MULTI2HYCAT

MULTI-site organic-inorganic HYbrid CATalysts for MULTI-step chemical processes

Enjoy reading the MULTI2HYCAT newsletter!

18 months ago, the MULTI2HYCAT research and innovation project has started developing hybrid catalysts for heterogeneously catalyzed cascade reactions. The project is coordinated by the University of Piemonte Orientale "Amedeo Avogadro" and funded by the EU Horizon 2020 program under GA no. 720783.

Our overall goal is to design, obtain proof of concept, upscale and reach industrial validation of a new class of hierarchically-porous organic-inorganic hybrid materials to be used as active catalysts in multi-step asymmetric catalytic processes.

SUMMARY

The MULTI2HYCAT Project is gaining momentum. In the last 18 months, the project has produced a number of great results which have been published in 7 scientific articles in peer-reviewed international journals.

At the beginning of July 2018 the ITQ-CSIC invited the EU expert, the EU officer and the partners to the 3rd biannual project meeting and the 1st MULTI2HYCAT Summer School, which were both held in Valencia (Spain).

A LOOK BACK AT THE FIRST 18 MONTHS – PROJECT RESULTS

Already at an early project stage, main **reactions were identified** following the needs of the industrial partners (Almirall and Solvay). Consequently, appropriate **catalysts were selected**, including Corey-Bakshi-Shibata for enantioselective syntheses or Pd- and Fe-containing catalysts for C-C-coupling, such as benzoin, aldol or Suzuki condensation.

The anchoring of these catalysts to the hierarchically nanoporous active supports, e.g., SAPO-5, SAPO-34 and ZSM-5, is one of the **main challenges** during the project. Therefore, the above-mentioned catalysts were grafted to a trialkoxysilane body, which enables the condensation to the support surface. Hitherto, a variety of these modified catalysts was synthesized by CAGE Chemicals. This **catalyst design** aims to provide structures with different structural rigidity, thus, influencing the catalytic activity by keeping the active group away from the support surface.

In the meantime, the ITQ-CSIC has prepared the nanoporous active support materials and anchored first catalysts, thus, synthesizing the **final hybrid catalysts** this year. Physico-chemical and catalytic properties were **characterized** by the University of Piemonte Orientale and the University of Southampton, respectively. Thus, the influence of pore width and organic loading on the conversion, selectivity and, not less important, the recyclability of the hybrid catalysts.

Now that the first set of acidic as well as alkaline hybrid catalyst is available, the CNRS also started its activities in January 2018 with validating the catalytic activity of these catalysts in the **syntheses of bio-based surfactants and ligands**.

In summary, **50 samples** have been synthesized and 40 of these samples have been exchanged among the partners for characterization and evaluation.

The synthetic research activity was supported by **computational studies**, also performed by the University of Piemonte Orientale, to assess the interactions of the organic catalytic moieties with the different support materials. This **in-silico catalyst design** showed the importance of the molecular structures towards the materials activity (Fig. 1).

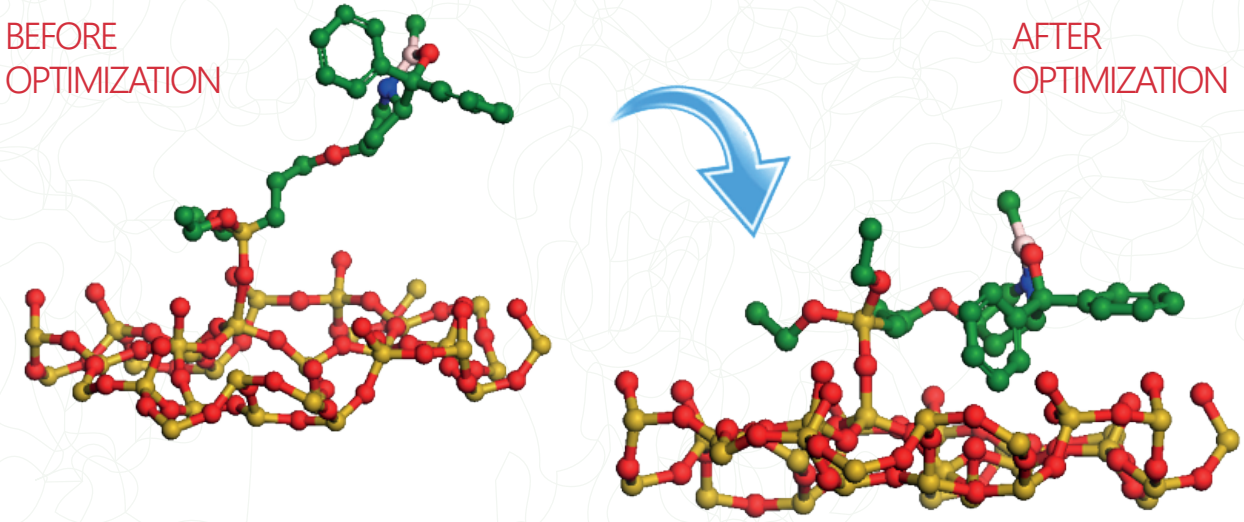


Fig. 1: Results of a computational study, showing that the organic moiety could stick to the support surface due to energetic advantages, if the anchoring is not fully completed. Thus, the overall catalytic activity could be decreased. Strategies to circumvent this drawback have already been developed.

SCIENTIFIC CONTRIBUTIONS

All the above-mentioned activities resulted in **7 scientific papers** (see below) and **20 oral and poster presentations** at international conferences.

- **Elucidation of the Interaction Mechanism between Organic Chiral Cages with Biomolecules through Nuclear Magnetic Resonance and Theoretical Studies**, Sara Sáez-Ferre et al., The Journal of Physical Chemistry C 122(29), 2018, DOI: 10.1021/acs.jpcc.8b05069
- **Combined solid-state NMR, FT-IR and computational studies on layered and porous materials**, Geo Paul et al., Chemical Society Reviews 47(15), 2018, DOI: 10.1039/C7CS00358G
- **Hierarchical SAPO-34 Architectures with Tailored Acid Sites using Sustainable Sugar Templates**, Ivana Miletto et al., Chemistry Open 7(4), 2018, DOI: 10.1002/open.201800001
- **Ab Initio Design of Low Band Gap 2D Tin Organohalide Perovskites**, Alberto Fraccarollo et al., The Journal of Physical Chemistry C 122(7), 2018, DOI: 10.1021/acs.jpcc.7b08928
- **Mesoporous silica nanoparticles incorporating squaraine-based photosensitizers: a combined experimental and computational approach**, Ivana Miletto et al., Dalton Transactions 47(9), 2018, DOI: 10.1039/C7DT03735J

- **First principles study of 2D layered organohalide tin perovskites**, Alberto Fraccarollo et al., The Journal of Chemical Physics 146(23), 2017, DOI: 10.1063/1.4985054
- **Mesoporous silica scaffolds as precursor to drive the formation of hierarchical SAPO-34 with tunable acid properties**, Ivana Miletto et al., Chemistry – A European Journal 23(41), 2017, DOI: 10.1002/chem.201701978

M18 MEETING AND COMING PERIOD

At the 18-month meeting of the MULTI2HYCAT project, that took place on July 3rd – 5th 2018 in Valencia (Spain), the achieved results have been discussed and **presented to the European Officer and the European Expert**. We can look back at a **successful and fruitful discussion** of the partners and with the delegates of the European Commission. Overall the project is slightly ahead the envisaged schedule and the first two milestones have been reached.

The partners will now focus on the preparation of **multi-site** hybrid catalysts and evaluate both their catalytic activity and their recyclability. Catalysts which will show outstanding results will be chosen for a larger scale preparation and tested in the specific, industrially-relevant reactions.

Finally, a first business and commercialization plan will be developed by PNO including a Life-Cycle-Assessment and a market analysis based on the stakeholder interviews, which will be finalized and evaluated by December 2018.

THE SUMMIT OF 18 PROJECT MONTHS – MULTI2HYCAT SUMMER SCHOOL

The achieved results and the project meeting were a good opportunity to organize a Summer School with tutorial character for PhD students, young researchers and Post-Docs. The Summer School was held directly after the end of the project meeting from July 5th to 6th at the Instituto de Tecnología Química (UPV CSIC) and consisted of 5 Tutorial Talks given by MULTI2HYCAT professors and local lecturers. Besides these talks, the participants presented 9 oral contributions and 6 posters related to catalyst preparation, characterization and application with a general relation to the MULTI2HYCAT project. The Summer School was a great opportunity for both young and experienced scientists to get together and discuss about their individual research and future potentials.

For more information about the speakers, the program and the book of abstracts visit www.multi2hycat-summerschool.eu. You can also find visual impressions on Facebook at www.facebook.com/MULTI2HYCAT and https://www.facebook.com/ITQ.UPVCSIC.

MEET MULTI2HYCAT

Are you interested to meet our partners? The next international events, where MULTI2HYCAT partners will be present and available for discussions are:

- **18th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC)**, 22 – 25 July 2018, Sydney, Australia, http://catalysis.org.au/events/ishhc-18
- **7th EuCheMS Chemistry Congress**, 26 – 30 August 2018, Liverpool, UK, http://www.rsc.org/events/euchems2018
- **CICAT 2018, XXVI Congresso Iberoamericano de Catàlise**, 9 – 4 September 2018, Coimbra, Portugal, http://cicat2018.eventos.chemistry.pt
- **SUSCHEM Brokerage Event**, 23. October 2018, Brussels, Belgium, http://www.suschem.org/events/save-the-date-suschem-brokerage-event-2018

Check event attendance and updates at www.multi2hycat.eu.

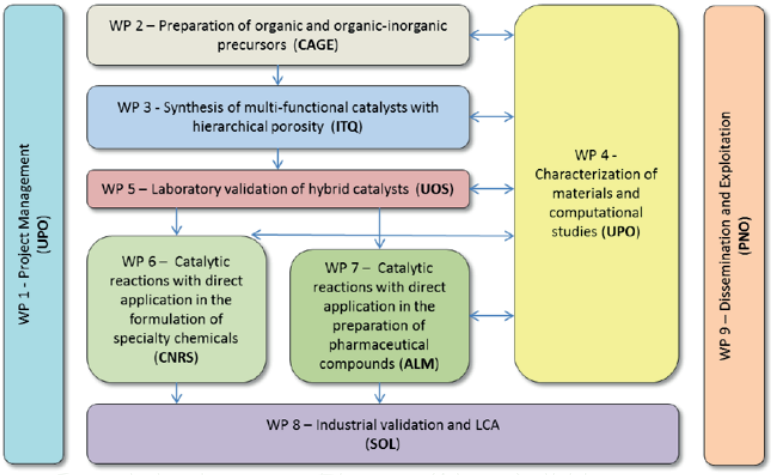
THE PROJECT IN BRIEF

MULTI2HYCAT – **"Multi**-site organic-inorganic **Hy**brid **Cat**alysts for **Multi**-step chemical processes" – is a research & innovation project funded by the **EU Horizon 2020 program under GA no. 720783**, to develop a new class of multi-site hierarchically-porous organic-inorganic hybrid materials for heterogeneously catalyzed multi-step asymmetric catalytic processes. Thus, multi-step catalytic processes with high conversions and selectivities towards the desired final products are expected for wide range of industrial applications.

The new materials will **rise the efficiency and sustainability** of heterogeneously catalyzed reactions by enabling one-pot syntheses and, consequently, **reduce costs** eliminating the necessity of purification steps correlated with high energy, solvent and time consumption.

The catalysts will be demonstrated for pharmaceutical and intermediate chemistry applications.

The MULTI2HYCAT consortium consists of **8 partners**: Four research centers (UPO, ITQ, UOS and CNRS) are carrying out **research activities**, while three companies (the SME CAGE, and the large companies SOL and ALM) will validate the proposed processes and products at the **industrial level.** Moreover, the innovation experts from PNO will guarantee a sound **dissemination** campaign and the **exploitation** of project results.



MULTI2HYCAT-RELATED PUBLICATIONS

- **Foundations and strategies of the construction of hybrid catalysts for optimized performances**, Ye et al., Nature Catalysis 1, 318-315, 2018 , https://www.nature.com/articles/s41929-018-0052-2
- **Recyclable organocatalysts based on hybrid silicas**, Ferré et al., Green Chemistry 18, 881-922, 2016, http://pubs.rsc.org/en/content/getauthorversionpdf/C5GC02579F
- **Co-immobilization of Laccase and TEMPO in the Compartments of Mesoporous Silica for a Green and One-Pot Cascade Synthesis of Coumarins by Knoevenagel Condensation**, Mogharabi-Manzari et al., ChemCatChem 10(7), 2018 1542-1546, https://onlinelibrary.wiley.com/doi/abs/10.1002/cctc.201701527
- **Assembly immobilized palladium(0) on carboxymethylcellulose/Fe3O4 hybrid: An efficient tailor-made magnetically catalyst for the Suzuki–Miyaura couplings**, Zhang et al., Applied Organometallic Chemistry 32(1), 2017, https://onlinelibrary.wiley.com/doi/abs/10.1002/aoc.3912
- **Effect of the pore size and surface modification of porous glass membranes on vanadium redox-flow battery performance**, Mögelin et al., Journal of Applied Electrochemistry 48(6), 2018, https://doi.org/10.1007/s10800-018-1201-7

KEEP INFORMED

If you want to learn more about the MULTI2HYCAT project, please visit the MULTI2HYCAT website or follow the project on Twitter, Facebook, LinkedIn and Researchgate. To get in touch with one of the MULTI2HYCAT partners, please e-mail info@multi2hycat.eu.

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For more info about the project visit the MULTI2HYCAT website at: www.multi2hycat.eu MULTI2HYCAT

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