyes on the catalysts, in the absence of PMS, were also conducted for both series, to study the contribution of the adsorption process to the removal of dye. The catalysts achieved the complete elimination of Orange II after 20-45 min of reaction in the presence of PMS. High degradation values of Orange II were achieved using lower PMS/Orange II ratios and amount of catalyst than other reported in the literature, showing the efficiency of cobalt-impregnated montmorillonites. Various parameters, including catalyst amount, dye concentration and reaction pH, were systematically investigated. The study of the dominant reactive oxygen species was also carried out. Furthermore, the stability and recyclability of the catalysts has also been studied in this work.

#### **References:**

<sup>1</sup>Gupta, V.; Ali, I.; Mohan, D. J. Colloid Interf. Sci. 2003, 265, 257-264.

<sup>2</sup>Guerra-Rodríguez, S.; Rodríguez, E.; Singh, D.N.; Rodríguez-Chueca, J. Water **2018**, 10, 1828.

<sup>3</sup>Kefeni, K.K.; Mamba, B.B.; Msagati, T.A.M. Sep. Purif. Technol. **2017**, 188, 399-422. <sup>4</sup>Huang, W.J.; Liu, J.H.; She, Q.M.; Zhong, J.Q.; Christidis, G.E.; Zhou, C.H. Catal. Rev. **2023**, 65, 929-985.

#### DEOXYGENATION AND DEHALOGENATION CATALYSIS WITH ACTIVATED BORANE – A POROUS POLYMERIC LEWIS ACID

#### **<u>B. Urbán</u>**,<sup>a</sup> A. Udnoor,<sup>b</sup> M. Horáček,<sup>a</sup> M. Lamač,<sup>a</sup> J. Demel<sup>b</sup>

<sup>a</sup> J. Heyrovský Institute of Physical Chemistry, ASCR, Dolejškova 2155/3, 18223 Prague 8, Czech Republic; <sup>b</sup> Institute of Inorganic Chemistry, ASCR, 25068 Řež, Czech Republic; E-mail: <u>martin.lamac@jh-inst.cas.cz</u>, <u>demel@iic.cas.cz</u>

Acid-catalyzed reactions are of general importance in chemistry. Heterogeneous catalysts possess many advantages in practical applications. On the other hand, molecular borane derivatives, such as  $B(C_6F_5)_3$  (BCF),<sup>[1]</sup> have been demonstrated to act as strong Lewis acid homogenous catalysts in a range of reactions, including the Frustrated Lewis pair chemistry. Recently, "Activated borane" (ActB)- a solid porous amorphous polymer prepared by co-thermolysis of decaborane(14) (*nido*-B<sub>10</sub>H<sub>14</sub>) and organic hydrocarbons was reported.<sup>[2]</sup> This material has been since demonstrated as a promising heterogeneous catalyst with distinct capabilities. It features Lewis acid centres likely of a tricoordinated borane character and is therefore suitable for similar transformations as BCF, but its behaviour seems to vary in certain cases.

We would like to present our studies into assessing the catalytic performance of **ActB** materials in selected reactions such as hydrosilylation/deoxygenation of various carbonyl substrates<sup>[3]</sup> and dehalogenation of aliphatic fluorides and chlorides,<sup>[4]</sup> typically with Et<sub>3</sub>SiH as the reductant. Selected reactions were tested also under flow conditions using an XCube microfluidics-based system.



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#### References

- (a) Piers, W. E.; Chivers, T. Chem. Soc. Rev. 1997, 26, 345-354; (b) Lawson, J.R.; Melen, R. L. Inorg. Chem. 2017, 56, 8627–8643.
- 2. Bůžek, D.; Škoch, K.; Ondrušová, S.; Kloda, M.; Bavol, D.; Mahun, A.; Kobera, L.; Lang, K.; Londesborough, M.G.S.; Demel, J. *Chem. Eur. J.* **2022**, *28*, e202201885.
- Lamač, M.; Urbán, B.; Horáček, M.; Bůžek, D.; Leonová, L.; Stýskalík, A.; Vykydalová, A.; Škoch, K.; Kloda, M.; Mahun, A.; Kobera, L.; Lang, K.; Londesborough, M.G.S.; Demel, J. ACS Catal. 2023, 13, 14614–14626.
- 4. Udnoor, A.; Urbán, B.; Škoch, K.; Hynek, J.; Horáček, M.; Lamač, M.; Demel, J. *Catal. Sci. Technol.* **2024**, *14*, 4458–4465.

#### MONTMORILLONITE – ECO-FRIENDLY AND EFFECTIVE CATALYST IN SYNTHESIS OF BIOLOGICALLY ACTIVE COMPOUNDS WITH BICYCLO[3.3.1] MOIETY

#### Eva Vrbková, Lucie Stoupová, Eliška Vyskočilová

#### Dpt. of organic technology, University of Chemistry and Technology Prague, Technická 6, Prague, Czech Republic

Compounds containing bicyclo[3.3.1] moiety are known for their biological activity (e.g., interaction with estrogen receptors) and they also possess usually some fragrant properties (described as amber wood fragrance)<sup>1,2</sup>. This work focuses on Prins reaction of limonene with crotonaldehyde, as a process to synthesize 2,2,6-trimethyl-4-(1-propenyl)-3-oxabicyclo[3.3.1]non-6-ene. Montmorillonite K10 – eco-friendly benign natural clay material is well known for its catalytic properties in Prins reaction<sup>3</sup>, therefore it was chosen to catalyze the reaction of limonene with crotonaldehyde (Fig. 1).

Fig. 1 Reaction scheme of Prins reaction of limonene with crotonaldehyde



Effect of montmorillonite modification (focused on the enhancement of its Brønsted acidity) was thoroughly studied – modification was performed by treatment with mineral acids or by modification using phosphotungstic and phosphomolybdic acid. All types of modifications of montmorillonite had positive influence on the reaction course – high limonene conversions (70-90%, 6h) and selectivity around 80% toward the desired product was obtained. Effect of other reaction course was also studied. Even mineral acid treated montmorillonite might be used for the production of the desired fragrant compound with high yield.

#### **References:**

<sup>1</sup> Costa, V. V.; da Silva Rocha, K. A.; Mesquita, R. A.; Kozhevnikova, E. F.;

Kozhevnikov, I. V.; Gusevskaya, E. V. ChemCatChem 2013, 5, 3022-3026.

<sup>2</sup> Cotta, R. F.; da Silva Rocha, K. A.; Kozhevnikova, E. F.; Kozhevnikov, I. V.; Gusevskaya, E. V. Appl. Catal., B **2017**, 217, 92-99.

<sup>3</sup> Vrbková, E.; Vaňková, M.; Lhotka, M.; Vyskočilová, E. Mol. Catal. **2023**, 542, 113143.

#### MONTMORILLONITE AS AN EFFICIENT CATALYST IN TERPINYL METHYL ETHER PREPARATION FROM DIFFERENT SOURCES

#### Eva Vrbková, Lada Dolejšová Sekerová, Eliška Vyskočilová

#### Department of Organic Technology, UCT Prague, Technická 5, 166 28 Prague 6

Terpinyl methyl ether (Figure 1) is a significant compound widely used in the food and pharmaceutical industries as a flavoring agent. It can be synthesized from readily available green sources—terpenes, specifically limonene and both isomers of pinene (Figure 1). Although zeolites are typically the materials of choice as heterogeneous acid catalysts for methoxylation reactions<sup>1</sup>, the accessibility and versatility of clay materials make them a compelling alternative<sup>2</sup>. Among these, montmorillonite K10 stands out due to its abundance and the ease with which its properties can be modified<sup>3,4</sup>, prompting us to explore its catalytic potential in the studied reaction.

In our work, we investigated the methoxylation of limonene and  $\alpha$ -pinene to produce the desired terpinyl methyl ether using acid-treated montmorillonite as a catalyst. Reactivity comparisons between the two terpenes revealed that  $\alpha$ -pinene exhibited higher reactivity due to its cyclic structure. However, the selectivity for the desired product was lower compared to reactions using limonene as the substrate.

The acidity of montmorillonite was enhanced through mineral acid treatments to increase Brønsted acidity or modified by iron loading to introduce additional Lewis acid sites. Our results confirmed the critical role of Brønsted acid sites in facilitating the formation of pinyl or terpinyl ions, essential intermediates in the reaction. The prepared catalysts were characterized using available analytical methods to assess acid site strength and type.

The highest yield of terpinyl methyl ether (72%) was achieved using montmorillonite treated with HCl, demonstrating the efficacy of acid-treated montmorillonite as a catalyst in this green chemistry approach.



Figure 1: From left –  $\alpha$ -pinene, limonene, terpinyl methyl ether

#### **References:**

<sup>1</sup>Hensen, K.; Mahaim, C.; Hölderich, W. F. Appl. Catal. A **1997**, 149 (2), 311-329.

<sup>2</sup>Catrinescu, C.; Fernandes, C.; Castilho, P.; Breen, C.; Carrott, M. M. L. R.; Cansado, I. P. P. Appl. Catal. A **2013**, 467, 38-46.

<sup>3</sup>Vrbková, E.; Vaňková, M.; Lhotka, M.; Vyskočilová, E. Mol. Catal. **2023**, 542, 113143.

<sup>4</sup>Mitsudome, T.; Matsuno, T.; Sueoka, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Tetrahedron Lett. **2012**, 53 (39), 5211-5214.

#### HIERARCHICAL ZEOLITES IN THE DIELS-ALDER REACTION OF FURFURAL AND ETHANOL: ROLE OF POROSITY AND ACID SITES

#### <u>Talat Zakeri</u><sup>1</sup>, Francesco Sandri<sup>2</sup>, Päivi Mäki-Arvela<sup>2</sup>, Mariya Shamzhy<sup>1</sup>, Dmitry Murzin<sup>2</sup>, Maksym Opanasenko<sup>1</sup>

#### <sup>1</sup>Charles University, Prague, Czech Republic <sup>2</sup>Abo Akademi University, Turku, Finland

**Background.** The production of aromatics from biorenewable sources has been extensively studied, with most research focusing on furan and its derivatives as dienes, and ethylene as dienophile. However, the high cost of furan production and ethylene petrochemical origin raise scalability and sustainability concerns. In contrast, furfural presents an attractive alternative as it is a primary substrate originated from biomass and can be selectively produced via the low-cost acid hydrolysis of nonedible lignocellulosic biomass. Gancedo et al. [1] investigated one-pot aromatic production from furfural and ethanol using conventional ZSM-5 zeolite, but the catalyst suffered from rapid deactivation and limited benzene, toluene, and xylene (BTX) yields. To address this, we investigated hierarchical zeolites with tailored acid site properties to enhance diffusion, active site accessibility, and catalyst stability for more efficient furfural-ethanol conversion to aromatics.

**Materials and methods.** Aluminum and gallium nanosponge zeolites (Al-MFI-nSP and Ga-MFI-nSP) were synthesized using  $[C_{22}H_{45}-N+(CH_3)_2-C_6H_{12}-N+(CH_3)_2-C_6H_{13}](Br^-)_2$  structure-directing agent (SDA). Characterization was performed by XRD, N<sub>2</sub>-physisorption, ICP-OES, SEM, and FTIR. Catalytic tests were conducted in a flow reactor with furfural and ethanol at a 1:2 molar ratio, at 500°C and 1 atm, using GC-FID and micro-GC for the analysis of the liquid and gas phases, respectively.

**Results and discussion.** The catalytic reaction was studied over 320 minutes, with complete substrate conversion observed for all catalysts. While conventional Al-MFI-Bulk achieved the highest initial BTX yield, it rapidly deactivated, consistent with previous studies. In contrast, hierarchical Al-MFI-nSP had a slightly lower initial BTX yield (11% vs. 13%) but maintained its activity in producing aromatics, particularly BTX throughout the reaction. This improved stability is attributed to its hierarchical porosity, which facilitates better diffusion and preserves active site accessibility, reducing the rate of deactivation. Ga-MFI-nSP showed both superior activity and greater durability compared to its bulk counterpart. Hierarchical zeolites also exhibited higher selectivity toward two-ring aromatics such as naphthalene and indene, likely due to their enhanced porosity, which promotes bulkier molecule formation through a secondary cycloaddition. Interestingly, Al-MFI-nSP outperformed Ga-MFI-nSP, despite prior studies suggesting Ga-containing zeolites should be more active [2]. Acidity analysis revealed that the Lewis-to-Brønsted acidity (LAS/BAS) ratio is a key factor in catalyst stability, with an imbalance accelerating deactivation.

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#### **References:**

<sup>1</sup> Gancedo, J.; Faba, L.; Ordonez, S. Sustain. Chem. Eng. **2022**, 10, 7752–7758.

<sup>2</sup> Uslamin, E. A.; Luna-Murillo, B.; Kosinov, N.; Bruijnincx, P. C. A.; Pidko, E. A.;

Weckhuysen, B. M.; Hensen, E. J. M. Chem. Eng. Sci. 2019, 198, 305–316.

#### Alberto Pinto<sup>1,2</sup>, Lidia Amodio<sup>1,2</sup>, Martin Kubů<sup>3</sup>, Jennifer Cueto<sup>1</sup>, Pavla Eliášová<sup>3</sup>, Patricia Pizarro<sup>1,2</sup>, Jiří Čejka<sup>3</sup>, <u>David P. Serrano<sup>1,2</sup></u>

<sup>1</sup>Thermochemical Processes Unit, IMDEA Energy, Avda. Ramón de la Sagra 3, 28935, Móstoles, Madrid, Spain

<sup>2</sup>Chemical and Environmental Engineering Group, Rey Juan Carlos University, Móstoles, Madrid, Spain

#### <sup>3</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 8, Prague, Czech Republic

The increasing accumulation of plastic waste and the inefficiency of conventional recycling methods have intensified interest in pyrolysis as a flexible route to convert heterogeneous and complex waste plastics into liquid fuels and valuable chemicals. However, the resulting oils typically contain high concentrations of halogenated compounds (specially Cl and Br) and heavy hydrocarbons, requiring further upgrading before use<sup>1</sup>. In this way, the present work focuses on the post-catalytic treatment of a pyrolysis oil, derived from real plastic waste, using zeolitic catalysts with different frameworks. Specifically, MWW and TNU were selected due to their unique pore architectures and acidity, which influence their catalytic behavior<sup>2</sup>. Catalytic tests were conducted in a fixed-bed reactor at 450 °C and WHSV of 5 h<sup>-1</sup>. The feedstock oil presented 290 ppm of chlorine and 43.5 wt% of heavy compounds.



Figure 1. (a) Global mass yields of the different fractions, (b) Global yield of the main families obtained in the oil: PAR (paraffins), MAH (mono-aromatics), OL (olefins), NAPH (naphtenes), PAH (poli-aromatics) and IND (indanes), (c) Cl concentration in the oil as a function of the reaction time on stream.

Figure 1 illustrates the comparative performance of five zeolite samples. The product yield analysis reveals that all catalysts primarily produce oil, with MCM-36 and MCM-56 achieving the lowest oil yields. Regarding the chemical nature of the upgraded oils, MCM-36 shows the highest production of monoaromatic hydrocarbons (MAHs), followed closely by MCM-56. Most notably, Cl concentration profile over time highlights superior and stable dechlorination performance of MCM-36 zeolite, maintaining Cl levels between 20 and 54 ppm throughout the experiment. In conclusion, MCM-36 is the most effective catalyst, thanks to its high external surface area and accessible Brønsted acidity, which enhance chlorine removal.

#### **References:**

<sup>1</sup>Marino, A.; Aloise, A.; Hector Hernando, H.; et al. Catalysis Today. **2022**, 390-391, 210–220.

<sup>2</sup> Opanasenko, M.; J. Roth, W.; Čejka, J. Catal. Sci. Technol. 2016,6, 2467.

#### Po23

#### SIMULTANEOUS DEHYDRATION OF METHANOL AND ETHANOL: EFFECT OF THE ZEOLITE STRUCTURE ON CONVERSION AND PRODUCTS DISTRIBUTION.

#### Giorgia Ferrarelli<sup>1</sup>, Enrico Catizzone<sup>1</sup>, Massimo Migliori<sup>1</sup>, Girolamo Giordano<sup>1</sup>

<sup>1</sup>University of Calabria, Via Pietro Bucci, 87036 Rende, Italy.

The increasing demand for sustainable, de-fossilized resources highlights the importance of nontraditional carbon-based feedstocks as a strategic solution to global fuel and chemical needs. Methanol and ethanol, which can be produced via CO<sub>2</sub> recycling processes, are promising platform molecules that could play a crucial role in advancing energy transition and achieving sustainability goals. While much research has focused on the individual dehydration of these alcohols, the simultaneous dehydration of methanol and ethanol remains largely unexplored [1]. A previous study investigated the effect of acid site distribution in MFI zeolites on the simultaneous dehydration of ethanol and methanol [2]. This research aims to explore the impact of zeolite structure on conversion and product distribution during the simultaneous dehydration of methanol and ethanol. Zeolites with 1D (EUO), 2D (FER), and 3D (MFI and BEA) channel systems, with varying Si/Al ratios in the synthesis gel, were synthesized and characterized by XRD,  $N_2$  adsorption isotherms, SEM, and FT-IR. The catalysts were tested for both pure alcohols and ethanol/methanol mixture dehydration reactions in an experimental setup equipped with a tubular reactor (140-240°C). XRD confirmed the crystallinity of the samples, and other physical and chemical properties were consistent with literature data [3,4]. For pure methanol, FER zeolite showed the highest activity, while for pure ethanol the trend was reversed. In the simultaneous methanol/ethanol dehydration, Brønsted acid sites were found to be more active than Lewis acid sites. Methanol dehydration produced dimethyl ether (DME), while ethanol dehydration yielded diethyl ether (DEE) and ethylene. When a methanol-ethanol mixture was used, methyl ethyl ether (MEE) was formed as a new product. MEE was the dominant product at low temperatures with 1D or 2D zeolites, while DEE was more prevalent with 3D zeolites. Additionally, the formation of DME was significantly inhibited in the presence of 3D zeolites. At low temperatures, the ratio of DME to total products (MEE, DEE, and ethylene) varied with zeolite structure, with the highest value for EUO zeolite (as shown in the figure below). In conclusion, zeolite structure plays a significant role in the reaction mechanism, affecting both alcohols' conversion and product distribution.



#### **References:**

- [1] Palčić, A.; Catizzone, E., Current Opinion in green and Sustainable Chemistry, 2021, 100393.
- [2] Catizzone E.; Ferrarelli G.; Bruno P.; Girolamo G.; Migliori M., Catalysis Today, 2024, 114436.
- [3] Catizzone E.; Cirelli Z.; Aloise A.; Lanzafame P.; Migliori M.; Girolamo G.; Catalysis Today, 2018, 39-50.
- [4] Catizzone E.; Aloise A.; Migliori M.; Girolamo G., *Microporous and Mesoporous Materials*, 2017, 102-111.

#### TOPOLOGY-ACIDITY-CATALYTIC ACTIVITY INTERPLAY IN HIERARCHICAL NANOLAYERED ALUMINOSILICATE ZEOLITES

# Oleksiy V. Shvets<sup>1</sup>, Michal Mazur<sup>2</sup>, Mykhailo M. Kurmach<sup>1</sup>, Petr Golis<sup>2</sup>, Pavel S. Yaremov<sup>1</sup>, Oleg Petrov<sup>3</sup>, Nataliya D. Shcherban<sup>1</sup>, <u>Mariya V. Shamzhy<sup>2</sup></u> and Jiři Čejka<sup>2</sup>

# <sup>1</sup>L.V. Pisarzhevskiy Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Ukraine

<sup>2</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Czech Republic

#### <sup>3</sup>Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, Czech Republic

Nanolayered (2D) zeolites are at the forefront of research as efficient catalysts for reactions involving bulky molecules. So far, s MFI, MOR, MWW, BEA zeolites have been synthesized in 2D form *via* direct hydrothermal crystallization using gemini-type surfactants. Furthermore, by adjusting synthesis conditions, the key characteristics of 2D zeolite catalysts, including external surface area and acid site concentration, have been

tailored for different catalytic applications.<sup>1</sup> Despite these advances, a fundamental understanding of how topology of 2D zeolite influences the distribution and strength of acid sites and how this interplay impacts catalytic performance remains limited.<sup>1</sup>

This study reports the first successful synthesis of 2D FER-type zeolite and addresses topology-acidity-activity relationships in nanolayered aluminosilicate zeolites with FER, MFI, MOR, and BEA topologies (Figure 1) using alkylation of mesitylene with benzyl alcohol as surfaceacid-site-demanding and acid-site-strength-sensitive model reaction. Spectroscopic and thermoprogrammed studies of the synthesized zeolites revealed a distinct topology-dependent distribution of tetrahedrally coordinated aluminum sites generating Brønsted acidity. These structural differences correlate with an increase in the strength of surface Brønsted acid sites and selectivity in the alkylation of mesitylene with benzyl alcohol, following the sequence: MFI < BEA < MOR < FER.

These results provide evidence of topology-driven modulation of acid site strength in nanolayered zeolites, which may open new avenues for the rational design of tailored hierarchical zeolite catalysts.



zeolites under study

#### **References:**

<sup>1</sup> Kadja, G.T.M.; Azhari, N.J.; Mardiana, S.; Culsum, N.T.U.; Maghfirah, A. Results Eng. **2023**, 17, 100910

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Airi A	РоОЗ
Alonso-Doncel M	OP4, OP26
Álvarez Izaguirre M.M.	Po12
Amodio L	OP30, Po23
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Asunción Molina M	OP15
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Barroso-Martín I.	OP21
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Benešová T	OP25
Benmebirouk-Pareja N	Po01
Bensaid S	OP1
Blanco R.M	Po02
Bohigues B	Po14
Bonadiman C	OP18
Bonino F	Po03, Po04
Bordiga S.	Po03, Po04
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Botas J.A	OP26, OP32
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Bruno P	OP11
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Carmo J.V.C.	OP38
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Caterina C	OP18
Catizzone E	OP11, Po24
Cavallo M	Po04
Cerpa-Naranjo A.	Po05, Po18
Císařová I.	OP16
Concepción P	Po14
Corma A	Po14
Corrao E	OP1
Crocellà V	Po03, Po04

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Dolejšová Sekerová L	OP27, Po21
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Erlebach A	OP25
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Essid S	OP20

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Flores-Escamilla G.A	OP21
Franc M	Po06
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### G

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Gabriele B.	OP11
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Giglio E	OP1
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Golis P	Po25
Gómez-Hortigüela L	_OP2, OP10, Po07, Po08

Gómez-Pozuelo G	OP26
Grajciar L	OP25, OP35
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Guerrero-Pérez O	OP21, Po17
Guilera J	OP24

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Mancuso R.	0	<i><b>JP11</b></i>
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Márquez-Álvarez C.	OP2, OP8, OP10, OP15, I	Po08
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Martos C.	/	Po15
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Mazur M	OP6, OP9, OP12, Po09, F	Po25
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Moliner M	I	Po14
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Soukup K OP32	7
Souza A <i>OP30</i>	0
Stoupová L Po20	0
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Charles University, Prague, Czechia				
Jiří Čejka	Pavla Eliášová			
Michael Franc	Lukáš Grajciar			
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Martin Kubů	Niccolò Lusiani			
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Jan Valenta				
Institute of Chamical Ducases Fundamentals				
Institute of Chemical Process Fundamentals, C	LAS, Czechia			
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I. Hevrovský Institute of Physical Chemistry, C	AS, Czechia			
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University of Chemistry and Technology Prag	ie. Czechia			
lva Paterová	Martina Pitínová			
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University of Par <u>dubice, Czechia</u>				
Roman Bulánek	Kateřina Knotková			
ZEOCHEM AG, Czechia				
David Hajdu				

#### University of Calabria, Italy

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University of Ferrara, Italy

Maura Mancinelli

#### Università di Napoli Federico II, Italy

Paolo Aprea Nicola Gargiulo

Domenico Caputo

University of Turin, Italy

Francesca Bonino

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Gisela Orcajo Patricia Pizarro de Oro Gabriel Morales Sánchez Marta Paniagua

#### University of Málaga, Spain

M. Olga Guerrero Perez Enrique Rodríguez-Castellón 09.06.2025

pondělí

	10.06.2025		11.06.2025		12.06.2025
	úterý		středa		čtvrtek
8:45	Opening				
9:00	PL1 Martínez	9:00	PL2 Otyepka	9:00	PL3 Giordano
9:45	OP1 Giglio	9:45	OP16 Kamlar	9:45	OP36 Orcajo
10:00	OP2 Sánchez-Morena	10:00	OP17 Pitínová	10:00	OP37 Topka
10:15	OP3 Shamma	10:15	OP18 Mancinelli	10:15	OP38 Rodríguez-Castellón
10:30	Break	10:30	Break	10:30	Break
11:00	OP4 López Alberto	11:00	OP19 Chirinos	10:50	KL2 Pérez-Pariente
11:15	OP5 Paniagua	11:15	OP20 Knotková	11.20	Closing
11:30	OP6 Olšovská	11.20	KI1 Shamzhy	11.20	
11:45	OP7 Kubů	11.50	KEI SHAHIZHY		
12:00	Lunch	12:00	Lunch	12:00	Departure
14:00	OP8 Arnaiz	14:00	OP21 Guerrero-Perez		
14:15	OP9 Kolesár	14:15	OP22 Pérez-Martín		
14:30	OP10 de la Serna	14:30	OP23 Veselá		
14:45	OP11 Bruno	14:45	OP24 Martín		
15:00	OP12 Xie	15:00	OP25 Grajciar		
15:15	OP13 de la Calle	15:15	OP26 Inés Ávila		
15:30	OP14 Zhang	15:30	OP27 Paterová		
15:45	OP15 Sánchez-Sánchez	15:45	Break		
		16:15	OP28 Moreno		
		16:30	OP29 Shafiq		
		16:45	OP30 Pizarro		
16.00	F	17:00	OP31 Moravčík		
16:00	Excursion	17:15	OP32 Linares		
		17:30	OP33 Vysloužil		
		17:45	OP34 Morales		
		18:00	OP35 Kendra		
20:00	Barbecue	19:00	Farewell Dinner		

18:00 - 21:00 Registration