MULTI2HYCAT
Summer School

# Hybrid Materials for Catalytic Processes

5th and 6th of July 2018
Valencia, Spain

## Book of Abstracts

# INDEX

# WELCOME

We welcome you to the **Summer School MULTI2HYCAT – 5th and 6th July 2018** in Valencia (Spain), organized by the Instituto de Tecnología Química (ITQ) in collaboration with the Università del Piemonte Orientale "Amedeo Avogadro" (Alessandria, Italy), University of Southampton, Solvay SA, PNO Consultants GMBH, Agencia Estatal Consejo Superior de Investigaciones Cientificas, Centre National de la Recherche Scientifique, Cage Chemicals SRL and Almirall SRL.

The objective of MULTI2HYCAT Summer School is to contribute to the implementation of the EU policies and Directives on competitiveness and sustainability (e.g. Climate Action, Energy Strategy, Green Growth, etc.), through the validation of novel concepts in hybrid materials design for heterogeneous catalysis. This includes the preparation and validation of innovative hierarchical porous organic-inorganic materials with several active sites (organocatalysts) perfectly located in specific structural positions in their framework, which will be used as single-solid reusable hybrid active catalyst to carry out multi-step catalytic processes with high conversions and selectivities towards the desired final products. The new materials will allow avoiding the extra-efforts associated with isolation of intermediate products, wastes and solvents elimination and purification processes thus enabling more efficient and sustainable catalytic routes from the economic, energetic as well as the environmental points of view.

These actions promises to solve the limits of current organosiliceous solids, while improving the flexibility and versatility and reducing costs of the obtained catalysts, making them attractive for a wide range of industrial applications. To this end, these type of hybrid catalysts will be demonstrated for pharmaceutical and intermediate chemistry applications, as a concrete prime-mover for subsequent replication.

Inside this field, MULTI2HYCAT Summer School event (5th and 6th July 2018, Instituto de Tecnología Química, UPV-CSIC) is destined to PhD students and young post-doc researchers. The program consist of Invited Tutorial lectures delivered by top experts in the field of heterogeneous catalysis, poster session and flash short oral communications by students from selected posters.

We hope that you will enjoy the scientific as well as the social programmes, and we wish all of you a fruitful and pleasant stay in Valencia.

## PROGRAMME

| | 5th July 2018 | | 6th July 2018 |
|---|---|---|---|
| | | 9:00 – 10:00 h | Tutorial Session 3<br>***R. Raja (UoS)*** |
| | | 10:00 – 11:00 h | Short Oral Presentations 2 |
| | | 11:00 – 11:30 h | Coffee Break |
| 13:45 – 14:45 h | Registration | 11:30 – 12: 30 h | Tutorial Session 4<br>***Maurizio Cossi (UPO)*** |
| 14:45 – 15:00 h | Welcome | 12:30 – 13:30 h | Tutorial Session 5<br>***Guillermo Mínguez (ICMol-UV)*** |
| 15:00 – 16:00 h | Tutorial Session 1<br>***L. Marchese (UPO)*** | 13:30 – 14:00 h | Concluding Remarks |
| 16:00 - 17:15 h | Short Oral Presentations 1 | 14:00 – 15:30 h | Lunch |
| 17:15 – 17:45 h | Coffee Break | | |
| 17:45 – 18:45 h | Tutorial Session 2<br>***M. Crespo (Almirall)*** | | |
| 18:45 – 20:00 h | Poster Session | | |
| 21:00 h | Summer School Dinner | | |

## MEETING PROGRAMME

### 5th July 2018

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|---|---|
| **13:45 – 14:45 h** | Registration |
| **14:45 – 15:00 h** | Welcome |
| **15:00 – 16:00 h** | Tutorial Session 1<br>***L. Marchese (UPO)***<br>**Multidisciplinary approach for the physico-chemical characterisation of porous and hybrid materials** |
| **16:00 - 17:15 h** | Short Oral Presentations |
| **16:00 h** | CREATING HIERARCHICAL SILICOALUMINOPHOSPHATES WITH TAILORED ACID SITES USING BOTTOM-UP SYNTHETIC STRATEGIES<br>Chiara Ivaldi (Univ. Piomente Orientale, Italy) |
| **16:15 h** | GROWING MODULATOR AGENTS FOR THE SYNTHESIS OF AL-MOF TYPE MATERIALS BASED ON ASSEMBLED 1D STRUCTURAL SUBDOMAINS<br>José María Moreno (ITQ-UPV/CSIC) |
| **16:30 h** | CHIRAL NON-ORDERED MESOPOROUS HYBRID CATALYST TO ENANTIOSELECTIVE MICHAEL ADDITION<br>Sebastián Llopis (ITQ-UPV/CSIC) |
| **16:45 h** | FEW LAYER 2D-PNICTOGENS (P & SB) CATALYZE THE ALKYLATION OF SOFT NUCLEOPHILES WITH ESTERS.<br>Vicent Lloret (Friedrich–Alexander–Universität Erlangen–Nürnberg, Germany) |
| **17:00 h** | Ag-ZEOLITES AS BIOCIDE AGENTS<br>Jose .L. Cerrillo (ITQ-UPV/CSIC) |
| **17:15 – 17:45 h** | Coffee Break |
| **17:45 – 18:45 h** | Tutorial Session 2<br>***M. Crespo (Almirall)***<br>**The journey of a medicine: from invention to the market** |
| **18:45 – 20:00 h** | Poster Session |

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| | THE IMPACT OF MODIFICATIONS WITH TRANSITION METALS OF VERMICULITES ON THE CATALYTIC PROPERTIES IN DENOX PROCESSES<br>Bogdan Samojeden (AGH University of Science and Technology, Poland) |
| | SYNTHESIS AND CATALYTIC APPLICATIONS OF ORGANOPALLADIUM CAGES WITHIN METAL ORGANIC FRAMEWORKS<br>R. Greco (ITQ-UPV/CSIC) |
| | SYNTHESIS OF A HOMOCHIRAL PERIODIC AROMATIC FRAMEWORKS BASED ON BINOL AND ITS APPLICATION IN ASYMMETRIC CATALYSIS<br>Beatriz Villoria-del-Álamo (ITQ-UPV/CSIC) |
| | MAGNETIC MOFS WITH TUNABLE ORDERING TEMPERATURES ABOVE 100 K<br>Cristian Martínez-Hernández (ICMol, Univ. Valencia, Spain) |
| | CARBON-SUPPORTED Au NANOPARTICLES: CATALYTIC ACTIVITY RULED OUT BY CARBON SUPPORT<br>Andrea Jouve (Università degli Studi di Milano, Italy) |
| | MIXED CERIUM MOFs: THE ROLE OF THE CERIUM OXIDATION STATE (III / IV) IN ITS CATALYTIC ACTIVITY TOWARDS SYNTHESIS OF AMINES<br>Antonio Valverde (ITQ-UPV/CSIC – ICMM/CSIC) |
| **21:00 h** | **Summer School Dinner**<br>*Restaurante La Ferradura*<br>*Av. Mare Nostrum, 42, 46120 Alboraia, València* |

## 6th July 2018

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| **9:00 – 10:00 h** | Tutorial Session 3<br>***R. Raja (UoS)***<br>**Catalysis with Functionalised Porous Architectures** |
| **10:00 – 11:00 h** | Short Oral Presentations 2 |
| **10:00 h** | AIR STABLE COBALT-AQUO CATALYSTS FOR ALKENE HYDROSILYLATION WITHOUT ADDITIVES AND NEW INSIGHT INTO ITS MECHANISM.<br>Silvia Gutiérrez (ITQ-UPV/CSIC) |
| **10:15 h** | ISOLATED Fe(III)–O SITES CATALYZE FRONT-END ACETYLENE SEMIHYDROGENATION<br>Maria Tejeda-Serrano (ITQ-UPV/CSIC) |
| **10:30 h** | PLATINUM CLUSTERS AND SINGLE ATOMS INSIDE MOFS AS HYBRID CATALYSTS FOR INDUSTRIALLY RELEVANT CHEMICAL REACTIONS<br>Miguel A. Rivero-Crespo (ITQ-UPV/CSIC) |
| **10:45 h** | HIGHLY ACTIVE AND FUNCTIONAL-TOLERNT ZEOLITE AS CATALYST FOR LIGNOCELLULOSIC BIOMASS VALORIZATION<br>Majd Al-Naji (Max Planck Institute of Colloid and Interfaces, Germany) |
| **11:00 – 11:30 h** | Coffee Break |
| **11:30 –12: 30 h** | Tutorial Session 4<br>***Maurizio Cossi (UPO)***<br>**Computational Techniques for the Characterization of Porous Materials** |
| **12:30 – 13:30 h** | Tutorial Session 5<br>***Guillermo Mínguez (ICMol-UV)***<br>**1D, 2D and 3D Hybrid Organic-Inorganic Crystalline Materials** |
| **13:30 – 14:00 h** | Concluding Remarks |
| **14:00 – 15:30 h** | Lunch |

## PLENARY CONFERENCES

**Prof. Leonardo Marchese**

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Università del Piemonte Orientale "Amedeo Avogadro"
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Leonardo Marchese graduated in Industrial Chemistry in 1985 and obtained the PhD in Chemistry in 1990 at the University of Turin (Italy). Full Professor of Physical Chemistry since 2005 at the Università del Piemonte Orientale (UPO), where he is the Director of the Department of Science and Technological Innovation. He is leading a research group of around 15 professors and young researchers focusing on the development of layered or porous materials, even with hybrid inorganic-organic character, for application in catalysis, gas storage and separation, photovoltaic cells and biomedicine. All these systems have been studied by a combined experimental (prominently FT-IR and ssNMR, also with the use of molecular probes) and computational approach. He has co-authored 235 articles and 8 patents collecting over 7000 citations (*h*-index 47).

### Talk Title:

### Multidisciplinary approach for the physico-chemical characterisation of porous and hybrid materials

Understanding the structure-property relationship of solids is of utmost relevance for efficient chemical processes and technological applications in industries. In this lecture, the concept of coupling three well-known characterization techniques (solid-state NMR, FT-IR and computational methods) for the study of solid state materials with 2D and 3D architectures and/or hybrid nature will be discussed. The integrated approach involving multiple spectroscopic and computational methods allows achieving an in-depth understanding of the surface, interfacial and confined space processes that are beneficial for the establishment of structure-properties relationships. The role of ssNMR/FT-IR spectroscopic properties of probe molecules in monitoring the strength and distribution of catalytic active sites and their accessibility at the porous/layered surface will be discussed. Both experimental and theoretical aspects will be considered by reporting relevant examples.

**Prof. Robert Raja**

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Professor Robert Raja, FRSC is Professor of Materials Chemistry & Catalysis at the University of Southampton (UK), following a research career at the University of Cambridge, Bayer Chemicals, Germany, the Royal Institution of Great Britain, as an 1851 Exhibition Fellow, and the National Chemical Laboratory, India. His multidisciplinary research Group at Southampton University are involved in the discovery, design and fabrication of novel catalytic materials, for application as heterogeneous catalysts, in chemical, pharmaceutical, fine-chemical and environmental sectors for developing sustainable technologies. He is the author of more than 150 research publications in peer-reviewed journals with an h-index of 45, in addition to being the inventor on over 50 International Patents. He is a *Fellow of the Royal Society of Chemistry* and his notable accolades include the Honeywell Inventors Award, Santander Universities Entrepreneurial Award, Erskine Fellowship, awarded by the University of Canterbury (New Zealand), and the Barrer Award by the Royal Society of Chemistry.

## Talk Title:

### “Catalysis with Functionalised Porous Architectures”

The utilisation of simple and readily available organic entities to effectively catalyse demanding synthetic organic transformations has inspired the development of more sustainable routes for the production of bulk and fine-chemicals. These catalysts are relatively easy to functionalise and can be engineered for specific carbon–carbon bond forming reactions. Active sites functionalised within microporous architectures have proved particularly proficient in facilitating shape-selective catalysis, where molecular transport can be controlled through a range of interconnecting channels and cages. However, despite these advantages, these catalysts have shortcomings, as the micropores which house the active sites can be easily blocked, leading to mass-transport and diffusional constraints, thereby impacting their durability and applicability.

In line with some of the objectives of MULTI2HYCAT, this talk will highlight some recent advances in our design strategy for tailoring active sites on porous architectures and how operando tools can be used for monitoring diffusion pathways during catalysis. The design and development of synthetic strategies for integrating isomorphous substituents and organocatalytic active sites within porous architectures for bulk and fine-chemical applications and in CO2 utilisation will be discussed. The potential of hierarchically porous materials to host multifunctional

active sites, traditionally found within the microporous architectures, for expanding substrate scope and targeting selectivity in heterogeneous catalysis will also be outlined in this lecture.

1. S.H. Newland, W. Sinkler, T. Mezza M.E. Potter., A.J. O'Malley., S. Chapman., J. Kezina., S.H. Newland., I.P. Silverwood., S.F. Parker., C.R.A. Catlow., R. Raja, *ACS Catalysis*, **2017**, 7, 2926.
2. A.M. Gill, C.S. Hinde, R.K. Leary, M.E. Potter, A. Jouve, P.P. Wells, P.A. Midgley, J.M. Thomas, R. Raja, *ChemSusChem*., **2016**, 9, 423.
3. S. H. Newland, W. Sinkler, T. Mezza, S. R. Bare, M. Carravetta, I. M. Haies, A. Levy, S. Keenan, R. Raja, *ACS Catal.,* **2015**, *5*, 6587.
4. M.E. Potter, A.J. Paterson, B. Mishra, S.D. Kelly, S.R. Bare, F. Cora, A.B. Levy, R. Raja, *J. Am. Chem. Soc*., **2015**, *137*, 8534.
5. R. Raja, M. E. Potter and S. H. Newland, *Chem. Commun. Feature Article*, **2014**, 50, 5940.
6. E. Gianotti, M. Manzoli, M.E. Potter, V.N. Shetti, D. Sun, A.J. Paterson, T.M. Mezza, A. Levy, R. Raja, *Chem. Sci*., **2014**, *5*, 1810.

**Prof. Maurizio Cossi**

Dipartimento di Scienze e Innovazione Tecnologica - DISIT
Universita' del Piemonte Orientale "Amedeo Avogadro"
(Alessandria, Italy)

Maurizio Cossi graduated and received his PhD at the Scuola Normale Superiore in Pisa (Italy); he's full professor in Theoretical Chemistry at the University of Piemonte Orientale (IT). He contributed to the development and implementation of some of the most used algorithms and codes for the inclusion of solvent effects in ab initio calculations (PCM). Presently his main interests regard the ab initio simulation of hybrid systems, often in connection with experimental studies: functionalized surfaces, gas adsorbed in porous materials, heterogeneous catalysts, hybrid photovoltaic materials. The techniques comprise DFT, with special attention to long range dispersion, molecular and coarse-grained dynamics, models of transport properties. He published more than 100 papers, with more than 23000 citations (h-index 37).

Lecture for MULTI2HYCAT Summer School (Valencia, 2-6 June 2018)

## Talk Title:

### Computational Techniques for the Characterization of Porous Materials

A number of different theoretical approaches and computational techniques are presented, which can be useful to support the design and the experimental characterization of various microporous materials. Some test cases will be discussed, including the adsorption of antibiotics and hydrocarbons into zeolites, the functionalization of silica surfaces with organic species for catalytic applications, the gas adsorption in various carbon materials.

We shall describe up-to-date ab initio and classical methods, particularly aimed to the description of hybrid systems, comprising organic molecules or functional groups and inorganic porous matrices (mainly silica, zeolites and porous organic frameworks). Most ab initio methos are based on Density Functional Theory (DFT), and we'll show the effect of functional and basis set choice; in addition, the weight of dispersion contributions, usually added as semiempirical corrections, will be presented and discussed. When classical methods are used, as in Monte Carlo simulation of gas adsorption processes, we'll discuss the optimization of specific terms in the force fields.

A part of the lecture will be devoted to a review of the experimental porosimetric techniques, involving DFT parameterization in their most recent versions, and to a combined experimental/theoretical study to deduce the microporous structure of an amorphous carbn material.

**Dra. Maribel Crespo**

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Dr. Maria Isabel Crespo has a Ph.D. in Organic Chemistry and a degree in Chemical Engineering from the Institut Quimic de Sarrià, Ramon Llull University (Spain). She joined Almirall S.A. in 1992 as a medicinal chemist. Since then, she has been involved in several projects covering most aspects of the Drug Discovery process. Since 2011, she has been working as Research Alliances Leader. She has published more than 40 articles and reviews in scientific publications, and patents.

## Talk Title:

### “The journey of a medicine: from invention to the market”

The discovery of new drugs starts in the laboratory by testing thousands of compounds that can be potential candidates for development as a medical treatment. However, only a small number of those compounds looks promising and call for further studies. The selected compound is evaluated by drug developers to gather information on potential benefits and efficacy compared with similar drugs, best dosage and route of administration, as well as possible adverse effects. Once a drug developer has evidences that the drug is efficacious and safe, the company asks regulatory authorities for commercialization approval and, finally, the drug reaches the market. In this talk, we will walk through the whole R&D process with a real case of an Almirall drug development.

**Dr. Guillermo Mínguez Espallargas**

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Guillermo Mínguez Espallargas (1981) was graduated in 2004 with Extraordinary Prize and Second National End-of-Career Award. Later he completed his PhD in 3 years at the University of Sheffield, for which he received the 2008 European Young Chemist Award (the only Spanish to receive it so far), as well as being the only European to receive the "Ludo Frevel Award" in 2007 of the International Center for Diffraction Data of the USA. He is currently a Ramón y Cajal researcher at the Molecular Science Institute of the University of Valencia (ICMol), where he leads four research projects.

The work of Dr. Mínguez Espallargas is aimed at the development of new porous materials conceptually different from those already existing, with the aim of being able to selectively store certain gases and, therefore, of their application in the separation of gases. The implementation of magnetic properties allows the detection of the incorporation of these gas molecules and the development of sensors. These achievements can have a significant positive impact in areas such as the environment or energy.

The high quality of his scientific work is clear when he received the "Dalton Young Research Award 2009" from the Royal Society of Chemistry, the "Real Academia Sevillana de Ciencias 2010 Award" to Young Researchers and the "Xavier Solans Award 2011" to the best scientific work in the area of Crystallography. In addition, he was selected to attend the prestigious meeting Lindau-Nobel meeting of 2013 where 35 Nobel prizes attended.
He is the author of more than 60 publications, and has been invited to present his work at several international conferences. Moreover, he has recently been awarded the Princess of Girona Prize in Scientific Research.

## Talk Title:

### 1D, 2D AND 3D HYBRID ORGANIC-INORGANIC CRYSTALLINE MATERIALS

Coordination polymers are a crystalline class of hybrid organic-inorganic materials that have received a lot of attention during the past years due to their high interest towards practical applications.

First, we will present a family of 1D coordination polymers that, despite the lack of permanent channels, can effectively trap a wide range of gas molecules into the internal cavities due to the flexible and dynamic nature of the framework.[1]

Second, we will present a general strategy for the synthesis of neutral layered coordination polymers, exhibiting magnetic order.[2] These 2D coordination polymers are robust enough in ambient conditions to be micromechanically exfoliated down to the mononalyer while preserving the crystallinity. Furthermore, the molecular composition of these compounds provide an unconventional route to tune at will the surface chemistry of the individual layers, an approach unfeasible in 2D inorganic materials, but easily achieved in 2D coordination polymers.

Finally, we will discuss a highly stable tetrathiafulvalene (TTF)-based 3D coordination polymer with a non-interpenetrated hierarchical crystal structure with mesoporous channels (~33 Å) disposed orthogonal to microporous channels (~10 Å).[3] The advantages of this MOF respect to widely used MOFs catalyst (MIL-100 and MIL-101) will be clearly demonstrated for a reaction of large applied interest (aerobic oxidation of benzothiophenes), illustrating the advantages of having a hierarchical MOF with large mesopores and high stability. In addition, **MUV-2** presents a continuous breathing behaviour upon solvent or gas adsorption, cause by the flexibility of the TTF-based ligands that show conformational changes, as unequivocally demonstrated by single crystal X-ray diffraction. The reversible swelling not only modifies the accessible space, but also the oxidation potential of the MOF.[4]

**References:**

[1] M. Giménez-Marqués et al, Chem. Sci. **2017**, 8, 3109.

[2] J. López-Cabrelles, S. Mañas-Valero, *et al,* Nature Chem. **2018**, accepted.

[3] M. Souto, *et al.,* Chem. Sci, **2018**, 9, 2413.

[4] M. Souto, *et al.,* submitted.

## ORAL COMUNICATIONS

### CREATING HIERARCHICAL SILICOALUMINOPHOSPHATES WITH TAILORED ACID SITES USING BOTTOM-UP SYNTHETIC STRATEGIES

**Chiara Ivaldi,[1] Ivana Miletto,[1] Geo Paul,[1] Stephanie Chapman,[2] Robert Raja,[2] Leonardo Marchese[1] and Enrica Gianotti[1]**

*1 – Department of Science and Technological Innovation and Nano-SiSTeMI Centre, Università del Piemonte Orientale, Viale T. Michel 11, 15121 Alessandria, Italy 2 – School of Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, SO17 1BJ. U.K. chiara.ivaldi@uniupo.it*

Hierarchical zeolites or zeotype materials, which combine both micro and mesopores in a multilevel pore network, strongly emerged as novel materials for catalytic applications to overcome typical drawbacks of traditional microporous materials such as poor mass transfer and hindered diffusion. A wide variety of innovative strategies to produce secondary porosity within the framework of microcrystalline structures has been developed, nevertheless, significant challenges are still ahead.

In this contribution, different synthetic strategies to prepare hierarchical SAPO-34 acid catalysts were explored. Two novel bottom-up routes were used to synthesize hierarchical SAPO-34 catalysts, mitigating the need of sophisticated surfactants or templates by using: (i) CTAB encapsulated within ordered mesoporous silica (MCM- 41) as both the silicon source and mesoporogen[1]; (ii) mono- and di-saccharides as structure directing agent to direct the mesopore network[2]. To get information on the nature, strength and the accessibility of the acid sites in the hierarchical zeotype catalysts, a fine physico-chemical characterization using FT-IR spectroscopy of adsorbed probe molecules together with solid-state NMR was performed. In addition, structural and textural properties of the hierarchical zeolites were also explored by means of PXRD and volumetric analyses. In this study, CO was used to assess the acidic properties of the hierarchical zeolites and bulky basic molecules such as pyridine, 2,4,6-trimethylpyridine and 2,6-di-tert-butylpyridine, which cannot enter the micropores, were used to get information on the enhanced accessibility of the active sites. Probe-based studies are particularly pertinent in catalysis for establishing structure-property relationships.

The hierarchical materials showed superior activity in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam (precursor of Nylon-6) with respect to the parent microporous systems. This superior catalytic activity can be explained by the overcoming of the diffusion constraints due to the introduction of mesoporosity, well documented by the volumetric analysis and by the enhanced accessibility of active sites.

**References:**

[1] Miletto I.; Paul G.; Chapman S.; Marchese L.; Raja R.; Gianotti E. Chem. Eur. J. **2017,** 23, 9952-9996.

[2] Miletto I.; Ivaldi C.; Paul G.; Chapman S.; Marchese L.; Raja R.; Gianotti E. ChemistryOpen **2018**, 7, 297-301.

*The project leading to these results has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N. 720783—MULTI2HYCAT*

# GROWING MODULATOR AGENTS FOR THE SYNTHESIS OF AL-MOF- TYPE MATERIALS BASED ON ASSEMBLED 1D STRUCTURAL SUB- DOMAINS

**José María Moreno, Alexandra Velty, José A. Vidal-Moya, Urbano Díaz and Avelino Corma**

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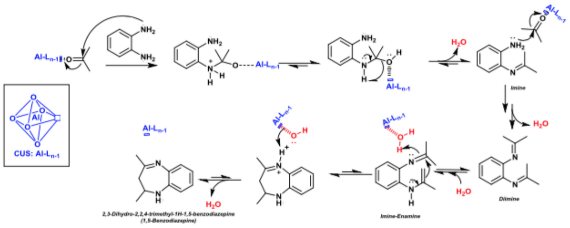
The use of suitable building blocks in optimal synthesis conditions has allowed the generation of new families of advanced porous materials with high gas uptake capacities, catalytic applications or technological functionalities.[1-2] Although, 1D nanoribbons and 2D lamellar architectures are very interesting due to the associated structural versatility that allows the spatial modification of their individual nanolayers to generate more accessible materials or novel nanocomposites, the number of 1D or 2D organized structures is reduced, especially for metalorganic networks[3].

Then, in this work, we propose the use of specific long-alkyl aromatic mono- carboxylate linkers, combined with metallic nodes, to favor the formation of 1D metalorganic ribbon-type structural sub-units which would be assembled to generate novel organized MOF-type solids under solvothermal conditions with different level of structuration and dimensionality. The combination of two solvents with different polarity during the synthesis process (DMF and water) was decisive to obtain Al-MOFs with several morphologies and particular textural properties. Particularly, it was obtained 3 different families with different morphologies: (I) isoreticular materials with MIL-53(Al)-type structure, (II) mesoscopic (Al-ITQ) and (III) lamellar materials (L- MOF). These solids were active as acid catalysts to the synthesis of 1,5-benzodiazepine.

Therefore, we have successfully prepared novel families of hybrid metalorganic materials based on the effective assembly of 1D organic-inorganic ribbon-type structural sub-units where the final structuration level was based on the polar nature of solvent. These hybrid materials carried out the production of 1,5-benzodiazipines with interest in fine chemistry related with pharmacological industry.



**Scheme 1.** Mechanism for 1,5-benzodiazepine formation.

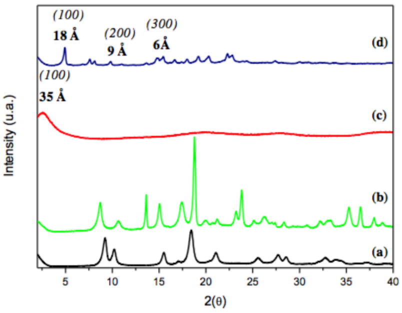


**Figure 1.** XRD patterns of: (a) MIL-53(Al), (b) isoreticular MIL-53(Al), (c) mesoscopic and (d) lamellar frameworks.

**References**:

[1] Chughtai, A. H.; Ahmad, N.; Younus, H. A.; Laypkov, A.; Verpoort, Chem. Soc. Rev. 2015, 44, 6804-6849.

[2] Getman, R. B.; Bae, Y. S.; Wilmer, C. E.; Snurr, R. Q. Chem. Rev. 2012, 112, 703- 723.

[3] Ródenas, T.; Luz, I.; Prieto, G.; Seoane, B.; Miro, H.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X.; Gascón, J. Nat. Mater. 2015, 14, 48-55.

# CHIRAL NON-ORDERED MESOPOROUS HYBRID CATALYST TO ENANTIOSELECTIVE MICHAEL ADDITION

**Sebastián Llopis, Teresa García, Ángel Cantín, Alexandra Velty, Urbano Díaz, Avelino Corma.**

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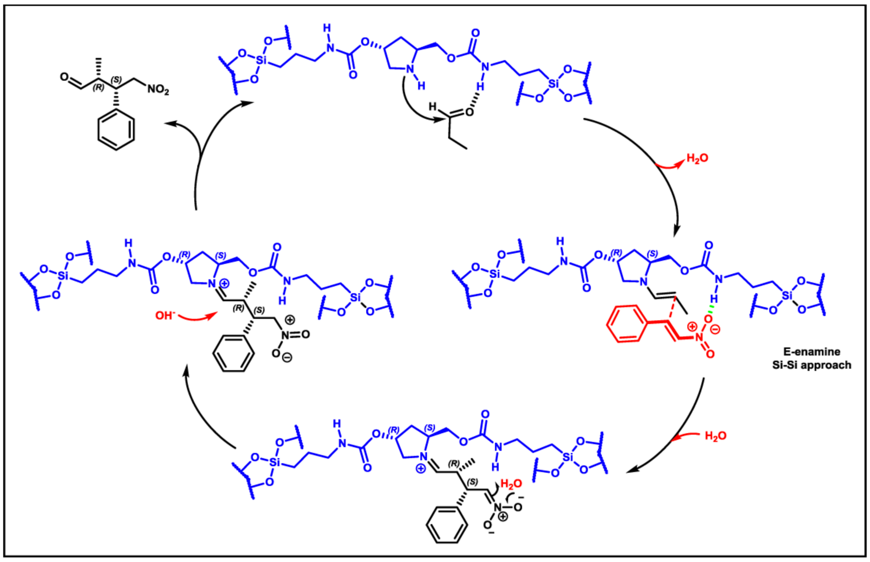
The aims of heterogenization of chiral organocatalysts[1] lie in industry implantation, the possibility of reducing the costs and facilitate the recovery, reuse and/or regeneration of the catalysts for several cycles. In this context, the development of new asymmetric hybrid materials offer new opportunities respect to the mechanical and chemical stability of the materials under process and regeneration conditions[2]. Hybrid materials have been of large interest for both scientific and industrial communities because of their commercial interest and because of the challenges posed by their synthesis. In this work, we report the preparation of chiral hybrid material based on methyl-(2S,4R)-4-hydroxypyrrolidine-2-carboxylate derivative for the enantioselective Michael addition of aldehydes to nitroolefins with high stereocontrol(see Scheme). The asymmetric Michael addition of carbonyl compounds to nitroalkenes is among the most useful synthetic methods for the C–C bond formation to produce nitroaldehydes, which constitute highly valuable synthetic intermediates in organic chemistry[3].



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# FEW LAYER 2D-PNICTOGENS (P & SB) CATALYZE THE ALKYLATION OF SOFT NUCLEOPHILES WITH ESTERS.

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The discovery of Graphene has given rise to a plethora of 2D-materials with applications in the field of electronics and spintronics.[1] Concerning to organic catalysis, Graphene and other 2D-materials have been studied due to their unique structural features and electronic properties, significantly increasing the range of catalytic applications.[2] The novel layered materials Black Phosphorus (BP) and Antimonene (Sb), corresponding to the pnictogens group, are formed by a single element in zero oxidation state and offer excellent properties for catalytic reactions due to their dimensionality and the lone pair of electrons located in every atom of their structure.[3],[4] Nevertheless, these materials rapidly oxidize or decompose under ambient conditions, hampering their applications in catalysis due to the difficulties in preparing well–structured catalytic precursors. In order to overcome this challenge, suspensions of highly exfoliated few layer 2D phosphorene and antimonene protected against oxidation in ionic liquids were prepared, with the native atoms ready to interact with external reagents while avoiding aerobic or aqueous decomposition pathways. Remarkably, these materials promote the selective cleavage of the $C_{alkyl}$–O bond of different esters with respect to the much more reactive neighboring C–C and C=O bonds, allowing the alkylation of nucleophiles. These 2D-pnictogens circumvent the extremely harsh reaction conditions which are associated with previous superacid– catalyzed alkylations, by enabling an

alternative mechanism on the surface, protected from the water and air by the ionic liquid. Thus, BP and Sb increase the straightforward access to abundant functional groups provided by cheap esters and succeed in the alkylation of a variety of acid–sensitive organic molecules.

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# AG-ZEOLITES AS BIOCIDE AGENTS

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Microorganisms as bacteria and fungi can be pathogenic living beings. Bacteria, for instance, are responsible of around $4{\cdot}10^6$ hospital associated infections (€7 billion economic impact per year in Europe) (1). But also, fungi are guilty of the waste of 40% of fruits and vegetables. According to these problems, the use of materials containing silver represent an inspiring generation of biocide materials. However, for an appropriate biocide action, silver must be supported on innocuous support to control the release of the biocide agent, guarantying a durable effect in time (2). For that purpose, zeolites seem to be adequate supports due to its properties and structure. This contribution studies the *in vitro* biocide activity of Ag-zeolites against different bacteria and fungi.

Two commercial Na-zeolites (FAU and LTA) have been used. They were ion exchanged with AgNO3 solutions during 16 hours at 298 K in darkness in order to obtain 2% wt. Ag zeolites (3). XRD studies of the samples did not show structural changes neither any peak related with Ag demonstrating that silver species are well-dispersed and no large silver clusters are formed. Bactericidal activity of Ag-zeolites was evaluated *in vitro* against two bacteria in TSB medium (*S.aureus* and *E.coli*), measuring the minimum inhibitory concentration (MIC). The results (Figure 1) showed a high biocide activity of the Ag-zeolites, being the most active the zeolite with large porous system (FAU). The HRTEM+EDX studies exhibited the release of silver cations to the biological medium and the change on the morphological structure of microorganism's cell, indicating the death of the bacteria.

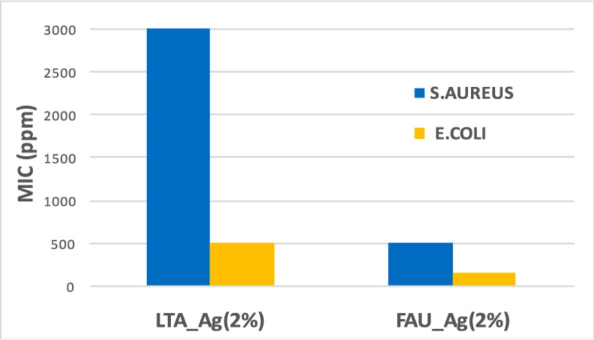

**Figure 1:** Biocide activity (MIC) of Ag zeolites against *S.aureus* and *E.coli*

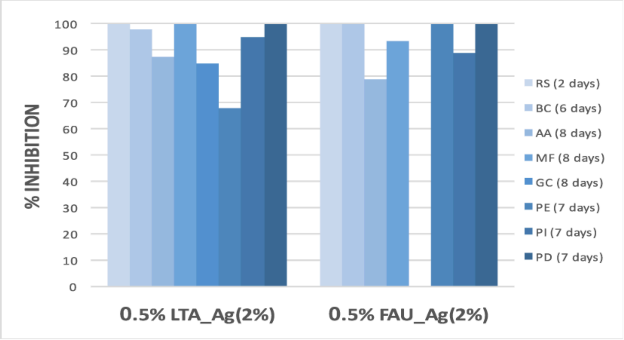

**Figure 2:** Biocide activity as % of inhibition of Ag-zeolites against several fungi

On the other hand, *in vitro* fungicide activity of the same zeolites was measured against some fungi: *Penicillium digitatum, P. italicum, P. expansum, Geotrichum citri-aurantii, Monilinia fructicola, Botrytis cinerea, Alternaria alternata,* and *Rhizopus stolonifera*. Figure 2 shows the biocide activity of Ag-zeolites incorporated in the fungi growing medium at 0.5% wt. The results revealed also excellent fungicide activity for almost all fungi. The differences in the fungicide activity of both Ag-zeolites are not significant.

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# AIR STABLE COBALT-AQUO CATALYSTS FOR ALKENE HYDROSILYLATION WITHOUT ADDITIVES AND NEW INSIGHT INTO ITS MECHANISM.

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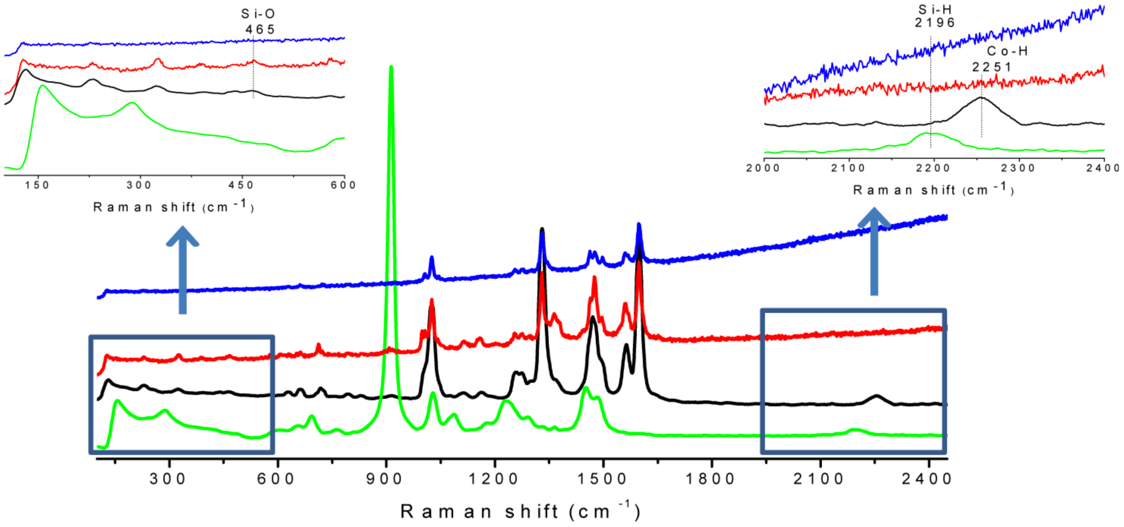
Hydrosilylation of alkenes catalyzed by transition metals is the most straightforward and atom-economic approach to synthesize organosilanes, which can be converted to alcohols or used as monomers for the production of silicon-based polymers. Some authors have reported complexes with Fe, Co and Ni which have been studied for the catalytic hydrosilylation of alkenes, but only a few studies reported hydrosilylation with hydroalkoxysilanes and hydrosiloxanes . Moreover, they were limited by their high sensitivity toward air and moisture. A desirable catalyst should contain stable and easily handled metal salts and ligands that are active without requiring strong co-catalysts.[1]

Herein, the development of air stable cobalt-aquo complexes as catalyst for the hydrosilylation of alkenes without additives is shown. The developed catalysts are based on commercial ligand and cobalt precursors. This discovery of highly active, selective and bench-stable cobalt precatalysts enabled exploration of the scope of the alkene substrates in the hydrosilylation reaction.

In-situ Raman spectroscopy was employed to elucidate the reaction mechanism between the catalyst and the two reagents. In this case, a strong band was detected, which was clearly shifted respect to the Si-H bond of the silane, and it was observed for a long period of time and disappeared when the alkene was added. This signal was assigned to a Co-H bond.[2] Based on the in-situ Raman and kinetic experiments, a plausible mechanism has been proposed.



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# ISOLATED Fe(III)–O SITES CATALYZE FRONT-END ACETYLENE SEMIHYDROGENATION

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Ethylene is one of the most important compounds for the chemical industry, with a worldwide production over 150 million tonnes in 2016.[1] Most of its production goes to synthetized polyethylene, the first plastic in terms of production volume (more than 80 million tons per year).[2] Ethylene is produced by the "stream cracking" method with some by-products. Specifically, raw ethylene contains around 1% (10000 ppm) of acetylene that must be reduced to 5 ppm for polymerization uses, higher levels of acetylene either poison or form explosive acetylides with the metal polymerization catalysts. Currently, this process is carried out with Pd supported on $Al_2O_3$, modified with Ag, K, Pb or Au additives.[3] These state-of-the-art catalysts operate in a wide window of temperatures typically from <100 to 150 oC, and give an ethylene purity >99.90%. Alternative catalysts based on non–noble metals supported on inorganic oxides have been developed but they operate at >250 oC with lower catalytic efficiency, often reducing acetylene to no less of 0.05%.[4] In a previous work, a supported planar iron oxide nanoparticle catalyst achieved similar activities and selectivities in flow than the state-of-the-art catalyst for the purification of ethylene flows by semihydrogentaion of acetylene (less than 100 ppm with 0.2% of ethane generated at 115-165 oC).[5] Interaction with the support helps the iron to perform the hydrogenation reaction. Further studies, which will be presented here, show that an isolated Fe(III)–O Sites is a better catalyst. Using a MOF and a more robust support (zirconia),[6,7] an isolated Fe(III)–O Sites converts acetylene to less than 100 ppm with 2-20% of ethane at 150 oC, under industrial conditions, comparable to commercial Pd supported on $Al_2O_3$. These results constitute a step forward toward the design of an efficient, robust, and versatile catalyst based on non-noble-metals for the purification of ethylene, operating under the industrial conditions of acetylene converters.

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# PLATINUM CLUSTERS AND SINGLE ATOMS INSIDE MOFS AS HYBRID CATALYSTS FOR INDUSTRIALLY RELEVANT CHEMICAL REACTIONS

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Heterogeneous catalysts are always preferred in industry due to several factors including easy separation from the reaction mixture, recyclability, stability at elevated temperatures and sustainability, among others. However, traditional synthesis methods (impregnation, co-precipitation, etc.) usually produce a mixture of species varying in size, morphology, electronic properties and environment, with the consequent disparity in reactivity and therefore, low selectivity. In order to overcome the lack of uniformity in heterogeneous catalysts, microporous supports provide the same environment for the metal species.[1-2] In particular, MOFs act as "nano-reactors" that drive the atomically precise synthesis of clusters or single atoms and stabilize them without strong interactions, maintaining the intrinsic catalytic activity of the metal. This, along with host-guest interactions similar to enzymes make clusters- and SAC-MOF hybrid materials promising heterogeneous catalysts.

In this work, $Pt^0_2$ clusters inside a MOF have been used as catalyst for the low temperature (25-140 oC) synthesis of cyanides, $CO_2$ methanation and olefin hydrogenation (Figure 1).[3] Naked $Pt^0_1$ prepared inside a different MOF, catalyse the low temperature (50-150 o C) water gas shift (WGS) reaction more efficiently than state-of-the-art catalysts (Figure 2). These catalysts present lower activation energy thanks to confinement and high activity of the metal particles. The catalysts have been thoroughly characterized by single crystal XRD, TEM, XPS, FTIR, NMR and DFT calculations.

This work shows the great potential of hybrid catalysts based on cluster/SAC-MOFs as very active and selective well-defined catalysts for a variety of industrially relevant chemical reactions. This concept can be expanded to other MOF structures and metals.

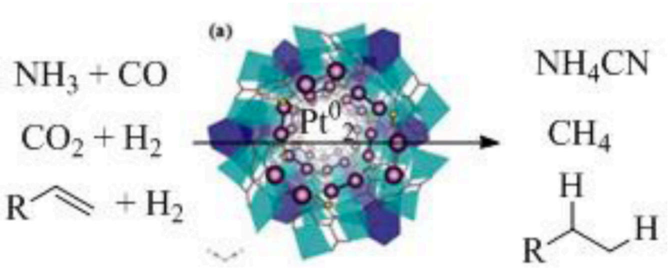

**Figure 1**. Crystal structure of $Pt^0_2$-MOF and reactions catalyzed.

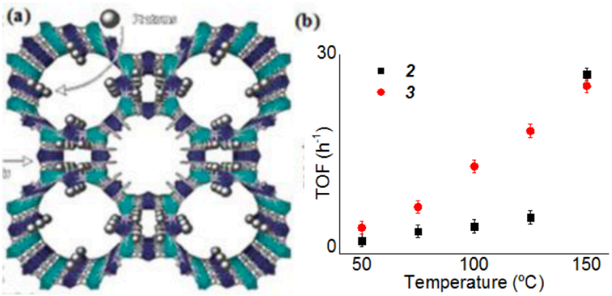

**Figure 2.** (a) Crystal structure of $Pt^0_1$-MOF. (b) Temperature profile for WGS of $Pt^0_1$-MOF (red) and $Pt^{2+}$-MOF (black).

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# HIGHLY ACTIVE AND FUNCTIONAL-TOLERNT ZEOLITE AS CATALYST FOR LIGNOCELLULOSIC BIOMASS VALORIZATION

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The associated resource stress and price volatility, as well as climate changing and polluting effects of our linear fossil based economy, necessitates a transition towards a sustainable circular economy based on renewable biomass resources. Particularly, lignocellulosic biomass which consists of cellulose, hemicellulose and lignin, represents the most abundant and low cost one. Nevertheless, the multi-functionalities of lignocellulosic biomass, e.g., -OH, -C=O, -COOH and -R-O-R-, due to the high oxygen content renders it highly reactive and not suitable for most of the classical standard catalysts which consequently suffer from rapid deactivation. Therefore, combining the development of novel active and functional-tolerant catalysts, i.e., zeolite and hierachichal zeolite, with integrated flow process in green solvents for lignocellulosic valorization, is our specific key approach for obtaining a sustainable process.[1,2]

In our group, we are working on designing strongly basic zeolite for the selective upgrading of easily accessible lignocellulosic biomass–derived γ-valerolactone (GVL) to a "methacrylic-like" monomer, i.e., α-methenylene-γ-valerolactone (MeGVL), over basic zeolite, e.g., Cs- or Mg containing zeolite, in the presence of formaldehyde (FA), cf. Figure 1. Additionally, we working on the upgrading of 2,5-dimethylfuran (DMF) into p-xylene over wide range of different acidic zeolites (ZSM-5, Beta and USY) in the presence of ethylene via solid acid-catalyzed dehydration step (Figure 2).

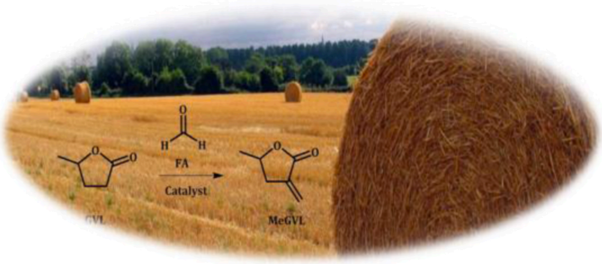

**Figure 1:** GVL upgrading to MeGVL over basic catalyst in the presence of FA.

Interestingly, p-xylene is a wanted platform chemical for large scale production of polyester such as polyethylene terephthalate (PET).

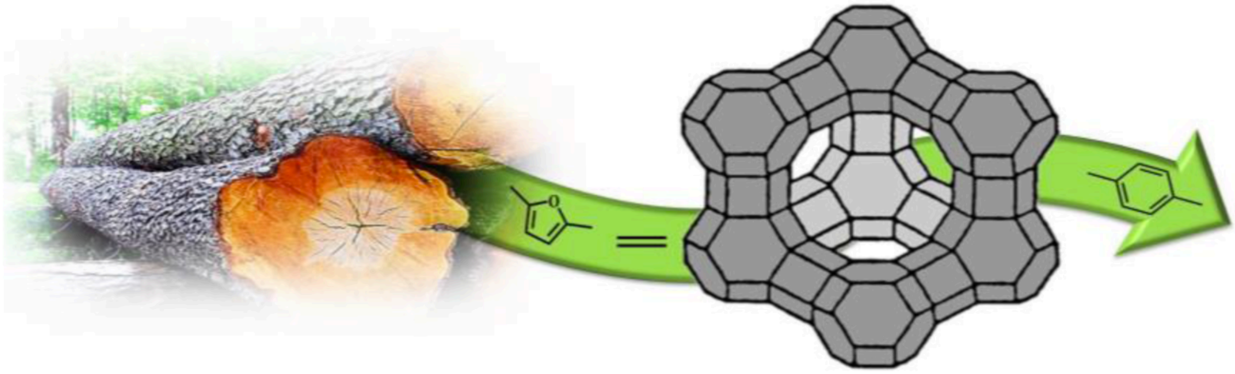

Figure 2: DMF conversion to p-xylene using zeolite in the presence of ethylene.

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## POSTER SESION

### THE IMPACT OF MODIFICATIONS WITH TRANSITION METALS OF VERMICULITES ON THE CATALYTIC PROPERTIES IN DENOX PROCESSES

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Natural aluminosilicate - vermiculite was given to the intercalation process according to the modified procedure of Kudła[1] . The resulting material was further modified (by the incipient wetness) with selected d-electron metals: Mn, Ni, Fe, Cu (5% wt) and Ce as the active material (0.5% wt.).

Treatment with azodicarboamide of vermiculites increased its surface area and pore volume (2 for pure vermiculite and 86 $m^2/g$ for modified and from 0.016 to 0.100 $cm^3/g$). Modification with Cu, Ni, Fe and Cu slightly decreased $S_{BET}$ (74, 64, 68 and 59 $m^2/g$ respectively). The addition of cerium slightly affects the surface area.

In XRD, characteristic reflection for introduced metals were observed in diffractograms, in FTIR, the modification with azodicarboamide decrease of the band attributed to OH vibrations.

Vermiculite modified with manganese and ceria, the highest value of NO conversion reached 96% at 300 ℃, while at 350 ℃ 89%. However, high $N_2O$ concentration values were recorded in the post-reaction mixture (about 240 ppm). This is due to the fact that the $Mn^{2+}$ manganese cations are highly oxidizing[2]. At high temperatures oxidation of NO to $N_2O$ is occured, where high concentrations of $N_2O$ were visible, as compared to other catalysts.

At slightly higher temperatures (350 and 400$^{O}$C), the addition of cerium causes the nickel catalyst which is inactive in the SCR reaction (10 and 18%, in 350 and 400$^{O}$C) to achieve a conversion rate of 66% and 53%, with a low concentration of $N_2O$ at these temperatures (61 and 63 ppm).

The iron-cerium catalyst also proved to be a good catalyst in the SCR reaction. The obtained values of NO concentration are low at 350 and 400$^{O}$C and reached average values in the recorded temperature ranges of 90 and 89 ppm NO.

This work was financed by Grant AGH 11.11.210.373

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Klinik, J.; Samojeden, B.; Grzybek, T.; Suprun, W.; Papp, H.; Glaeser, R. Catalysis

# SYNTHESIS AND CATALYTIC APPLICATIONS OF ORGANOPALLADIUM CAGES WITHIN METAL ORGANIC FRAMEWORKS

**R. Greco[1], R. Adam[1], M. Mon[2], J. Ferrando-Soria[2], D. Armentano[3], E. Pardo[2], A. Leyva-Pérez[1]**

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Coordination chemistry offers endless possibilities to design unique supramolecular complexes with interesting physical and chemical properties and applications for example in catalysis, where they can even mimic the active sites of enzymes. In the last years, impressive advances have been performed in this field and it has been possible to obtain a huge variety of increasingly complex self-assembled discrete supramolecular constructs. Thus, a variety of metallacycles and metallacages with very well defined shapes and nanoscopic sites have been constructed.

Simultaneously to the development of supramolecular chemistry, a type of porous crystalline materials, so-called metal-organic frameworks (MOFs), have experienced a remarkable growth in chemistry due to its interesting host guest properties and their applications in catalysis.

Herein, we propose a unique template-directed strategy, involving the use of solid state post–synthetic methods for the step–by–step sequential synthesis of different supramolecular constructs, like metal– organic polyhedra or metal–organic polygons (MOPs). For this purpose, we first selected a highly crystalline MOF, of formula [Pd$^{II}$(NH ) ][Pd$^{II}$ (i–O)(NH ) )(NH ) ] {Ni$^{II}$ [Cu$^{II}$ (Me mpba) ] } · 52H O 34 2 36 420.5 4 2 3 23 2

**1** with large octagonal pores which are occupied by Pd$^{II}$ dimers, located in preferential positions of the 2

channels and leaving enough room to further react (**Figure 1**). Then, crystals of **1** were soaked in solutions of the selected appropriate pyridine containing ligands (**Figure 1**, **L$_1$** and **L$_2$**). Using this strategy we could unprecedently obtain MOF-driven MOPs within the pores. These uncommon structures could be synthesized due to the confined state provided by the channels of the MOF and the presence of such uncommon dinuclear oxo-bridged palladium(II) entities.

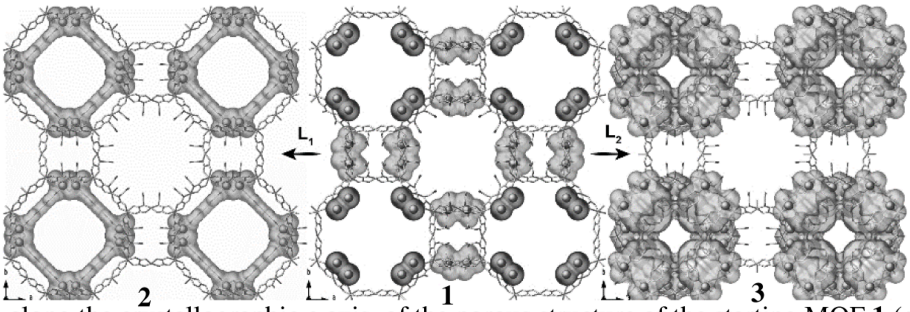

**Figure 1-** . Views, along the crystallographic c axis, of the porous structure of the starting MOF **1** (center), as well as the structures of the MOF-containing $Pd_8$ square **2** (left) and the $Pd_{24}$ cage **3** (right).

The oxidative coupling of organoboron compounds is one of the most powerful protocols for the construction of carbon – carbon bonds in synthetic chemistry, due to the availability and low toxicity of organoboranes. We have evaluated the catalytic activity of the new structures **2** and **3** in the homocoupling of 2-thienylboronic acid to afford 2,2'-bithiophene (**Figure 2**). To our delight, both catalysts **2** and **3** resulted active in the homocoupling of boronic acids, being the activity of MOF **3** superior.

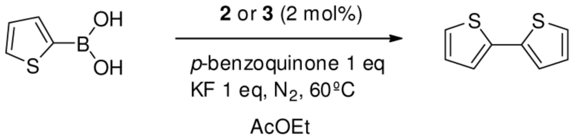

**Figure 2- 2** and **3** catalyzed homocoupling of 2-thienyl boronic acid.

**Acknowledgements**
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# SYNTHESIS OF A HOMOCHIRAL PERIODIC AROMATIC FRAMEWORKS BASED ON BINOL AND ITS APPLICATION IN ASYMMETRIC CATALYSIS

**Beatriz Villoria-del-Álamo**, **Pilar García-García, Avelino Corma**

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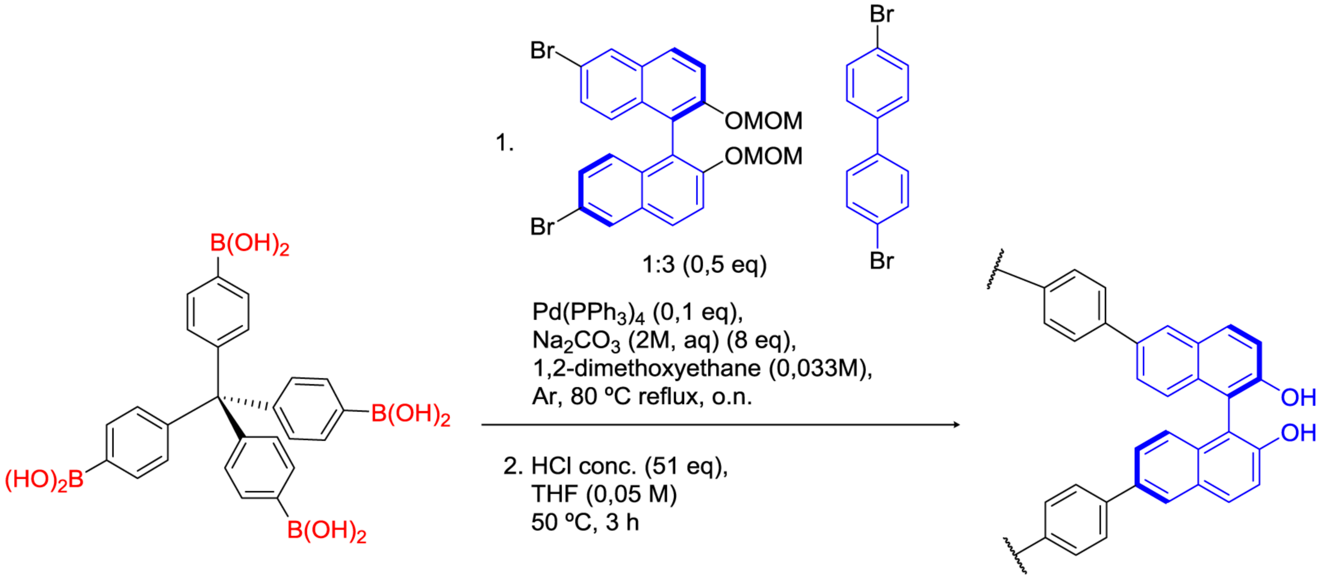
Periodic Aromatic Frameworks (PAFs) are a novel group of organic, robust, porous and stable materials whose research has increased in recent years.[1] They are based exclusively on organic aromatic rigid blocks connected together by covalent bonds. This type of solids finds applications in adsorption, gas storage, separation, catalysis and sensors devices. We report here the synthesis of the first pre-functionalised homochiral PAFs with (R)-BINOL using (methanetetrayltetra-4,1- phenylene)tetrakisboronic acid[2] through a Suzuki cross-coupling reaction.[3] This PAF was characterized by several techniques (TGA, nitrogen absorption isotherms, MAS $^{13}C$ NMR). The homochiral PAF catalyst was tested in asymmetric catalysis, in the enantioselective addition reaction of diethylzinc to aromatic aldehydes.[4]



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# MAGNETIC MOFS WITH TUNABLE ORDERING TEMPERATURES ABOVE 100 K

**Cristian Martínez-Hernández, Samia Benmansour, Carlos J. Gómez-García**

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Here we show the synthesis, structure and magnetic characterization of a family of anilato-based magnetic MOFs with tunable ordering temperatures above 100 K. These families of magnetic layered MOFs can be formulated as $[(H_3O)(phz)_3][M^{II}M^{III}(C_6O_4X_2)_3]\cdot nH_2O$ (phz = phenazine, $M^{II}$ = Mn and Fe; $M^{III}$ = Fe and Cr; X = Cl and Br; n ≈ 12) have been reduced with Li or Na to obtain 2D lattices formulated as $[M^{II}M^{III}(C_6O_4X_2)_3]^{n-}$. These reduced compounds maintain the 2D honeycomb lattices observed in the oxidized forms (Figure 1a) and show long range magnetic orderings at high temperatures thanks to the strong magnetic coupling observed between the metallic centers and the radical semiquinone form of the anilato ligands. Thus, the ordering temperatures increase from *ca*. 2.5 K in the oxidized forms of the $[Fe^{II}Fe^{III}(C_6O_4X_2)_3]^-$ lattices [1] to more than 100 K in the reduced ones (Figure 1b). In the case of the $[Mn^{II}Cr^{III}(C_6O_4Cl_2)_3]^-$ lattice, the ordering temperature increases from *ca*. 6 K to *ca*. 50 K (Figure 1c).[2]

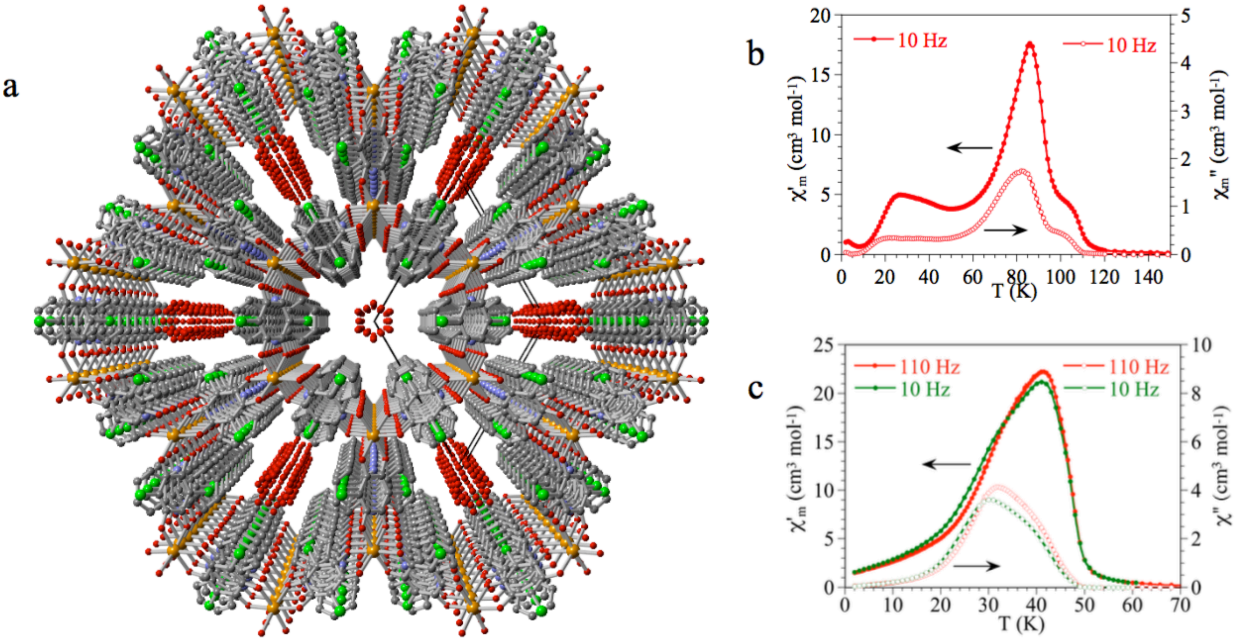

**Figure 1.** (a) 2D honeycomb lattice in the family $A[M^{II}M^{III}(C_6O_4X_2)_3]\cdot G$. (b) Magnetic properties of the reduced lattice $[Fe^{II}Fe^{III}(C_6O_4Cl_2)_3]^{n-}$. (c) Magnetic properties of the reduced lattice $[Mn^{II}Cr^{III}(C_6O_4Cl_2)_3]^{n-}$.

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# CARBON-SUPPORTED AU NANOPARTICLES: CATALYTIC ACTIVITY RULED OUT BY CARBON SUPPORT ANDREA

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**Background.** The catalytic oxidation of glycerol produces high added value chemical products [1; 2]. Gold NPs have been shown to be active, selective and stable against deactivation [3]. Particle size and shape affects the catalytic activity [4]. Complementarily, the role of the support showed to be decisive in modulating gold activity and stability [5]. Demirel-Gulen et al. investigated the liquid phase oxidation of glycerol over carbon supported gold catalysts; comparing carbon black and activate carbon, they found that the activity was higher for the first mentioned support [6]. Other studies on the specific interaction between Au and graphite reported about the change of the catalyst structure and stability of Au clusters [7]. Overall, the whole catalyst properties come from the specific properties of the support together with the synthesis approach for depositing NPs. Gold-supported carbon materials have been deeply explored, but the range of possibilities for modulating their properties still require efforts.

Here, we deposited Au NPs on three different commercial carbon supports (Vulcan-XC72R, X40S and Norit GSX) by SMAD technique for investigating the support effect on size, dispersion, catalytic activity/selectivity and catalyst stability in glycerol oxidation. In addition, in order to better clarify the influence of the preparation technique, we also prepared Au catalyst on the same supports by Sol Immobilization (SOL) technique in the presence of polyvinyl alcohol (PVA) as stabilizing agent. The morphological and structural features of each catalyst were deeply investigated disclosing the importance of the synthetic procedure on the whole material physico-chemical properties. These latter were related to the catalytic results in the selective glycerol oxidation highlighting that also the nature of the support play an important role.

**Experimental.** In SMAD, gold vapors generated by resistive heating of an alumina crucible filled with ca. 100 mg of gold (beads) were co-condensed with acetone. After, the Au- SMA solution was added to the relative suspensions containing each carbon support. Each catalyst contained 1.0 wt.% of Au. Sol method requires the preparation of an aqueous solutions of metal precursor (HAuCl4·3H2O) and PVA (1 % w/w). Then we dripped NaBH4 (0.1 M) and Au reduced immediately. Immobilization of Au NPs occurred by adding each carbon support under magnetic stirring.

A LIBRA 200FE ZEISS at 200 kV equipped with a high- angle annular dark field detector (HAADF) provided HRTEM and STEM measurements. Gold loadings were determined by ICP-OES (ICAP6300 Duo purchased from Thermo Fisher Scientific). XPS (KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber) scanned the surface composition and oxidation state of the metals.

Glycerol oxidation occurred in a glass reactor, at 50 °C and oxygen pressure of 3 atm. The catalyst was suspended in 10 ml of a glycerol solution 0.3 M and NaOH/glycerol molar ratio 4, having a glycerol/metal molar ratio of 2000. Sample was analyzed by HPLC (Alltech OA-10308, 300 mm × 7.8 mm).

**Discussion.** TEM and XPS analyses showed that the size and distribution of the AuNPs on the different supports varied according to the density of surface oxygen-containing groups.

However particle size also depends on the immobilization time, being the longer producing larger particles. Sol-derived catalysts always showed higher activity in the glycerol reaction (Figure 1).

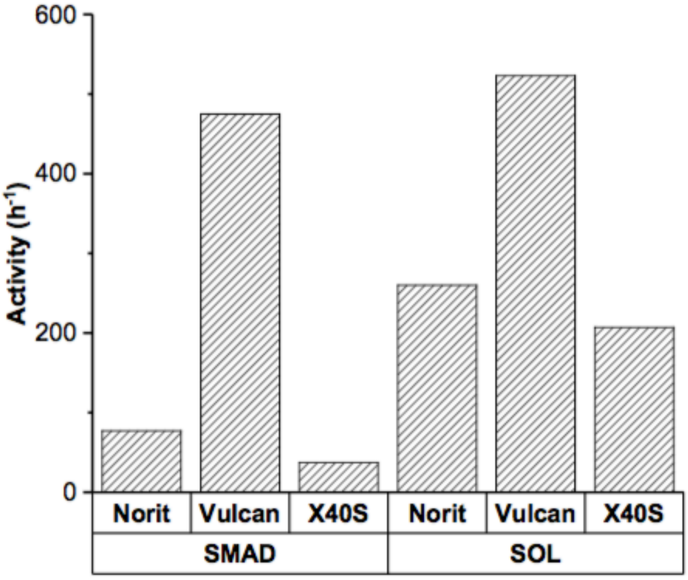

**Fig. 1** Comparison of the initial activities for i) Norit, ii) Vulcan and iii) X40S carbon by SMAD and Sol method, respectively. Reaction conditions: 10 ml 0.3 M; NaOH/GLY 4:1; GLY/Metal molar ratio 1:2000, P(O2) 3 atm, T=50 °C, $^{a}$Activity calculated at 15 min as moles converted/moles of metal · h.

**Conclusions.** We observed that the higher O-containing functionalities of the support determines a higher exposure of Au nanoparticles at the surface but also an increase of particle size due to a lower rate of immobilization on the support.

We found that the highest activity was shown by AuNPs on Vulcan, samples that showed the lowest exposure of Au but the smallest particle size. Comparing SMAD and SOL prepared samples on Vulcan, beside a very similar particle size and distribution, a different activity and also selectivity was observed. Moreover, SOL sample on Vulcan showed a pretty good stability on recycling.

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# MIXED CERIUM MOFS: THE ROLE OF THE CERIUM OXIDATION STATE (III / IV) IN ITS CATALYTIC ACTIVITY TOWARDS SYNTHESIS OF AMINES.

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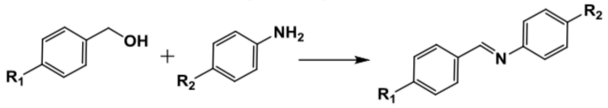
**1. Introduction –** Introduction of various metal cations in metal-organic frameworks provides an interesting strategy to tune the properties of porous materials towards practical applications. Zr-based metal-organic frameworks have a large specific surface area and pore size, which result in desirable properties for catalytic applications [1]. Furthermore, cerium is an attractive candidate for substitution of Zr into UiO-66 derivatives because of its introduction can provide redox properties in the framework [2]. This fact, along with the Zr(IV) Lewis acidity, makes this novel type of bimetallic MOFs an excellent candidate as catalyst in the direct synthesis of imines from alcohols.

**2. Experimental –** Zr(Ce)-MOF (1) and Ce-MOF (2) were synthesized by direct synthesis under solvothermal conditions in a teflon lined vessel at 120 °C for 24 h and 100 oC for 4 hours, respectively, in DMF as solvent. Zr(Ce)-MOF was prepared from $ZrCl_4$ and $CeCl_3.7H_2O$ as precursors and naphthalene- dicarboxylic acid (NDC) and 4-amino-naphthalene-dicarboxylic acid ($NDC-NH_2$) as linkers. Whereas Ce-MOF was obtained from $(NH_4)_2[Ce(NO_3)_6]$ and NDC.

**Table I.** UiO-66-catalyzed synthesis of amines.



| Entry | Cat. | $R_1$ | $R_2$ | Con.(%) (h)[(c)] | Sel.(%)[(d)] |
|---|---|---|---|---|---|
| 1 | **(1)**[a] | H | H | 84 (8) | 91 |
| 2 | **(1)**[a] | $CH_3O$ | H | 62 (8) | 62 |
| 3 | **(1)**[a] | H | Br | 9 (8) | 100 |
| 4 | **(2)**[b] | H | H | 100 (4) | 100 |
| 5 | **(2)**[b] | H | $CH_3O$ | 100 (3) | 99 |
| 6 | **(2)**[b] | H | Br | 87 (5) | 100 |

General reactions conditions: 0.12 mmol of alcohol, 0.1 mmol of amine, 150 ºC MW. (a) 6.0 mg of **(1)** and 0.5 mL of toluene. (b) 8.0 mg catalyst **(2)**, 0.15 mmol of *t*-BuOK and 0.5 mL of chlorobenzene. (c), (d) Determined by GC-MS.

**3. Results and Discussion –** XPS analysis of mixed (1)-catalyst indicates that Ce(III) is the most abundant species. PXRD patterns show typical peaks for isostructural UiO66 MOF. Both MOFs were also characterized by $^{13}$C-NMR spectroscopy.

Table I shows that (2) has better reactivity than mixed Zr(Ce) (1) in all cases. This fact is coherent with the higher activity as an oxidant of Ce(IV) than Ce(III). As can be observed, the acidity of Ce(IV) is comparable to that of Zr (IV). When amines with electron withdrawing groups at the aromatic ring are used as substrates (entries 3 and 6) the conversion obtained is lower, being significantly lower when mixed Zr(Ce) was the catalyst.

**4. Conclusions -** This work describes the construction of Ce-MOFs isostructural with UiO-66 family, which present high catalytic activity in the N-alkylation of benzyl alcohols. It was further demonstrated the Lewis' acid capacity of cerium (III) in contrast to the cerium (IV). This last one resulted in a more appropriate catalyst for this type of reaction affording higher selectivity towards imine in lower reaction times.

**5. References**

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