



6th WINTER MEETING 
Diciembre 2023

LIBRO DE RESÚMENES

15 de diciembre de 2023

*Salón de Actos del Edificio Nexus
de la Universitat Politècnica de València*



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Prólogo:

El "ITQ Winter Meeting", iniciado en el año 2018, es un encuentro nacido con el propósito de reunir una muestra del trabajo realizado en el Instituto de Tecnología Química (ITQ) a lo largo del año. La finalidad de este evento es dar difusión a las líneas y trabajos de investigación desarrollados por los distintos grupos que conforman el ITQ, así como dar la oportunidad a las nuevas generaciones de estudiantes de compartir su trabajo en formato de comunicaciones orales y pósteres, ampliando su experiencia y conocimiento.

Este proyecto está creado con el objetivo de ser también un encuentro anual entre el ITQ y el resto de la comunidad científica y universitaria, para generar un buen ambiente que sirva para compartir y discutir ideas, esperando a su vez, que pueda ser la fuente de nuevas colaboraciones, así como visibilizar los avances realizados en el instituto y en la ciencia de cara al público.

Comité organizador y coordinación: Cora Pardo Asunción, Anaïs Atalaya Córdoba, Sonia Remiro Buenamañana y Jose Luis Jordá Moret.

Comité científico ITQ (UPV-CSIC): Jose M. Serra, Antonio Chica, Cristina Martínez, A. Eduardo Palomares, Alfonso Carrillo, Marisa Marín, Marta Mon, Judit Oliver, Pascual Oña, Sonia Remiro y Jose L. Jordá.

El 6th ITQ Winter Meeting es una actividad organizada por la Comisión de Divulgación Científica del ITQ (UPV-CSIC), con financiación del Programa de Centros de Excelencia Severo Ochoa (CEX2021-001230-S)



VI WINTER MEETING

Viernes 15 diciembre 2023 – Edificio Nexus

- 08:30-09:30 *Registro y colocación de las comunicaciones en cartel en los paneles*
- 09:30-09:45 *Apertura, bienvenida del director y presentación ITQ - Jose M. Serra*
- Primera Sesión**
- 09:45-09:52 *Catálisis de reacciones orgánicas sostenibles - Antonio Leyva*
- 09:52-09:59 *Química sintética y terapéutica de productos naturales - Miguel A. González Cardenete*
- 09:59-10:06 *Conversión y almacenamiento de energías renovables y fósiles - Jose Manuel Serra*
- 10:06-10:13 *Nanomateriales para Optoelectrónica, fotónica y energía - Pablo P. Boix*
- 10:13-10:20 *Diseño molecular de catalizadores - Cristina Martínez*
- 10:20-10:27 *Fotocatálisis - Ana Primo*
- 10:27-10:34 *SINGAS - Agustín Martínez*
- 10:34-10:41 *CATREDOX - Jose Manuel López*
- 10:41-10:48 *Nanomedicina - Pablo Botella*
- 10:48-10:55 *Activación selectiva y valorización de moléculas pequeñas - Gonzalo Prieto*
- 10:55-11:02 *Fotoquímica Orgánica y Biológica - Virginie Lyria Lhiaubet*
- 11:02-11:09 *Materiales porosos para adsorción, separación y aplicaciones medioambientales - Fernando Rey*
- 11:09-12:01 *Pausa para café y posters (Fuera del Nexus)*
- Segunda Sesión**
- 12:01-12:11 *Programa de Excelencia Severo Ochoa - Hermenegildo García*
- 12:11-12:26 *Unidad administrativa - Mónica Asunción*
- 12:26-12:33 *Servicios científicos - Caracterización - Antonio Chica*
- 12:33-12:40 *Formación - Eduardo Palomares*
- 12:40-12:47 *Transferencia - Clara Fornés*
- 12:47-12:54 *Charlas divulgativas premiados 2023 - Andrés López*
- 12:54-13:01 *Charlas divulgativas premiados 2023 - Marta Mon*
- 13:01-14:01 *Actividad "Desata tu potencial"*
- 14:01-14:05 *Cierre de las comunicaciones orales*
- 14:05-15:30 *Pausa para catering, posters y coloquio (Fuera del Nexus)*
- 15:30-15:40 *Entrega de premios*
- 15:40-16:00 *Conclusiones, feedback y clausura del evento*

RESÚMENES

Stable redox electrodes for their application in proton ceramic electrochemical reactors

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Ceramic proton electrochemical cells present a promising avenue to improve hydrocarbon conversion processes through on-site hydrogen (H_2) extraction, as depicted in Figure 1. However, these cells operate in non-oxidative conditions, leading to potential coke formation. This coke formation poses a significant challenge, causing catalyst deactivation and a decline in electrode performance. To solve this problem, oxidative regeneration cycles become necessary, demanding that the electrodes remain stable under redox conditions.

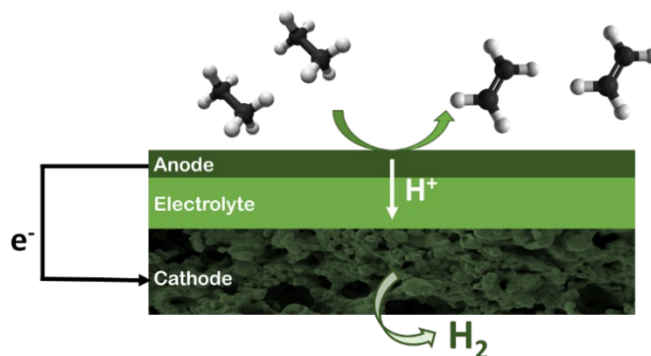


Figure 1. Intensify hydrocarbon conversion processes by in-situ H_2 extraction whit PCECs.

The principal objective of this investigation is to design and evaluate various materials as potential redox-stable electrodes for integration into proton ceramic cells. These cells enable operation under both non-oxidative H_2 removal and coke oxidation conditions. The investigated composite materials feature BZCY as the protonic phase, with doped $LaCrO_3$ and $LaMnO_3$ perovskites serving as the electronic phase.

In order to optimized the electrode performance, an alternative strategy is proposed, involving the catalytic activation of the electrode surface through the incorporation of Pt and CeO_2 nanoparticles. The research encompasses several critical aspects, including assessing chemical and structural compatibility, employing electrochemical impedance spectroscopy, evaluating stability under redox cycling conditions, and studying coke formation on the electrodes in hydrocarbon atmospheres.

The outcomes of this study underscore the significant potential of Mn and Cr perovskite-based electrodes for non-oxidative hydrocarbon upgrading and

redox-regenerative cycling. This research contributes to the advancement of clean and efficient hydrocarbon conversion technologies, offering a promising pathway for enhancing the performance and sustainability of these electrochemical systems.

Agradecimientos

The work leading to these results has received funding from Spanish Government (RTI2018-102161 grant) and has been supported by the WINNER project. This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 101007165. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation program, Hydrogen Europe and Hydrogen Europe Research.

MULTI-COMPONENT MATERIALS BASED ON MWW-TYPE ZEOLITES LAYERS AND MgAlCe HYDROTALCITES

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The development of sustainable and efficient chemical processes is one of the highest priorities in contemporary society. For this reason, using heterogeneous catalysts with the reusable capability of performing such processes in a single step could avoid the isolation of intermediates and the recovery and disposal of by-products and solvents. For this purpose, this study aims to link different components in the same structure to benefit from the advantages and physicochemical characteristics of each component and to generate new properties due to the synergy and cooperative effects established between them.

Lamellar materials are crucial to obtaining these multifunctional catalysts.[1] These materials are versatile in modifying their morphology and textural properties by altering the order and spatial arrangement of the individual sheets that form them. Likewise, their composition and reactivity can be changed by including organic or inorganic compounds on the surface and interlamellar space.[2]

Mg-Al oxides are one of the most widely used solids in catalysis. It is due to their number of basic sites, high thermal resistance, and high specific surface area. In addition, Mg-Al layered double oxides (MgAl-LDH) are usually modified by the incorporation of a third atom. This could be improving the catalytic properties, modifying the acid-base sites. [3]

In this study, different multi-component materials have been prepared from MWW-type zeolitic layers. Considering its silicoaluminate nature and using the appropriate synthesis conditions, it was possible to prepare in situ nanometric sub-domains of MgAlCe hydrotalcite-type on the surface and inside the semi-cavities and microporous channels present in the individual MWW layers, favoured by the tetrahedral units of aluminium present in the zeolitic structure.

The different materials have been characterised by Powder X-Ray Diffraction (PXRD), Chemical Analysis (ICP and EA), Solid State NMR, thermogravimetry and electronic microscopy.

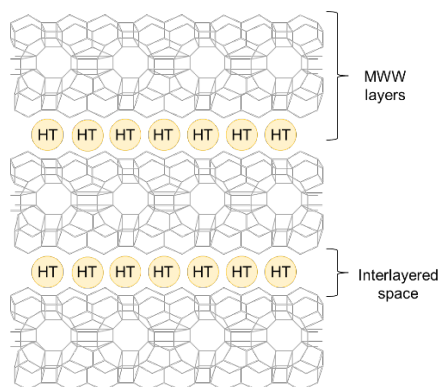


Figure 1. Scheme of the structure of materials.

Agradecimientos

The authors acknowledge support from Grant PID2020-112590GB-C21 and from Severo Ochoa excellence program CEX2021-001230-S, both funded by MCIN/AEI/10.13039/501100011033. This study forms part of the Advanced Materials program and was supported by MICIN with funding from European Union Next Generation (PRTR-C17.11) and by Generalitat Valenciana (MFA/2022/003). C. E. acknowledges financial support from the Spanish Government by FPI predoctoral scholarship number PRE2019-089547 under project SEV-2016-0683-19-3.

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PROMOTING GADOLLINIUM-DOPED CERIA VIA EXSOLUTION OF METALLIC ALLOYED NANOPARTICLES

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Exsolution is lately emerging as a promising alternative to other classic functionalization methods, such as impregnation. This method is based on the promotion of metallic nanoparticles to the surface of a material (metallic oxides such as perovskites, for instance) under reducing conditions and, typically, medium-high temperatures (600-1000 °C). This way, metallic atoms migrate from the structure of the material itself into the surface, where they nucleate and grow, until the formation of "socketed", partially embedded nanoparticles [1]. This anchoring of the metallic nanoparticles to the oxide backbone brings several advantages, like increased resistance to high temperature issues (sintering of the nanoparticles) or to coke formation [2]. Besides, exsolution provides better control over distribution and size of the nanoparticles and the possibility of obtaining alloyed metallic nanoparticles. In this case, doping CeO₂ based materials with different metallic atoms led to the exsolution of bimetallic nanoparticles on the surface, which appears to be an interesting strategy to improve the catalytic performance [3].

In this work, Ce_{0.8}Gd_{0.2}O_{2-δ} was doped with different metallic atoms (Ru, Rh or both) in order to exsolve alloyed metallic RuRh nanoparticles. For this purpose, (Ce_{0.8}Gd_{0.2})_{0.94}M_{0.06}O_{2-δ} was exsolved at 700 °C for 4 hours under 5% H₂/Ar flow. This treatment resulted in well dispersed, between 2-4 nm exsolved metallic nanoparticles of Ru, Rh for single metal doped cerias. In the case of (Ce_{0.8}Gd_{0.2})_{0.94}Ru_{0.03}Rh_{0.03}O_{2-δ}, we proved alloyed Ru-Rh nanoparticle exsolution

via TEM characterization for the first time in these materials. Each material was tested as catalyst in methanation reaction to prove the enhanced catalytic activity and high selectivity with exsolved nanoparticles. These tests also proved the stability of these nanoparticles under reaction conditions, showing no loss in number or changes in sizes, according to the *post-mortem* SEM characterization performed. Our results show a promising method to effectively functionalize the surface of ceria oxides with highly dispersed, stable nanoparticles and the possibility of easily obtaining metallic alloys.

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Optimization of a stacked catalytic membrane reactor using computational fluid dynamics modelling

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The use of catalytic membrane reactors, which combines chemical reactions with membrane separation technology, offers an alternative for enhancing the fuel conversion of equilibrium-limited reactions, leading to process intensification [1-2]. The electrochemical membrane in the reactor serves as a selective barrier, allowing certain species to pass through while retaining others. This selective permeability can enhance the efficiency of the reaction by removing products as they are formed, shifting the equilibrium. This technology has already been successfully applied using proton-conducting cells in various catalytic systems such as methane reforming [3-4] ammonia cracking [4-5], or direct conversion of methane to aromatics [6].

When designing stacks with a larger number of stages operating in parallel (see Figure 1), it is essential to ensure that the fuel flow is uniform at each stage. Otherwise, the conversion in some stages/channels would be different than others, and H₂ extraction would not be homogeneous along all stages, leading to inefficiencies from the kinetic and thermal point of view. At this point, some questions arise regarding the flow nonuniformity, such as the recommended particle/pellet size within the catalyst bed, the maximum flow rate that the reactor can handle, or the number of stages that can be assembled in parallel. Utilizing computational fluid dynamics (CFD) simulations, it is possible to study in-depth this kind of systems, providing valuable information and possible solutions to these inquiries.

In this work, multiple CFD simulations are performed by varying the number of stages, catalyst bed particle size, and feed flow rate. The fuel velocity distribution obtained from CFD allows the quantification of the flow polarization among the

stages for a given conditions. Therefore, some geometry modifications are proposed based on the above-mentioned parameters, in order to mitigate flow polarization, aiming to get a uniform velocity among the stages and channels. Finally, some guidelines are created to aid in the decision-making step for selecting the appropriate geometry and operating parameters, which can also be extrapolated to larger scale systems.

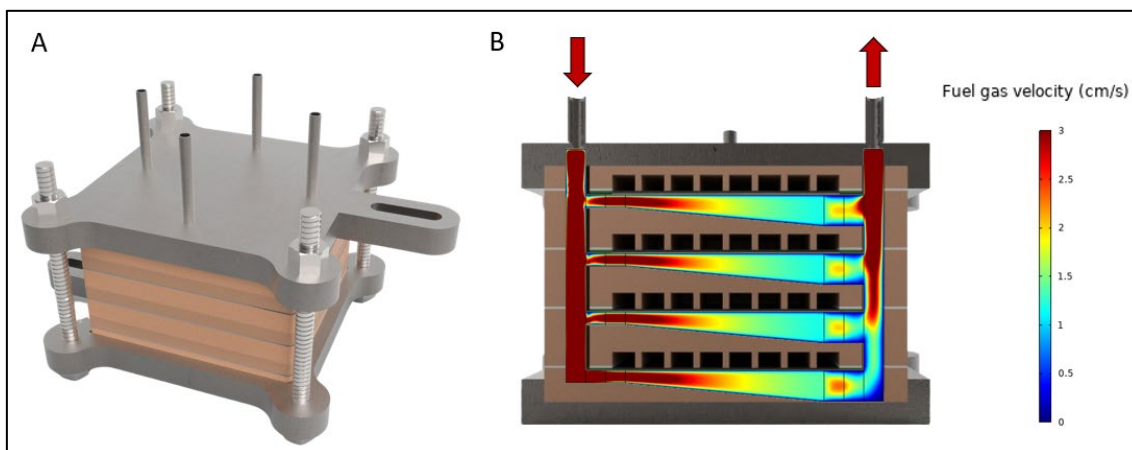


Figure 1: A) Depiction of a 4-cell catalytic membrane reactor stack. B) Cross-section view with flow gas velocity distribution.

Agradecimientos

This work was supported by the Spanish government (FPU20/06919). Total Energies OneTech is thanked for sponsoring this project.

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**EVALUATING THE EFFECTS OF A-SITE DOPING IN SUB-STOICHIOMETRIC
 $\text{Sr}_{1.9}\text{Fe}_{1.3}\text{Ni}_{0.2}\text{Mo}_{0.5}\text{O}_{6-\delta}$ DOUBLE PEROVSKITE ELECTRODE
NANOPARTICLE EXSOLUTION**

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In the last few decades, there has been a progressive change to sustainable energies, due to the need of an energetic system independent from fossil fuels. To overcome the environmental problematic their use implies and due to the seasonal nature of renewable energies, it is imperative to develop more efficient energy storage and conversion technologies. Among the latter, fuel cells have emerged as one of the main lines of research, especially Solid Oxide Fuel Cells (SOFC). These devices work under high temperatures (up to 800°C) and have great advantages over other types of cells, including higher efficiencies.

In SOFCs a redox reaction takes place in the electrodes where a catalyst, usually Ni-based, is necessary. Perovskites proved to be great materials when employed as electrodes and can be functionalized with nanocatalysts by different methods. Exsolution is one of them, which is in its early stages of development. During this process, metallic cations migrate from the bulk of the metal oxide under reducing conditions and medium-high temperatures, nucleating and growing until the formation of partially embedded metallic nanoparticles (NP) over the surface. Exsolution brings several advantages over other more traditional functionalization methods, like impregnation. It can prevent high-temperature issues, i.e., nanoparticle sintering, and provides a better control over size and dispersion of the nanoparticles, among others [1].

In this context, double perovskites from the $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ family are widely studied as electrodes for SOFC [2], and its structure can be easily modified to improve the exsolution process. For example, A-site deficiency is generally employed to enhance the amount of exsolved nanoparticles [3]. In this work, $\text{Sr}_{1.9}\text{Fe}_{1.3}\text{Ni}_{0.2}\text{Mo}_{0.5}\text{O}_{6-\delta}$ double perovskite is studied, but NiO is formed during the synthesis, which detrimentally affects the NP exsolution. To fix this, A-site doping

with La, Gd, Pr, Nd was performed, aiming at a crystal phase stabilization. Our results proved a decrease in the NiO impurities (La and Pr), and an improvement in electrical conductivity, in all cases. In summary, this work provided compositional guidelines for an optimized synthesis of A-site deficient double perovskites. This can lead to a better control of NP exsolution, besides an improvement of electrochemical properties, heading to an enhancement of the efficiency of SOFCs.

Agradecimientos

The development of this work is supported by the Master's Thesis Scholarship from the "Sociedad Española de Catálisis" (SECAT).

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Unveiling the Potential of 2D-Co MOFs as Cost-Effective and Efficient Catalysts for Oxygen Evolution Reaction in PEMFC

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Hydrogen-based fuel cells are renowned for their environmental friendliness, producing only water as a by-product and emitting zero carbon dioxide. However, the primary challenge lies in the catalysts used for the essential chemical reactions at the anode and cathode. Platinum serves as the main catalyst due to its efficacy in accelerating the electrochemical reactions. Nevertheless, its high cost and susceptibility to be poisoned by other gases such as carbon monoxide and sulfur-derived compounds mixed with hydrogen necessitate alternative solutions. In this sense, the development of active and selective non-noble metal-based catalysts is explored. [1]

The objective is focused on first-row transition metals, which are known for their activity, robustness and cost-effectiveness. Cobalt metal organic frameworks hold promise as electrocatalysts due to their favorable properties and are good candidates to replace platinum. Herein, we study a 2D-Co-MOF with excellent properties in the oxygen evolution reaction (OER) as electrocatalyst used in a PEMFC's anode. [2] Some of the explored variables are ink composition, hot pressing MEA preparation and the influence of metal support.

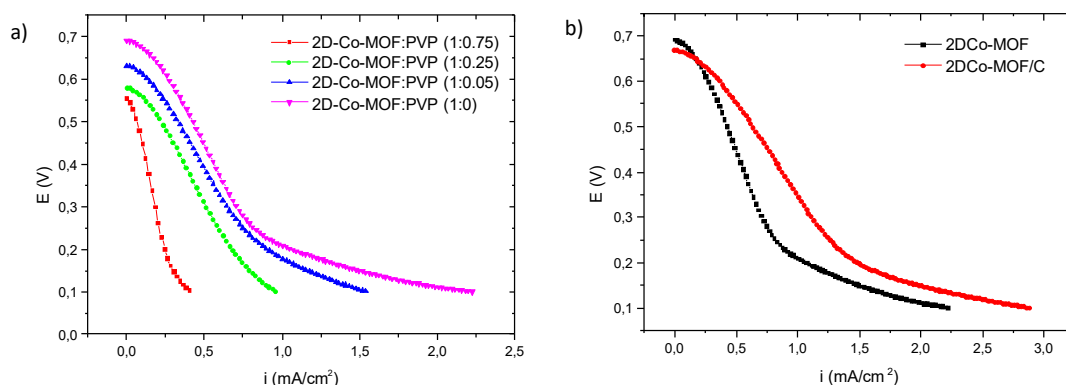


Figure 1. Polarization curves of (a) 2D-Co-MOF electrocatalyst and different PVP binder ratios (b) 2D-Co-MOF and 2D-Co-MOF/C

ACKNOWLEDGMENTS

J.L. Río-Rodríguez thanks the Ministry of Universities for his predoctoral contract FPU21/2562.

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MOF-Triggered Synthesis of Subnanometer Ag₀² Clusters and Fe³⁺ Single Atoms: Heterogenization Led to Efficient and Synergetic One-pot Catalytic Reactions

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The direct catalyst conversion of alkenes to alkynes is an unmet synthetic pathway with high potential impact in organic synthesis.^[1] Alkynes are pluripotential building blocks for organic synthesis, which engage in a multitude of reactions such as hydrogenation, hydroaddition, cross-coupling, metathesis and pericyclic reactions. However, alkynes are generally expensive and difficult to implement in kilogram studies since their synthesis often relies on highly energetic intermediates. In this contribution we will show how the synthesis of different metal species in well-defined solid catalyst has allowed to carry out the challenging direct conversion of styrenes to phenylacetylenes in one pot.^[2]

The solid Fe³⁺Ag₀²@MOF is capable of catalyzing the oxidative cross-coupling of styrenes with phenyl sulfone, to give vinyl sulfones in yields up to >99%. Vinyl sulfones can be transformed, in situ, to the corresponding phenylacetylene products in high yields, after filtration of the catalyst, which can be reused.

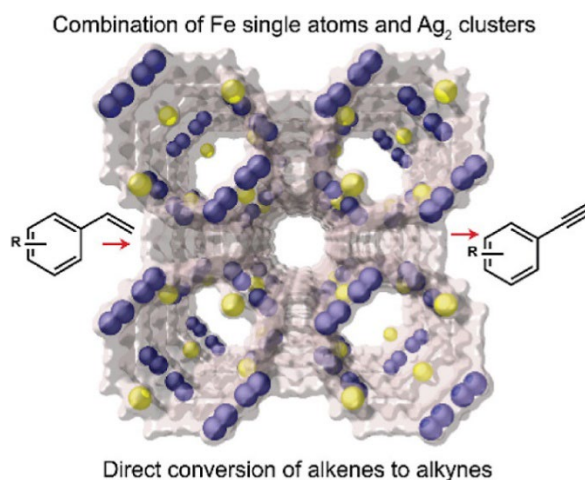


Figure 1: Reaction scheme for the formation of alkynes from alkenes.

Acknowledgments

Y.Z. thanks to the China Scholarship Council (CSC No: 202009350009) for a Ph.D.Fellowship. C.B. thanks ITQ for a contract. M.M. and J.O.-M. acknowledge MICIIN from a contract under the Juan de la Cierva program (FJC2019-040523-I, and IJC2018-036514-I, respectively). Thanks to MICINN (Spain, Project TED2021-130465B-I00).

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Generation of new lamellar phases and order alteration through soft exfoliation processes of MWW-type zeolites

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Layered zeolites have traditionally been perceived as covalently bonded frameworks that extend across two dimensions. Simultaneously, the growth of crystals is confined in the third direction. The connectivity between these zeolite layers is achieved through hydrogen bonding, primarily involving silanol groups located on the surface of each layer, and potentially ionic or hydrogen bonding interactions with organic template molecules that are encased within the interlayer spaces.^[1]

A 2-D layered zeolite precursor can be transformed to a 3-D zeolite (when the layers condense after removing the organic molecules present in the structure by calcination) or to a 2-D zeolite by the delamination or exfoliation of the individual zeolitic layers.

The process of delaminating layered zeolite precursors results in the formation of zeolites with a distinct advantage: it enables the entry of bulky molecules to access the catalytically active sites on the zeolite surface. Typically, these sites are limited to small molecules due to their location within microporous frameworks.^[2]

In this work, we have found a procedure to transform the structure of the MCM-22(P) into a new layered zeolitic material, being also observed a partial disorder between MWW layers. That procedure consists of mixing the zeolite layered precursor with a surfactant like tetrabutylammonium fluoride and a metallic salt like zinc nitrate and applying a suitable temperature.

Later, the new material has been characterized using various techniques such as X-ray powder diffraction, nuclear magnetic resonance and elemental analysis.

The structural modifications has been observed with transmission electron microscopy.

Acknowledgments

The authors are grateful for financial support for Spanish Ministry (project PID2020-112590GB-C21). J. Torr o has been partially supported by the Spanish Government by FPI pre-doctoral scholarship number PRE2021-098576.

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FUNCTIONALIZATION OF POLYETHYLENE USING HYDROLYTICALLY-STABLE ESTER GROUPS

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Polyethylene (PE) is the longest linear alkane known, with an estimated annual production of 100 million tonnes, which accounts for 34% of the total plastics market. This extremely cheap and very long alkane is used on a daily basis in bags, caps, etc. However, its disposal has created a significant environmental problem, due in large part to the lack of upcycling strategies.[1] We show here that low-density (LD) and high-density polyethylene (HDPE), recycled or not, incorporates up to 7 wt% of ester groups after reacting either with ethyl diazoacetate (EDA) under catalytic and solvent free-reaction conditions,[2] or with maleic anhydride (MA) and acrylates (AC) under catalytic radical conditions (Figure 1). The resulting upcycled polyethylene esters are hydrolytically stable at extreme pH (0–14) and can be further transformed into carboxylic acids, carboxylates, other esters and amides.[3] In this regard, three necessary advances towards the applicability objectives are made: scaling-up, high ester functionalization (up to a 7 wt% compared to just 1 wt% before) and functionality of the upcycled material (hydrolytically stable).

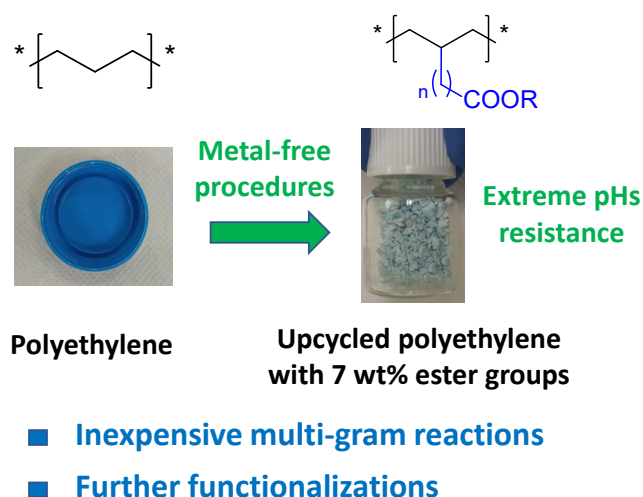


Figure 1. Current polyethylene (LDPE and HDPE) and polypropylene (PP) disposal.

Agradecimientos

Financial support by the projects PID2020-115100GB-I00 and TED2021-130465B-I00 (funded by Spanish MCIINN, MCIN/AEI/10.13039/501100011033MCIIN) is acknowledged. The work has also been funded by Generalitat Valenciana, Grupos Emergentes (GV/2021/138). AIMPLAS and ITQ authors thank Agencia Valenciana d'Innovació (AVI) and the European Union the founding of the project INNEST/2022/18. J. O.-M. acknowledges the Juan de la Cierva program for the concession of a contract (IJC2018-036514-I). S. H.-A, C. B. and P. M.-V. thank ITQ, UPV-CSIC for the concession of a contract (FPI-2022-S2-42040 and PAID 01-20, respectively).

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Hydroformylation reaction of 1-alkenes using heterogeneous Ru catalyst

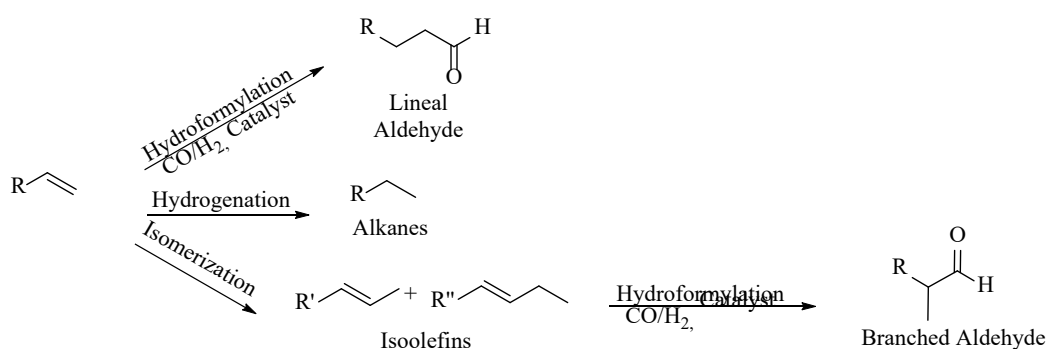
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Hydroformylation of linear 1-olefins with syngas is one of the most important C–C coupling reactions used on an industrial scale to manufacture high value linear aldehydes. These compounds are important chemicals (as perfumes and flavouring agents) or as intermediates to produce linear carboxylic acids, amines, or alcohols (used in the manufacture of detergents, plasticizers, and so on). [1]

In the hydroformylation reaction towards linear aldehydes, different by-products such as isoolefins, branched aldehydes as well as alkanes are formed and its proportion is dependent of the nature of the catalyst as well as on reaction conditions. (Scheme 1).



Scheme 1. Hydroformylation reaction

Traditionally the reaction has been mainly performed using homogeneous catalysis based on rhodium (Rh) [2], however in the last years the develop of heterogeneous catalysts based on the cheapest and abundant Ru has been of increased attention. In this work, we present an heterogeneous Ru based catalyst consisting of Ruthenium nanoparticles with a core-shell structure formed by a core of metallic ruthenium and a shell of ruthenium carbide that have been

synthesized by a mild and easy hydrothermal treatment starting from RuO₂ and glucose. [3] Taking as reaction model the hydroformylation of 1-hexene, high regioselectivity and remarkable activity, have been obtained operating at 40 bar, 100 °C, and CO/H₂ ratio 1:1. Moreover, the effect of addition of promoters such as K salts in the reaction media on the regioselectivity has been studied. The applicability of the catalyst has been extended to other linear 1-olefins with good success. Finally, a one-pot cascade reaction to obtain secondary amines has been designed starting from 1-olefins, syngas and amines. These results open an opportunity for heterogeneous Ru catalysts.

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Enhancing Redox Properties of Solid-State Materials through Low-Temperature Microwave Irradiation

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Hoy en día, el hidrógeno se utiliza como vector energético para ahorrar el exceso de energía renovable. Las técnicas más utilizadas para generar hidrógeno son los bucles termoquímicos, los electrolizadores y el reformado de hidrocarburos. Sin embargo, todas estas técnicas presentan varios inconvenientes, a saber, las altas temperaturas necesarias, el uso de maquinaria sofisticada y los largos tiempos de operación requeridos para la producción de hidrógeno. Recientemente, se ha informado de la posibilidad de generar hidrógeno verde utilizando energía eléctrica, como la radiación de microondas. Este proceso utiliza óxidos metálicos como catalizadores, por ejemplo, CeO_2 , y se produce en un reactor a temperaturas inferiores a 250 °C en menos de cinco minutos.

El mecanismo de producción de hidrógeno se produce en dos pasos. En primer lugar, el material es irradiado con un campo electromagnético de microondas, produciéndose la reducción del material, liberándose oxígeno. Esta radiación es capaz de estabilizar las vacantes de oxígeno en la estructura de la fluorita a temperaturas más bajas que los procesos convencionales, como es el caso de la termosolar (>1000 °C). Cuando se elimina la radiación, en presencia de agua, el material divide la molécula de H_2O , liberando así una corriente de hidrógeno molecular y llenando sus vacantes de oxígeno. Un ejemplo de este proceso se observa en el material $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$.¹

La liberación de oxígeno va acompañada de un aumento de la conductividad eléctrica del material. Además, se ha observado que puede deducirse un comportamiento diferente de la conductividad en función de la potencia de irradiación de microondas. Si la potencia de irradiación de microondas es inferior a la energía de activación (P_{TH}), la conductividad del material se comporta de forma similar al proceso de calentamiento convencional. En

cambio, para una potencia de radiación de microondas superior a la P_{TH} , el material experimenta un repentino aumento de la conductividad.² Este aumento se atribuye principalmente a un incremento de la conductividad electrónica. La conductividad iónica puede ajustarse dopando la red de ceria con cationes aliovalentes. En el caso concreto de la ceria dopada con lantánidos trivalentes, la conductividad iónica es predominante en todo el intervalo de temperaturas. Esto depende del parámetro de red, cuando este valor es próximo al de la ceria pura, existe una menor energía de enlace entre las vacantes de oxígeno y los dopantes trivalentes, dando lugar a una baja energía de migración que facilita el movimiento de los iones oxígeno a través de la red iónica. En este trabajo, hemos sintetizado y caracterizado un conjunto de ceria dopada con lantánidos, por ejemplo, $Ce_{0.9}M_{0.1}O_{2-\delta}$ ($M = La, Y, Yb, Sm, Nd, Er, y Gd$), con el fin de estudiar cómo el campo electromagnético interactúa con el material, dando lugar a la reducción de estos. Para ello, se han utilizado técnicas ópticas y medidas dieléctricas para monitorizar el proceso en cada paso. Por último, con el fin de aumentar la cantidad de hidrógeno producido, se ha estudiado en cada uno de ellos el proceso de water splitting asistido por microondas.

Agradecimientos

Apoyo financiero del MICINN (PRE2019-090959)

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RHODIUM SINGLE-ATOM CATALYST DESIGN THROUGH OXIDE SUPPORT MODULATION FOR A SELECTIVE GAS-PHASE ETHYLENE HYDROFORMYLATION

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The selective, gas-phase hydroformylation (HF) of light (C_{2-4}) olefins remains a long-lasting challenge in the realm of heterogeneous catalysis. This process has been demonstrated with excellent selectivities on Co or Rh molecular catalysts in solution^[1], or dissolved in supported ionic liquids (SILP). In this regard, several research efforts have been devoted over the years to the design of solid HF catalysts, although all-solid catalysts have hitherto shown lower activity and particularly poorer selectivity compared to their homogeneous counterparts, primarily owing to the promotion of undesired olefin hydrogenation side-reaction. Single Atom Catalysts (SACs) have recently attracted much scientific interest as a way to bridge the gap between the realms of homogeneous and heterogeneous catalysis^[2]. Herein, we address metal oxide support effects in Rh-SACs for ethylene ($C_2^=$) gas-phase HF and present a Rh_1/SnO_2 SAC which enables an extraordinary performance so far exclusive for molecular catalysts.

A series of Rh_1/MO_2 catalysts with a surface metal content of $1.0 Rh_{atom} nm^{-2}$, $M=Ce, Zr$ and Sn has been synthesized via impregnation and subsequent oxidative metal redispersion and atom trapping^[3] at 1073 K in air. A polynuclear catalyst Rh_n/SiO_2 ($0.4 Rh_{atom} nm^{-2}$) has been synthesized via impregnation and calcination at 823 K. The catalysts have been characterized via XRD, HAADF-STEM and *in situ/operando* XAS, CO-FTIR and Raman spectroscopies. HF tests were performed at 20 bar ($CO:H_2: Ethylene$ 1:1:1) in the temperature range of 383-503 K.

HAADF-STEM and XAS in combination with DFT-derived structural models have demonstrated the atomic dispersion of Rh species on all the oxide supports except for SiO_2 (example for Rh_1/ZrO_2 in Figure 1.a-c). Gas phase $C_2^=$ HF tests revealed poor activities ($TOF < 4 h^{-1}$) and reduced HF selectivities ($< 70 mol\%$) for Rh species when supported on CeO_2, ZrO_2 and SiO_2 , which is in good accordance

with previously reported performances for solid HF catalysts. In marked contrast, Rh_1/SnO_2 displayed a TOF of 225 h^{-1} and with a HF selectivity value over 95 %, which constitute record values for all-solid catalysts and are comparable to those so far only achieved with homogeneous catalysts (see Figure 1.d). Further *in situ* spectroscopic investigations and DFT calculations related the unique performance of Rh_1/SnO_2 to the energetically facile formation of oxygen vacancies on the surface of SnO_2 , which enable the formation of Rh sites that resemble those in benchmark catalysts in solution.

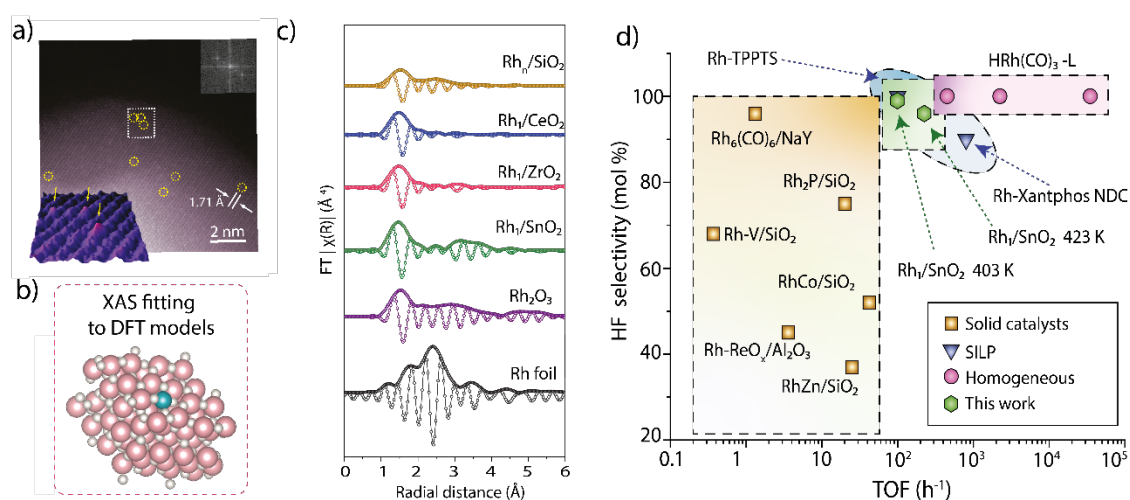


Figure 1. AC-HAADF-STEM micrograph (a) and DFT-optimized model for the best fitting with the experimental EXAFS data (b) for the as-synthesized catalyst Rh_1/ZrO_2 . (c) Fourier Transform of the k^3 -weighted EXAFS function for the as-prepared Rh/MO_2 catalysts. (d) Comparison of the catalytic performance of the Rh_1/SnO_2 catalyst (this work) with state-of-the-art solid and molecular ethylene HF catalysts.

The results highlight that modulation of support effects on solid SACs unlocks catalytic performances so far only within reach for molecular complexes in solution. The results may pave the road to a long sought-after, gas-phase, fully selective light olefin hydroformylation process, of significance as direct functionalization and reactive separation.

Acknowledgements:

ERC-CoG-864195, FPU17/04701 & ALBA (CLAESSBL22 Exp 2020024197, IH-2021085234)

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DESHIDRATACIÓN SELECTIVA DE XILOSA CATALIZADA POR ÓXIDOS METÁLICOS MIXTOS

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En la actualidad, la creciente demanda mundial de energía y la disminución de los recursos fósiles, junto con las regulaciones ambientales, impulsan la necesidad de adoptar procesos sostenibles. La biomasa lignocelulósica se perfila como una fuente renovable crucial para la producción de energía y productos químicos. En este contexto, el furfural, derivado de la despolimerización de la fracción hemicelulósica, destaca por su versatilidad en diversas aplicaciones [1]. A pesar de los desafíos inherentes al proceso industrial, como el uso de catalizadores corrosivos, se requieren innovaciones tecnológicas para avanzar hacia una industria química basada en bio-compuestos furánicos [2]. Estas mejoras no solo superarán las limitaciones actuales, sino que también fomentarán la sostenibilidad en la producción energética y química. En el ITQ (UPV-CSIC), se han desarrollado óxidos metálicos mixtos con propiedades texturales específicas y funciones ácidas, ideales para procesos en medio acuoso. Este estudio se centra en óxidos metálicos y mixtos basados en W y Nb como catalizadores para la deshidratación de xilosa a furfural, comparando su rendimiento con catalizadores de referencia, ácido sulfúrico y zeolita H-USY.

Procedimiento experimental

Los óxidos metálicos fueron preparados comparativamente mediante coprecipitación y síntesis hidrotermal, partiendo de precursores metálicos. Se caracterizaron utilizando ICP, XRD, isothermas de adsorción de N₂, HR-TEM, SEM-EDX, FT-IR y TPD-NH₃, y se calcinaron a 450-550°C antes de los ensayos catalíticos. Estos se realizaron en un reactor autoclave con agitador magnético, control de presión y temperatura, y válvulas para inyección/extracción de muestras. Se introdujo 4g de xilosa (al 10% en relación con el disolvente) con el catalizador cerrando herméticamente el reactor. La deshidratación se realizó a 160°C durante 3 horas. Tras enfriar, se filtraron los líquidos y se analizaron por HPLC

(Agilent 1200 con detector RI y columna Bio-Rad Aminex HPX-87H, fase móvil H₂SO₄ 5 mM a 60°C).

Resultados y discusión

Se prepararon distintos óxidos metálicos simples y mixtos basados en W y/o Nb (y también con otros metales); y se ensayaron en la deshidratación catalítica selectiva de xilosa diferentes óxidos metálicos, comparando su actividad catalítica con catalizadores de referencia tanto homogéneos (<5% p/p H₂SO₄ en agua) como heterogéneos (zeolita H- USY). Como puede observarse en la **Figura 1**, la deshidratación de xilosa ocurre rápidamente en todos los casos dando lugar a la formación de furfural y productos no deseados (resinas) si los sitios activos poseen menor o mayor acidez (**Fig. 1A**). De entre todos los catalizadores ensayados, los óxidos mixtos de W-Nb, con una adecuada combinación de sitios ácidos de Brönsted y Lewis, ofrecieron muy buenos resultados en términos de conversión del azúcar (≈95%) y selectividad al furfural (>36%), valores superiores a los obtenidos con óxidos metálicos simples, comparables a los de zeolita comercial H-USY y cercanos a los alcanzados con ácido sulfúrico diluido (cat. industrial) en las mismas condiciones (**Fig. 1B**). Además, se ha comprobado que el catalizador WNb-O es estable y activo para la producción de furfural incluso después de varios re-usos. Estos resultados son muy promisorios y actualmente se está optimizando la composición del óxido mixto de WNb-O para maximizar el rendimiento a furfural. En definitiva, es posible llevar a cabo la deshidratación selectiva de xilosa a furfural con catalizadores basados en óxidos mixtos de W y Nb, con adecuada combinación de sitios ácidos B/L y elevada estabilidad en condiciones de reacción.

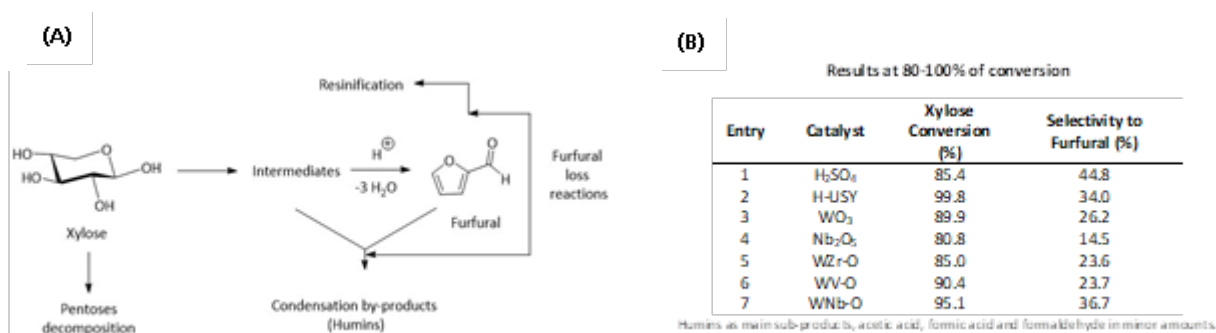


Fig.1. A)Reacción genérica para la síntesis de furfural mediante hidrólisis/deshidratación de xilosa; B)Resultados catalíticos con una conversión del 80-100%.

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Agradecimientos

Los autores agradecen el apoyo financiero del Gobierno español (PID2021-125897-B-I00) y de la Comisión Europea, Programa H2020 (Proyecto HIGFLY: este proyecto ha recibido financiación del programa de investigación e innovación Horizonte 2020 de la Unión Europea bajo el acuerdo de subvención N°101006618).

MXenes as heterogeneous catalysts. Computational insight into the regioselective anti-Markonikov hydroamination of terminal alkynes.

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Two-dimensional metal carbides (MXenes) are a group of recently discovered materials, which have attracted growing interest over the last years due to their 2D morphology and the large possibilities in chemical composition, which might allow a vast applicability in heterogeneous catalysis, among other fields.

We report that Ti_3C_2 Mxenes, synthesized by exfoliation of Ti_3AlC_2 with a NH_4F/HCl mixture, exhibit catalytic activity for hydroamination of terminal alkynes, being very selective to the anti-Markonikov product, both in the case of aliphatic amines as well as in the less reactive aromatic amines. According to XPS analysis, the Ti_3C_2 surface is functionalized by oxygen and fluorine groups, accompanied by both vacancies and defects that confer this material unique Lewis-acid catalytic properties for this reaction [1].

These unique structural properties have been modelled computationally, by means of quantum chemical DFT calculations at the B3LYP/Def2SVPD [2,3] level of theory. After modelling a 35-atom cluster of the described Mxene, a full reaction coordinate analysis has been carried out in order to determine the underlying reaction mechanism, and to explain the specific regioselectivity that has been described experimentally.

Three transition states have been characterized for this mechanism, with their respective energies:

- Cycloaddition of the alkyne on the catalyst.
- 1st proton transfer on the product.
- 2nd proton transfer on the product.

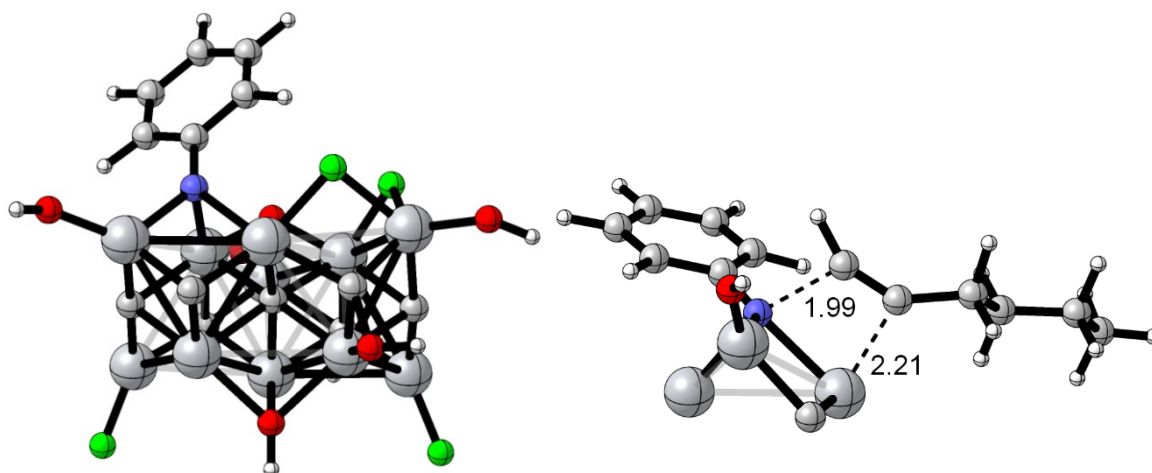


Figure 1: Representation of the proposed catalyst cluster (left) and the first transition state(right) of the anti-Markonikov hydroamination reaction.

Acknowledgements

We thank ASIC-UPV and SGAI-CSIC for the use of computational facilities. We also thank MICIN for Severo Ochoa Excellence research grant, and BASF for PhD sponsorship.

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One pot glycerol valorization of glycerol into acrylic acid: a catalytic and spectroscopic study

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Introduction.

Multifunctional materials based on Nb/V-doped hexagonal tungsten bronzes (HTB) have demonstrated to be outstanding catalysts in the glycerol dehydration to acrolein [1]. Additionally, molybdenum based mixed oxides presenting the so-called M1 phase showed interesting properties in the partial oxidation of propane [2] and acrolein [3] to acrylic acid. Therefore, the aim of this work is to study the effect of using a single or double bed configuration by combining these two families of catalysts in order to optimize the selectivity to acrylic acid in a one pot aerobic transformation directly from glycerol.

Experimental/methodology.

Nb/V-doped HTB (h - $W_{0.71}Nb_{0.29}O_3$ and h - $W_{0.8}V_{0.2}O_3$) and M1 (MoVO, MoVTeO and MoVTeNbO) catalysts have been prepared hydrothermally at 175°C/72h and finally heat-treated afterwards at 550 (tungsten bronzes), 400 (MoVO) or 600°C (MoVTeNbO) for 2h under N_2 stream. The physicochemical characterization of these oxides includes: XRD, NH_3 -TPD, N_2 -adsorption, Raman and XPS spectroscopies. *In situ* IR studies of adsorbed intermediates have been also carried out over selected catalysts. In addition, the catalytic tests were carried out in a fixed-bed reactor (alternating one or two subsequent catalytic beds) at 320°C and ambient pressure, with products being analyzed by both liquid and gas chromatography [3].

Results and discussion.

Characterization results indicate that both Nb^{5+} and V^{5+}/V^{4+} enter the HTB structure through isomorphic substitution of the Me^{n+} cations for lattice W^{5+} (**Fig. 1A**), while M1 oxides displayed differences in the XRD peaks, related to dissimilar shape of the crystals (**Fig. 1A**). However, regarding the catalytic results, for a single bed configuration, modified hexagonal tungsten bronzes showed a selectivity to acrolein (h - $W_{0.71}Nb_{0.29}O_3$) and acrylic acid (h - $W_{0.8}V_{0.2}O_3$) notoriously higher than M1 catalysts (**Fig. 1B**). Nevertheless, by using a double bed configuration consisting of a first acidic bed (h - $W_{0.71}Nb_{0.29}O_3$) followed by an oxidizing bed (M1-phase catalysts), excellent catalytic performance can be achieved by modulating the second bed (**Fig. 1C**), with tetrametallic M1-MoVTeNb oxide presenting the best results (yield to acrylic acid up to 65%). The

nature of active sites is also discussed by considering the *in situ* IR studies of adsorbed acrolein.

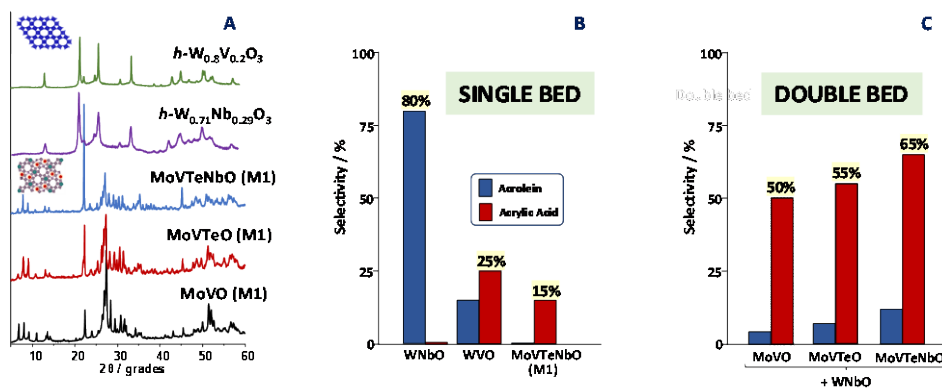


Figure 1. XRD patterns (A) of both Nb/V doped-Hexagonal Tungsten Bronze and M1-MoV(Te,Nb)O catalysts, and selectivity to acrolein/acrylic acid at 100% glycerol conversion of selected W- and Mo-based bronze catalysts in single (B) and combined bed (C) configurations.

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3D printing for the manufacturing and customization of electrochemical cells

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Electrochemical cells have significant potential in different fields such as batteries, electrolysis, fuel cells or sensors. Most of them are related to the transformation and storage of renewable energy. One of the most remarkable technological developments during the last decades has been the invention and commercialization of 3D printing. This technology can also have a strong impact in the development of new electrochemical cells.

3D printing consists in constructing three-dimensional objects by depositing successive layers of raw material. This type of manufacturing, also known as additive manufacturing, has been on a rise in the last years as it allows the production of complex designs with lower manufacturing cost and material waste [1][2].

There are many options for the application of 3D printing in electrochemistry, research groups are working in the production of electrodes and electrochemical cells among others [3]. Our goal is to design and print electrochemical cells that are adapted to the needs of the laboratory. We want to reduce the cost of the cells, improve the design of those currently in use and finally create prototypes for new applications. 3D printing allows us to scale functional models at low cost, optimize designs by performing low-cost tests and create our own library with customized designs.

The printer we are using is the Photon M3 Plus model from Anycubic, this printer uses a photopolymerizable resin as printing raw material. Resin printers offer higher resolution of details than filament printers [3], Anycubic Photon M3 Plus achieves an accuracy of 34 μm .

Not all the parts of an electrochemical cell can be 3D printed. Our designs focus on being able to integrate standardized parts such as screws and O-rings.

Below can be seen a 3D printed electrochemical cell that replaces the previous glass version and reduces the cost. An electrode holder has been incorporated into the design and the standardized threads allow the use of commercially available lids.



Figure 1. 3D printed cell with electrode holder

We are currently designing a reactor for the production of green hydrogen that can be incorporated into a solar cell module to test its efficiency. And as future work we want to develop stack cells like those used for industrial applications.

Acknowledgements

This research was supported by the project PID2021-123163OB-I00 funded by MCIN/AEI/10.13039/501100011033/and FEDER A way of making Europe and Severo Ochoa Centre of Excellence Program (CEX2021-001230-S).

E.B: This work has been made possible thanks to the JAE Intro 2023 research grant awarded by CSIC (Consejo Superior de Investigaciones Científicas). The work carried out is part of the JAEINT23_EX_0500 research program.

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OXIDOS METÁLICOS SOPORTADOS PARA LA DESHIDROGENACIÓN OXIDATIVA DE ETANO CON CO₂ COMO AGENTE OXIDANTE

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El etileno es una de las materias primas más importantes de la industria petroquímica. Actualmente la producción mundial de etileno se lleva a cabo mediante pirólisis con vapor (steam cracking) de hidrocarburos [1]. Sin embargo, el impacto ambiental y energético (como consecuencia de una temperatura de reacción elevada ≈ 900 °C) es importante, y supone la producción de una gran cantidad de CO₂ asociada al proceso (1.8 kgCO₂/ kgC₂H₄) [1]. Una alternativa interesante es la reacción de deshidrogenación oxidativa de etano a etileno en presencia de O₂ (ODHE-O₂) [1], en la que es posible valorizar el CO₂ y emplearlo como agente oxidante en la reacción de ODH en lugar del O₂ (ODHE-CO₂) [2]. De entre todos los sistemas catalíticos estudiados, los catalizadores de óxido de cromo soportado presentan resultados catalíticos de interés [3,4], aunque el mecanismo de reacción no está completamente explicado. La falta de conocimiento sobre la posible formación de hidrógeno y los pocos estudios in situ que muestran los cambios en la superficie del catalizador durante la reacción son algunas de las áreas a estudiar. En este trabajo se muestra un estudio comparativo de catalizadores de óxido de cromo soportado sobre alúmina (dopados con NiO), en el que se ha llevado a cabo un estudio pormenorizado de los diferentes productos de reacción. Además, se ha realizado un estudio in situ (XPS y Raman) sobre los catalizadores más selectivos. Para ello, se han preparado tres series de catalizadores con o sin NiO (este último, 2% en peso de Ni, incorporado antes o después de la incorporación de la sal de Cr. Los catalizadores se denominan como aCrOx/Al₂O₃, aCrOx/2NiO/Al₂O₃ o 2NiO/aCrOx/Al₂O₃ (donde "a" representa el contenido en cromo en % en peso, en el rango de 4-8%). Los catalizadores se han preparado por el método de impregnación húmeda y finalmente fueron calcinados a 600°C durante 5 horas en atmósfera de aire. La caracterización fisicoquímica de los mismos se ha realizado mediante DRX, TPR-H₂, y espectroscopias Raman y

XPS. El estudio de las propiedades catalíticas se ha llevado a cabo en un reactor de lecho fijo con una mezcla de reacción, C₂H₆/CO₂/N₂ de relación molar 1/2/7, una masa de catalizador de 0.4 g, flujo total de 50 mL min⁻¹, en el rango de temperaturas de 625-675°C. El análisis de los productos de reacción se realiza por cromatografía de gases en línea. Con fines comparativos, se ha realizado el estudio de la reacción de deshidrogenación catalítica (sin CO₂), empleando una mezcla de reacción C₂H₆/N₂ de relación molar 1/9.

Los resultados de caracterización indican la ausencia de cristales de CrO₃ (DRX), para catalizadores con contenidos de Cr inferiores al 8% en peso. Mientras que los resultados de Raman sugieren la presencia de especies poliméricas CrO₃ altamente dispersas en la superficie del soporte. En ningún caso se observa la presencia de cristales de NiO. Además, los resultados de TPR-H₂ (Figura 1) indican cambios en la reducibilidad de las especies de Cr de acuerdo con la composición del catalizador y el contenido de Cr. En el caso de los catalizadores con 6% de Cr, el orden de reducibilidad es: 6Cr/Ni/AL (284°C) > Ni/6Cr/AL (293°C) > 6Cr/AL (303°C). Esta secuencia es similar para el resto de catalizadores estudiados.

En la Figura 2 se muestra la variación de la conversión de etano y de CO₂ (a 103mol h⁻¹g⁻¹), así como la selectividad a etileno, para los catalizadores 6Cr/Ni/AL, Ni/6Cr/AL y 6Cr/AL obtenidos durante la conversión de etano en presencia de CO₂ a 650 °C y un tiempo de reacción de 170 min, empleando un flujo total de 50 mL min⁻¹ y una alimentación C₂H₆/CO₂/N₂ con una molar de 1/2/7. El catalizador sin níquel (6Cr/AL) presenta una conversión de etano y CO₂ inferior (y una selectividad a etileno ligeramente inferior) al catalizador 6Cr/Ni/AL. Además, se observa una relación CO/C₂H₄ de 1,1 y 1,2, y una relación H₂/C₂H₄ de 0,7 y 0,8, respectivamente. Estos resultados sugieren que, en ambos casos, se produce tanto la deshidrogenación catalítica como el ODH de etano, superior en el caso del catalizador promovido con óxido de níquel.

Sin embargo, en el caso en el que el óxido de níquel se incorpora sobre el óxido de cromo (Ni/6Cr/AL) se observa un gran consumo de CO₂ (2,5 veces al observado para el catalizador 6Cr/Ni/AL). Además, se observa una gran producción de CO e H₂ respecto a la formación de etileno (con relaciones CO/C₂H₄= 28,4 y H₂/C₂H₄= 16,3) lo que indica que, en este caso, se produce el reformado seco de etano.

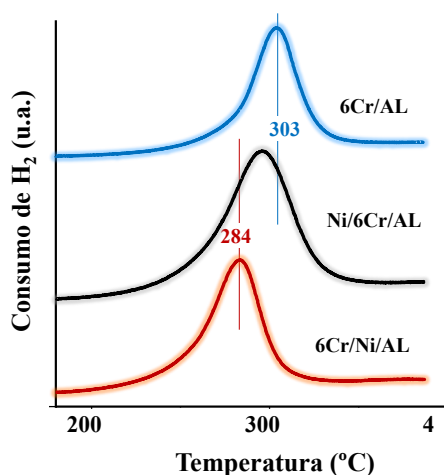


Figura 1. Resultados de TPR-H₂ de catalizadores de óxido cromo (6% en peso) soportado sobre Al₂O₃ con o sin óxido de níquel (2% en peso).

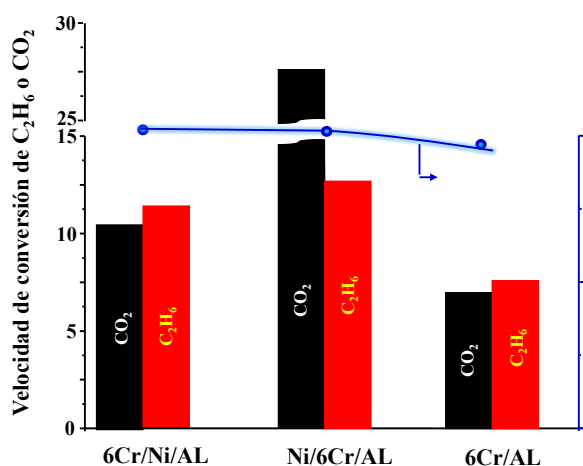


Figura 2. Variación de la conversión de C₂H₆ o CO₂ y de la selectividad a etileno en catalizadores estudiados.

Hay que destacar así mismo, que en ausencia de CO₂ en la alimentación se observa la formación mayoritaria de etileno, pero con gran formación de H₂ y una mayor desactivación del catalizador (deshidrogenación catalítica), lo que confirma el papel positivo de la presencia de CO₂ en la reacción. Los resultados de XPS in situ indican cambios en el estado de oxidación del Cr durante la reacción, como consecuencia de la presencia/ausencia de NiO en el catalizador y/o las condiciones de reacción, así como la importancia de la etapa de incorporación del níquel al catalizador para obtener las propiedades catalíticas adecuadas.

Agradecimientos

Se agradece la financiación de MINECO/FEDER (Proyectos: PID2021-126235OB-C31, y TED2021-130756B-C32).

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PROTONIC CERAMIC ELECTROCHEMICAL CELLS FOR SUSTAINABLE HYDROGEN PRODUCTION

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Solid oxide electrochemical cells based on oxygen-ion conductors have been demonstrated for efficient green hydrogen production. [1] However, due to the relatively high activation energy of oxygen-ion conduction high operational temperatures (>600 °C) are needed. These required temperatures have slowed down the scale-up and commercialization of ceramic electrochemical cells. Protonic ceramic electrochemical cells (<450 °C) [2] offer an alternative to the use of high temperatures due to proton conduction having a lower activation energy than oxygen-ion conduction. By extracting H₂ from the catalytic chamber, the equilibrium of the reaction is shifted, resulting in higher conversions at a lower temperature, and enhancing the selectivity of the reaction. At the same time, this technology allows for obtaining compressed high-purity H₂, intensifying the process. The proton-conducting cell technology has been successfully applied for the sustainable hydrogen production by means of different reactive systems such as methane reforming [3-4], ammonia cracking [4], or water electrolysis [5].

In this work, an innovative multifunctional flat protonic membrane is presented. On one hand, and on the frame of the EU-funded project SYMSYTES (101058426) the flat BZCY membrane will be used in a protonic membrane reactor (PMR) to optimize H₂ production by steam methane reforming (SMR) coming from pyrolysis gas waste streams (Figure 1). On the other hand, EU-funded project ALL-IN ZERO (101069888) aims to develop a compact membrane reactor (CMR) based on the flat BZCY membrane to produce hydrogen from zero or carbon negative fuels like ammonia, natural gas, biogas or alcohols. The hydrogen will be consumed in situ by internal combustion engines (ICE) or fuel cell systems (FCS) to generate electrical and mechanical power with zero emissions (Figure 2).

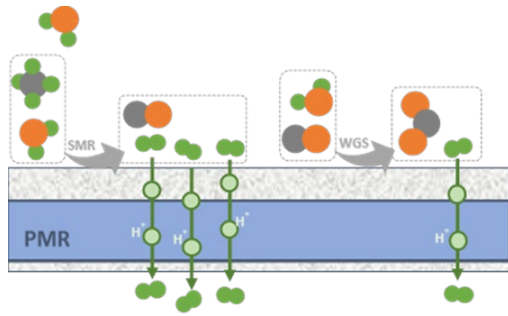


Figure 1: Schematics of the PMR

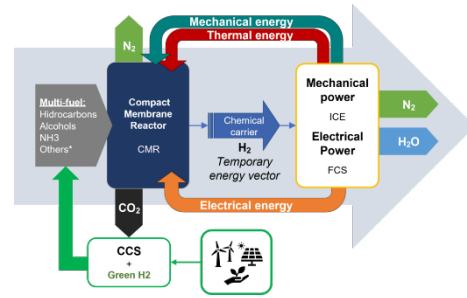


Figure 2: ALL-IN Zero concept layout

Acknowledgments:

This work has received European Union's Horizon 2020 research and innovation funding under grant agreement N° 101069888 and N° 101058426.

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Different Zeolite Phases Obtained with the Same Organic Structure Directing Agent in the Presence and Absence of Aluminum

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Zeolites constitute a diverse group of crystalline microporous materials primarily composed of silicate and aluminosilicate. The synthesis of each zeolite topology is possible in a specific range of aluminum content, $Al/(Si+Al)$, falling within the [0-0.5] interval. Predicting this interval for individual structures is generally challenging.[1, 2] The interplay between aluminum and organic structure directing agents (OSDAs) is crucial in determining the resulting zeolite phase during synthesis under specific conditions. This study endeavors to elucidate the role of aluminum as a structure directing agent in zeolite synthesis, employing computational chemistry. The investigation is grounded in criteria of energetic stability, employing force field methods such as Monte Carlo simulations and single point energy calculations. By carefully selecting cases where different zeolite phases emerge with the same OSDA, the study aims to rationalize how aluminum influences the relative stability of various competing zeolite phases, considering both the presence and absence of aluminum.

To achieve that, we proposed a new parameter called "synthesis energy" to compare the stabilities of zeolites with different Si/Al ratios based on the following concept. If the synthesis of two distinct zeolites can be expressed using identical reactants, the resultant product energies can be compared directly, as they are expected to have equivalent overall chemical compositions. Using the synthesis energies we were able to predict the most stable zeolite under pure silica and aluminosilicate conditions for most of the cases we considered in this work which emphasizes the potential of this newly proposed parameter to predict the phase selectivity of the zeolites in the future.

Acknowledgements

We thank GVA for PROMETEO/2021/077 project as well as ASIC-UPV and SGAI-CSIC for the use of computational facilities.

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MULTI-CONTRAST AGENT PLATFORM FOR T_1 - T_2 DUAL MAGNETIC RESONANCE IMAGING

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Introduction. Signal Intensity (SI) in Magnetic resonance imaging (MRI) depends on longitudinal (T_1) and transversal (T_2) relaxivity times [1]. Unfortunately, the intrinsic contrast changes associated to a pathologic condition are often too limited for accurate diagnosis. Here, MRI contrast agents (CA) improve image resolution based on their selective accumulation in the region of interest [2]. These CAs are classified as positive (T_1 -weighted) or negative (T_2 -weighted) image contrast promoters. The acquisition of MRI weighted in T_1 and T_2 could improve the safety of diagnosis [3]. In this context, it has been reported that Prussian Blue (PB) derivatives with general molecular formula $K_xGd_{1-x}(H_2O)_n[Fe(CN)_6]$ and nanosized crystallites present high performance as dual T_1 - T_2 CAs [4]. Unfortunately, their clinical use is precluded by the partial solubility in physiological medium. In this work, we have synthesized a novel hybrid material by monitoring the formation of PB analogue $Gd(H_2O)_4[Fe(CN)_6]$ (GF) nanoparticles with tailored shape and size, and further protection with a thin amorphous silica shell (GFS) by polymerizing the silicate at neutral pH. This results in a stable CA with constant Gd:Fe atomic ratio able to improve positive and negative contrast in MRI. In addition, nanoparticle stability and biocompatibility has been improved by conjugation of a short polyethylene glycol molecule at surface (GFS@PEG).

Results. The combination of Gd and Fe magnetic centers closely packed at the same crystalline structure leads to a magnetic synergistic effect, which results in an outstanding improvement of longitudinal relaxivity with regards to soluble Gd^{3+} chelates, whilst keeping the high transversal relaxivity inherent to iron oxide

nanoparticles. This CA improves positive and negative contrast in T_1 - and T_2 -weighted MR images, both in *in vitro* and *in vivo* systems. Furthermore, this novel hybrid presents a high biosafety profile and has strong ability to incorporate organic molecules on surface, displaying great potential for further clinical application.

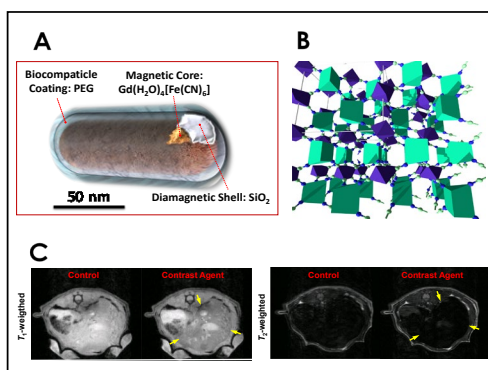


Figure 1: (A) Artistic representation of GFS@PEG na-noparticle with rod morphology. (B) Network topology of GF presenting the closely packaging of magnetic centers (Gd^{3+} and Fe^{3+}) in this structure. (C) *In vivo* coronal T_1 - and T_2 -weighted images acquired from a male Sprague-Dawley rat at 7 T magnetic field before (Control) and after (Contrast Agent) administration of $0.05 \text{ mmol kg}^{-1}$ of GFS@PEG.

Conclusion. The incorporation of T_1 and T_2 active moieties in a CA for dual-modal MRI provides complementary information that can help to improve the safety of diagnosis. In this sense, GFS@PEG magnetic nanoparticles show long-term stability in physiological fluids because of the protecting non-porous outer shell. With regards other proposed T_1 - T_2 dual mode CAs, these nanoparticles present very homogeneous composition and constant Gd:Fe atomic ratio, providing reproducible quality in MRI signal. With regards other proposed T_1 - T_2 dual mode CAs, these nanoparticles present very homogeneous composition and constant Gd:Fe atomic ratio, providing reproducible quality in MRI signal.

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AMINE COVALENT ORGANIC FRAMEWORKS FOR SAFE DELIVERY OF CAMPTOTHECIN

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Introduction: Covalent organic frameworks (COFs) are a new target for research in porous materials, due to their several attractive features, such as, large external surface area, defined pore size, tunable pores [1]. All these properties make these materials promising for multiple applications such as molecular separation, energy storage, catalysis, small molecules adsorption, and drug delivery. 20-(S)-camptothecin (CPT) is a natural alkaloid with strong antitumor activity against a broad spectrum of cancers [2]. Unfortunately, this molecule has found no clinical application, due to its presents some major limitations. Here, we present novel amine functionalized COF's prepared by direct incorporation of nucleophilic groups (e.g., primary amines) on pore wall during the synthesis of a 2D-COF (COF-5) due to the substitution of original monomers for its later use as drug delivery system for covalently bonded camptothecin (CPT).

Methods: All COFs derivatives (CF-x (substituted with primary amine groups) were synthesized by an optimized microwave-assisted method. The CPT prodrug (CPT-succinate) was conjugated with primary amine groups by amide bond. Moreover, stability assays in water were carried out in order to investigate the effect of the CPT on the structure (Figure 1). In addition, internal trafficking was investigated by flow cytometry (FC) due to the incorporation of Alexa Fluor 647 in the structure of COFs (Figure 1).

Results: COF-25-CPT and COF-25 conjugates show efficient particle cell internalization. It is noted that COF-25-CPT show strong cytotoxic activity over HeLa and MCF-7 cell lines, even at low dose. On the other hand, the introduction of functional groups during the synthesis of two dimensional COFs (2D COFs) is highly discouraged, as they can interfere with the π - π stacking forces, compromising framework integrity [3]. In this case, the presence of the CPT improve the stability of the structure due to the drug protect the B-O bonds and hydrolytically susceptible backbones through kinetic blocking.

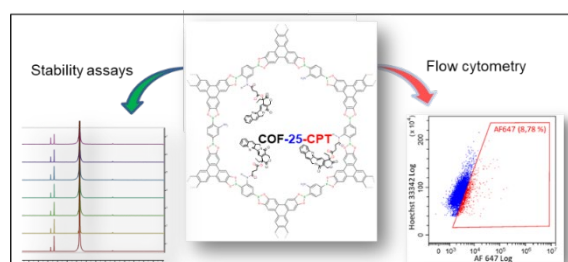


Figure 1. Schematic illustration of COF-25-CPT

Conclusion: COF-25-CPT is a novel type of drug delivery system based on covalent linking of a therapeutic molecule in COF structure, by coupling CPT molecules over primary amine functions. These new COF nanoparticles constitute a new stable vehicle for the safe delivery to cancer cells of the CPT or other chemotherapeutic molecules.

Acknowledgements

Financial support of the Spanish Ministry of Economy and Competitiveness (projects TEC2016-80976-R and SEV-2016-0683) is gratefully acknowledged.

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STRUCTURE DETERMINATION OF AS-MADE ZEOLITE ITQ-52 BY THREE-DIMENSIONAL ELECTRON DIFFRACTION

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The study of the crystalline structure of microporous zeolites by conventional X-ray diffraction techniques can be challenging since these materials commonly present complex structures with low symmetries and large unit cell volumes. [1,2] Single crystal X-ray diffraction (SCXRD) typically requires crystals larger than 10 μm which are difficult to grow for many zeolite samples, while powder X-ray diffraction (PXR) data usually present strong peak overlapping, which makes it difficult to achieve a satisfactory unit cell determination and structure solution. The advent of a new Transmission Electron Microscopy (TEM) based technique called 3D Electron Diffraction (3D ED) provides an interesting alternative, as it allows the use of any conventional TEM to collect single crystal-like diffraction data on nanocrystals of a few nanometers. [3] This method can be combined with precession electron diffraction (PED), minimizing dynamical effects and integration of reflections along the excitation error, which enables obtaining the superior quality diffraction data required for ab-initio structure solution. [4] The combination of 3D ED with beam precession allows the collection of a large set of 2D diffraction patterns while the crystal is rotated under the electron beam, enabling the reconstruction of a large fraction of the 3D reciprocal space in a very short span of time (e.g., in less than half an hour). As zeolites tend to be beam sensitive materials, a special data collection protocol (data collection time within few minutes instead of half an hour) has been developed in ITQ to provide a fast data collection capacity in order to determine complex novel zeolite structures. [5,6,7]

In this work, we have used the ultrafast 3D ED data collection protocol as developed in ITQ to determine the structure of two zeolitic borosilicates with ITQ-

52 structure [8] (IFW framework type), where phosphonium and aminophosphonium cations has been used as their respective organic structure directing agents (OSDA). They both present a structure with monoclinic space group $I2/m$ (No. 12) with unit cell parameters $a = 17.3446 \text{ \AA}$, $b = 17.7129 \text{ \AA}$, $c = 12.2535 \text{ \AA}$, $\beta = 90.628^\circ$, and $a = 17.4810 \text{ \AA}$, $b = 17.9008 \text{ \AA}$, $c = 12.3250 \text{ \AA}$, $\beta = 90.525^\circ$ respectively, containing 64 TO_2 units per unit cell (Figure 1 and 2).

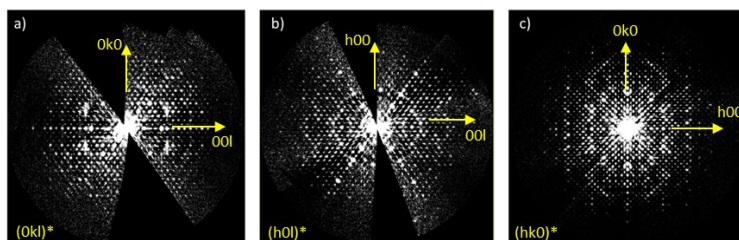


Figure 1. Cuts of the 3D ED volume reconstructions from the data collected on the phosphonium cation containing zeolite ITQ-52 sample. (a) $(h00)^*$ plane, (b) $(0k0)^*$ plane, (c) $(00l)^*$ plane.

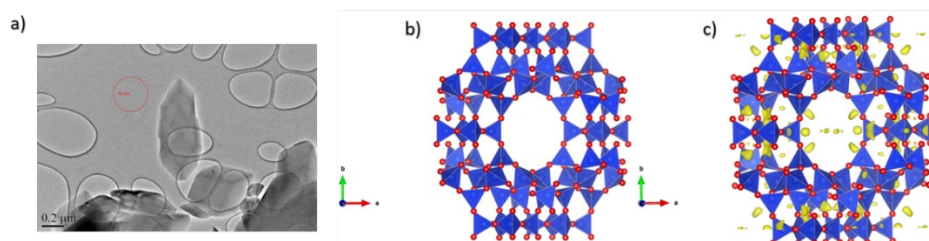


Figure 2. (a) TEM image of the phosphonium cation containing zeolite ITQ-52 crystal used for ultrafast 3D ED data collection; (b) Silicon framework structure of synthetic ITQ-52 (with phosphonium organic template) solved using ultrafast 3D ED Data; (c) Difference Fourier map after Silicon framework structure was determined.

Agradecimientos

This research was supported by projects RTI2018-101784-B-I00 and SEV-2016-0683-18-3 and grant PRE2018-083623 from the Spanish government, and project PROMETEO/2021/077 FROM Generalitat Valenciana.

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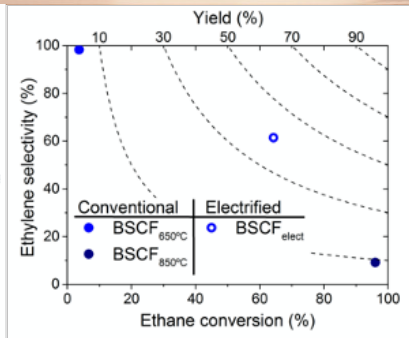
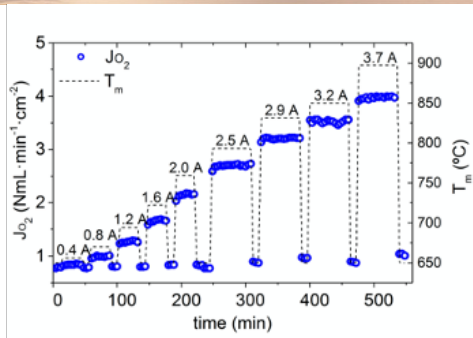
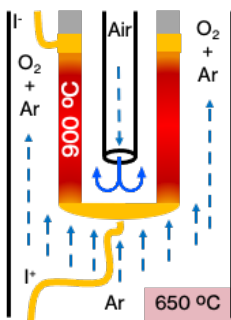
Lowering operational temperatures in traditional oxygen transport membranes

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Abstract

The industry decarbonization requires the development of highly efficient and flexible technologies based on renewable energy resources. In the case of pure oxygen production, oxygen transport membranes (OTMs) appear as an alternative technology for the cryogenic distillation of air, the most common technology for oxygen production. Also, OTMs could provide oxygen from different sources (air, water, CO₂, etc.), and they are more flexible to adapt to current processes, producing oxygen at 700-1000 °C. Furthermore, OTMs can be integrated in catalytic membrane reactors, providing new pathways for different processes, like oxidative dehydrogenation, partial oxidation, etc. The first part of this study focuses on electrification on a traditional OTM material (Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ}) imposing different electric currents/voltages along a capillary membrane. Thanks to the emerging Joule effect, the membrane-surface temperature, and the associated O₂ permeation flux can be adjusted. Here, the OTM is electrically and locally heated and reaches 900 °C on the surface, whereas the surrounding of the membrane was maintained at 650 °C. The O₂ permeation flux reached for the electrified membranes was ~3.7 mL/min·cm², corresponding to the flux obtained with an OTM non-electrified at 900 °C. In this study, it was also compared the effect of the electrification in oxidative dehydrogenation of ethane (ODHE). In this reaction, electrified OTM achieves improve the yield to ethylene in contrast to non-electrified OTM, 40% and 10% respectively.



CATALIZADORES DE Ni Y Co SOPORTADOS EN SEPIOLITA NATURAL APLICADOS AL REFORMADO CON VAPOR DE AGUA DE BIOETANOL

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Introducción

La invasión de Ucrania por parte de Rusia en el 2022 ha dejado patente la dependencia energética europea del gas natural y ha puesto de manifiesto la importancia de buscar alternativas sostenibles y descentralizadas de la energía cuanto antes. Esto, unido a la búsqueda de fuentes de energía renovables competentes para reducir el impacto sobre el clima ha hecho que en estos últimos años se esté planteando con mayor fuerza el uso del hidrógeno como vector energético [1,2]. El bioetanol podría ser una excelente opción para producir hidrógeno a través del reformado con vapor de agua (ESR) por los beneficios ambientales que conlleva [3]. En este proceso, el papel del centro activo resulta crítico, ya que no solo debe de tener una buena actividad en la rotura del enlace C-C sino que, además, debe ser selectivo en la producción de hidrógeno y minimizar la formación de coque [4]. Así pues, en este trabajo, se ha explorado la actividad, selectividad y estabilidad de catalizadores en el reformado con vapor de agua de bioetanol (RVAE), utilizando Ni y Co como metales activos soportados sobre sepiolita natural.

Experimental

La síntesis de los catalizadores de Ni y Co se ha llevado a cabo por impregnación húmeda avolumen de poro empleando como precursores los nitratos correspondientes. Estos materiales han sido caracterizados por diferentes técnicas (DRX, Área BET, TPR, AE, Raman) para conocer sus propiedades fisicoquímicas más relevantes. La actividad catalítica se ha estudiado en un reactor de lecho fijo de acero refractario. Previa a la reacción, se reduce el catalizador a 600°C (2h, 100mL/min H₂). El estudio catalítico se realiza a 400-600°C con una vuelta a 400°C para comprobar si existe desactivación.

Resultados y discusión de resultados

En la Tabla 1 se muestran los resultados obtenidos para ambos catalizadores en el RVAE. Como se puede ver, los dos catalizadores convierten por completo el bioetanol en todo el rango de temperaturas estudiado (400-600°C). No obstante, encontramos una diferencia importante en la selectividad a productos de reacción, especialmente a bajas temperaturas. El catalizador de Ni presenta selectividades a hidrógeno sensiblemente mayores a 400°C, y bajas producciones de CO, lo que podría estar relacionado con una mayor actividad en la reacción de "water gas shift" del Ni comparado con el Co. En cuanto a la estabilidad, el catalizador de Ni presenta una cierta desactivación, como se deduce de la pérdida de actividad cuando se vuelve a la temperatura inicial de reacción (Ni/Sep, 400R).

Tabla 1 – Variación de la conversión de bioetanol y selectividad a productos de reacción con la temperatura de reacción. Condiciones de reacción: presión atmosférica, WHSV 5,05 h⁻¹ y S/C = 6,5.

Catalizador	T. (° C)	Conv. mol %	Sel., H ₂ mol %	Sel., CH ₄ mol %	Sel., CO mol %	Sel., CO ₂ mol %	Sel., C ₂ H ₄ mol %	Sel., C ₂ H ₄ O mol %
Co/Sep	400	100	55	9,10	16,61	18,81	0,18	0,70
	500	100	73	3,25	2,23	21,79	0,00	0,00
	600	100	73	3,32	4,62	19,54	0,00	0,00
	400R	100	63	10,12	18,23	7,54	0,00	1,43
Ni/Sep	400	100	68	11,11	0,32	20,88	0,07	0,12
	500	100	73	3,08	2,11	21,70	0,00	0,00
	600	100	73	1,68	4,00	21,69	0,00	0,00
	400R	93	56	14,11	18,98	8,99	0,21	1,92

Conclusiones

Se han preparado catalizadores de Ni y Co soportados en sepiolita natural de alta actividad en el RVAE en todo el rango de temperaturas estudiado (400-600°C). Sin embargo, ambos catalizadores presentan signos claros de desactivación, especialmente el basado en Ni. La incorporación de dopantes, que eviten/inhiban la formación de compuestos precursores de coque será necesaria si se quiere aprovechar el gran potencial que presentan estos catalizadores para la producción de H₂ a partir del reformado de bioetanol.

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ESPINELAS DE NI-AL Y CO-AL COMO CATALIZADORES PARA REFORMADO DIRECTO DE BIOGÁS. EFECTO DEL MÉTODO DE SÍNTESIS Y LA INCORPORACIÓN DE K SOBRE LA ACTIVIDAD, SELECTIVIDAD Y ESTABILIDAD DEL CATALIZADOR.

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Introducción

La invasión de Ucrania por parte de Rusia en el 2022 ha dejado patente la dependencia energética europea del gas natural y la necesidad de buscar alternativas sostenibles y descentralizadas de la energía. Una de las fuentes alternativas y sostenibles más interesante es el uso de biogás en el reformado seco de metano para la producción de H₂, dado que este gas contiene los reactivos de partida (CH₄ y CO₂) en una relación adecuada, y con la ventaja medioambiental de que se consume CO₂ en el proceso [1]. El reformado seco de metano (DR) tiene muchos retos, siendo uno de ellos la búsqueda de un catalizador activo y resistente a la deposición de coque. Los metales más utilizados por su precio, disponibilidad y actividad son principalmente níquel y cobalto [2]. Los dopantes alcalinos, como el potasio, que mejoran la dispersión del metal y aportan una basicidad adecuada para gasificar el carbón formado sobre la superficie, pueden formular un catalizador más resistente manteniendo la actividad catalítica [3][4]. En este trabajo, enmarcado dentro del proyecto ZEPPELIN¹, se ha estudiado la actividad catalítica y estabilidad en el proceso de DR de una familia de espinelas de Ni-Al y Co-Al. Para ello, se ha estudiado el efecto del método de síntesis (*Pechini* y Co-precipitación) y la adición de dopantes (K) sobre la actividad, selectividad y estabilidad de los catalizadores resultantes.

Material y métodos

La síntesis de espinelas se ha llevado a cabo por dos métodos: *Pechini* (p) y co-precipitación (cp). Para ello, se han utilizado como reactivos los nitratos metálicos correspondientes, además de PEG y ácido cítrico para la de tipo *Pechini*. Estos materiales han sido caracterizados por diferentes técnicas antes de reacción (DRX, Área BET, ICP, TPR) y una vez usados (DRX, AE, Raman) para conocer sus propiedades fisicoquímicas más relevantes. La actividad catalítica se ha estudiado empleando un equipo con un reactor de lecho fijo de acero refractario (aleación SS-310). Previo a la reacción, se reduce el catalizador a 800°C (2h, 100mL H₂). El estudio catalítico se realiza a 800°C y 1atm durante 9h y se mantiene una ratio CH₄/CO₂ = 2,2, WHSV_{biogás} = 5,05 h⁻¹ y GHSV_{biogás} = 8000h⁻¹.

Resultados y discusión

En la Tabla 1 se puede ver que los materiales sintetizados por co-precipitación tienen un área superficial superior a las espinelas sintetizadas por *Pechini*, siendo mayor las de Ni con respecto a las de Co. Además, estos materiales de Ni-Al presentan más de un 75% de metal activo disponible tras la reducción a 800°C. La incorporación de potasio en la espinela p-Ni-Al, parece desplazar parte del

Ni de la espinela para formar el óxido correspondiente, además de aumentar su área superficial mientras que mantiene la disponibilidad del metal activo.

Tabla 1. Propiedades físico-químicas de las espinelas Ni-Al y Co-Al sintetizadas por ambos métodos. *Valor obtenido a partir del ICP de las aguas madres resultantes del lavado y filtrado.

Catalizador	% metal (Ni, Co)	Área BET (m ² /g)	% metal reducido 800°C
p-NiAl ₂ O ₄	33% Ni	80	80%
cp-NiAl ₂ O ₄	*33% Ni	142	77%
p-CoAl ₂ O ₄	33% Ni	35	47%
cp-CoAl ₂ O ₄	*33% Ni	75	70%
p-3%K-NiAl ₂ O ₄	3%K, 32%Ni	95	75%

Reacción

La actividad catalítica de estos materiales se ha probado en DR y se muestran en la Tabla 2. En ella se puede observar cómo tanto las espinelas de Ni como de Co, por ambos métodos de síntesis, son activas en el reformado seco de metano. Sin embargo, todas ellas sufren una rápida desactivación por la formación de coque. La adición de un 3% de K en el catalizador p-NiAl₂O₄, mejora la conversión de CO₂ de un 14% a un 80% en la primera hora de reacción, y hasta un 96% a las 9h de reacción. Es por ello que cabría esperar una disminución en la cantidad de coque formado; a la vez que mantiene la selectividad hacia los productos de interés (H₂ y CO) en una relación muy próxima al equilibrio (1:1).

Tabla 2. Variación de la conversión de CO₂ a 1h y 9h de reacción, y selectividad a productos con los diferentes métodos de síntesis y dopado con potasio. *Tiempo hasta obstrucción del reactor.

Catalizador	Tiempo (h)	Conv. CO ₂ mol % 1h	Conv. CO ₂ mol % 9h	Sel., H ₂ 1h mol %	Sel., CO 1h mol %	Sel., C ₂ H ₄ mol %	Sel., C ₂ H ₆ mol %
p-NiAl ₂ O ₄	*1,50	14	0	68,7	16,9	0,0	0,0
cp-NiAl ₂ O ₄	*0,25	52	0	68,1	23,9	0,0	0,0
p-CoAl ₂ O ₄	*0,25	42	0	72,1	27,9	0,0	0,0
cp-CoAl ₂ O ₄	*0,75	0	0	73,1	24,0	0,0	0,0
p-3%K-NiAl ₂ O ₄	9,00	80	96	55,6	44,4	0,0	0,0

Conclusiones

Se ha conseguido sintetizar las espinelas de Ni-Al y Co-Al por ambos métodos de síntesis, siendo la de tipo *Pechini* la más interesante por su sencillez. La incorporación de K en el método *Pechini*, que se ha realizado sin añadir nuevas etapas, se ha visto que modifica la estructura del catalizador final combinando las fases de NiO y NiAl₂O₄, además de aumentar el área BET. Los materiales sintetizados son activos en el reformado seco de metano, sin embargo, todos ellos sufren una rápida desactivación por coque. La incorporación de K mejora significativamente la resistencia de la espinela Ni-Al frente al coque, con conversiones de CO₂ del 96%. Esto es debido a la mejora en la dispersión del metal y a la capacidad básica del K de gasificar el carbón formado en la superficie.

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COMISIÓN DE IGUALDAD DEL ITQ: INFORME 2023

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Siguiendo la costumbre establecida en 2021, la Comisión de Igualdad del ITQ presenta en el Winter Meeting un breve resumen de las principales actividades realizadas a lo largo del año que finaliza.

Tal y como llevamos haciendo algún tiempo, para planificar las necesidades y las actividades a desarrollar en nuestro instituto, y para tratar los asuntos planteados por el personal del ITQ, se ha establecido un sistema de reuniones periódicas (junio, octubre, enero y abril); como novedad, desde este año antes de las reuniones se envía a itqist un formulario para que se puedan enviar solicitudes, comentarios y sugerencias.

Un año más hemos organizado charlas en centros educativos con motivo del Día Internacional de la Mujer y la Niña en la Ciencia, para fomentar y reforzar posibles vocaciones científicas. En la edición de 2023 la participación ha bajado bastante, pero aun así hemos contado con 12 personas del ITQ que dieron charlas en 11 centros para 857 niñas y niños desde Educación Infantil hasta 2º de bachillerato.

Otra actividad ya tradicional es la jornada "Mujeres y Ciencia", con motivo del Día Internacional de la Mujer. Este año la jornada se celebró los días 2 y 3 de marzo, en la Casa de la Ciencia del CSIC en Valencia y en la CPI-UPV, y contó con la participación de M^a Ángeles Durán Heras (socióloga), M^a Rosa Cerdá Hernández (técnica de igualdad UPV), Carmen García García (física) y Pilar Mateo Herrero (química).

La Comisión también ha continuado con la realización de estadísticas de género en el ITQ, incluyendo el análisis de las tesis doctorales realizadas en el centro.

Además, desde 2022 la Comisión promueve la participación en programas de tutoría (mentoring) para fomentar el interés hacia la ciencia y la tecnología entre la juventud, especialmente entre las chicas. Actualmente, las mentoras del ITQ participan en dos programas de tutoría, uno para estudiantes de primaria en colaboración con el programa Inspira STEAM de la Universidad de Deusto, y otro para estudiantes de doctorado asociados a centros de investigación del CSIC, especialmente chicas, en el marco del programa Camino del CSIC desde 2023.

Por último, y como novedad de este año, se ha realizado la jornada Maternidad y Ciencia. La jornada se celebró el 23 de noviembre, aprovechando la Semana de la Ciencia del CSIC. En esta mesa redonda cuatro investigadoras y técnicas del instituto, así como la coordinadora de PRL del ITQ, nos hablaron acerca de cómo el hecho de ser madres ha afectado tanto a su carrera profesional como a su vida personal, cómo han funcionado las medias de conciliación, qué recursos han encontrado disponibles, y qué cambios y mejoras les gustaría ver.

Esta jornada pretende ser el inicio de una serie de mesas redondas y charlas periódicas que acerquen distintos temas que puedan ser de interés. Actualmente estamos preparando nuevas temáticas para continuar con las jornadas, como "Discapacidad y ciencia" o "Maternidad y ciencia: 5 años después". Y por supuesto esperamos propuestas de más temas.