

Title	Informed design of heterogenous catalysts: a combined experimental-ML approach
--------------	---

Proponent	Paolo Dolcet
Research Group	Wet Chemistry and Colloids Group
Contact	web: https://wwwdisc.chimica.unipd.it/silvia.gross/dolcet.html email: paolo.dolcet@unipd.it
Co-Proponent	Sergio Rampino
Research Group	Theoretical Chemistry
Contact	web: https://www.chimica.unipd.it/sergio.rampino/ email: sergio.rampino@unipd.it

International Secondment	
PI	Jan-Dierk Grunwaldt
Institute	Karlsruhe Institute of Technology
Place, country	Karlsruhe, Germany
# months (min.3)	6

Project description (2 page max):

The selective oxidation of propylene to acrolein is a highly impactful industrial process, due to the importance of acrolein as e.g., the monomer for the production of acrylic and super absorbent polymers, as pesticide or for the production of methionine for animal nutrition. The global annual acrolein production reaches 5 Mt. Bi-Mo mixed oxides are well-known catalysts for this reaction, due to their high selectivity towards acrolein¹. Even though Bi and Mo sites are assumed to be the key active centers for the catalytic reaction, the addition of further metals (e.g., Fe, Co) favors a synergistic effect of different coexisting oxide phases, leading to dramatic increases in activity. The presence of these additional transition metals not only influences the specific surface area, but strongly affects the electronic conductivity and the extent of the lattice oxygen participation in the catalytic event^{1,2}. The α -Bi₂Mo₃O₁₂, β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ phases are all significant for the selective oxidation of propylene to acrolein, but their activity and selectivity towards acrolein is still giving rising to conflicting conclusions. Whereas some reports claim that the α -Bi₂Mo₃O₁₂ is the most active phase, most agree that the β -phase outperforms the other. On the other hand, there is a general consensus that the preparation method plays a crucial role in determining the catalytic performances.

These materials are most commonly prepared via co-precipitation, spray-drying or sol-gel synthesis, but these methods usually require a calcination step at temperatures greater than 400 °C to yield crystalline materials, and this might lead to a decrease of the catalytic activity, due to the consequent enrichment with bismuth of the catalyst surface. As an alternative, hydrothermal synthesis overcomes these issues, since it usually yields high purity, highly crystalline materials with controlled size and specific surface area, with the possibility of controlling the nanostructures morphology^{3,4}. For example, crystalline α -Bi₂Mo₃O₁₂ and γ -Bi₂MoO₆ with relatively higher surface area (8-10 m² g⁻¹) can be obtained already at 140°C using a hydrothermal approach⁴, avoiding a high temperature calcination step that would strongly decrease the specific surface area and therefore limit the catalytic activity. Controlling the pH value and Bi/Mo molar ratio in the starting reagent feed allows the selective formation of either phases. Low pH values and low molar Bi/Mo ratio favor the α -phase, vice versa high pH values and high molar Bi/Mo ratio yield preferentially the γ -phase. The β -Bi₂Mo₂O₉ phase, on the other hand, is challenging to obtain and usually requires a calcination step at 540°C min; recently Le and coworkers, however, were able to prepare crystalline β -Bi₂Mo₂O₉ already at low temperatures (175°C) by employing a microwave-assisted hydrothermal method⁵, instead of conventional heating. Overall, the hydrothermal approach has been proven as a promising method for pre-

paring these Bi-Mo oxides with good control on crystallinity, size distribution and aggregation, but several challenges are still present, for example a tighter control on phase purity is desired, as well as easier routes to the promising β - $\text{Bi}_2\text{Mo}_2\text{O}_9$ phase.

The focus of the PhD project is to advance the state-of-art of the informed design of these Bi-Mo oxides, towards improved structure-activity understanding, via the combination of controlled preparation, characterization, machine-learning modelling of the chemical space and catalytic activity monitoring. The overall aim is to minimize the need of a time-consuming trial-and-error exploration and acquire an holistic view on the targeted ad-hoc preparation.

Through a campaign of selected controlled syntheses and multi-approach characterizations (XRD, Raman, BET, TPR), coupled with an extensive literature analysis, a detailed curated synthesis dataset will be created with the aim of identifying the key structural descriptors regulating the catalytic activity (e.g., phase, particle size, specific surface area, presence of co-catalysts, etc.) and the associated synthesis parameters (e.g., max synthesis temperature, pH, molar ratios, duration of the thermal treatment, etc.). This dataset will serve as training and validation dataset for different machine-learning models that will be compared in regards of both (a) predicting the outcomes of different synthesis parameters (e.g. in terms of phase purity and particle size), and especially (b) determining the optimal synthetic parameters for a product with the desired chemico-physical and structural properties.

Further syntheses will be performed following the recommendations obtained from the machine-learning models, not only serving as a benchmark for the validity of these models, but also yielding optimized catalytic materials, that will be tested for their activity in selective oxidation of acrolein also through a secondment of 6 months at the Karlsruhe Institute of Technology (Karlsruhe, Germany), in the group of Prof. Jan-Dierk Grunwaldt (<https://www.itcp.kit.edu/grunwaldt/english/index.php>). During the secondment, further advanced characterizations (e.g., synchrotron-based X-ray absorption spectroscopy and X-ray diffraction, also under *operando* conditions) are also planned. Altogether, this will allow us to gain a full detailed understanding of the investigated systems, bridging the informed preparation (also thanks to the machine-learning models giving the possibility to predict potential synthesis outcomes), the complete structural and functional characterization, and the catalytic activity assessment.

The PhD project will develop in three years and will be organized as follows: M1-4 bibliography research, collection of literature parameters; M2-12 targeted syntheses and characterization; M8-16 development of machine-learning models; M16-24 validation of machine-learning models; M20-26 targeted syntheses for validation, advance characterization; M24-30: secondment at Karlsruhe Institute of Technology; M30-36: concluding experiments, writing of publications and thesis.

Overall, the project is highly multidisciplinary, encompassing the preparation and characterization of inorganic materials, their catalytic investigations, and the development and validation of machine-learning models for materials discovery. The PhD student could strongly benefit from this fertile research environment, gaining multifaceted know-how.

References

1. Stehle, M. *et al.* Complementary *operando* insights into the activation of multicomponent selective propylene oxidation catalysts. *J Catal* **408**, 339–355 (2022).
2. Sprenger, P., Kleist, W. & Grunwaldt, J.-D. Recent Advances in Selective Propylene Oxidation over Bismuth Molybdate Based Catalysts: Synthetic, Spectroscopic, and Theoretical Approaches. *ACS Catal* **7**, 5628–5642 (2017).
3. Schuh, K. *et al.* Bismuth Molybdate Catalysts Prepared by Mild Hydrothermal Synthesis: Influence of pH on the Selective Oxidation of Propylene. *Catalysts* **5**, 1554–1573 (2015).
4. Beale, A. M. & Sankar, G. In Situ Study of the Formation of Crystalline Bismuth Molybdate Materials under Hydrothermal Conditions. *Chemistry of Materials* **15**, 146–153 (2003).
5. Le, T. M. N., Guillou, N., Elkaïm, E., Aouine, M. & Millet, J. M. M. $\beta(\text{L})\text{-Bi}_2\text{Mo}_2\text{O}_9$: A new, highly active and selective, mild oxidation bismuth molybdate catalyst. *J Catal* **408**, 413–422 (2022).