

NATURE, ABUNDANCE AND DYNAMICS OF HYDROGENOUS SPECIES IN METAL SUPPORTED CATALYSTS UNDER HYDROGENATION REACTION CONDITIONS

Heterogeneous hydrogenation catalysts are strategic in a large number of industrial processes of practical importance. Understanding the hydrogen behaviour at the catalyst surface is fundamental to improve the catalyst performances, but is far from being understood. This project is aimed to the investigation of the structural and surface changes underwent by Pd and Pt-based hydrogenation catalysts in the presence of hydrogen during industrially relevant hydrogenation reactions. The attention will be focused on two main aspects: 1) the formation and stability of metal hydrides; and 2) the dynamic of the hydrogenous species in reaction conditions, including spill-over phenomena on the supports.

The main purpose of the present project is to reveal the changes occurring at the surface of industrial Pt- and Pd-based heterogeneous catalysts under the influence of hydrogen at low and high hydrogen pressure, and during industrially relevant hydrogenation reactions in both gas-phase and liquid-phase processes. To this aim, we intend to adopt a multi-technique approach that combines neutron scattering techniques and DFT modelling (carried out at ILL) with FT-IR spectroscopy, H₂ adsorption and HR-TEM measurements (performed at UniTO) and CO chemisorption and TPR measurements (carried out by our collaborators in Chimet S.p.A). Synchronous DRIFT/XAS measurements (proposal submitted at BM26 at ESRF) and SAXS measurements are also foreseen.

The catalysts investigated within this project will be provided by our industrial partner Chimet S.p.A. Pd and Pt will be exploited as active metals, while activated carbons (differing in origin, activation and post-activation treatments), metal oxides (alumina, silica-alumina), porous polymers (with different functionalities), and metal-organic frameworks will be used as supports. Half of this PhD project work will be conducted at ILL and will be devoted: 1) to use INS as best suited technique for investigating the metal-hydride formation and hydrogen spillover to the supports, complemented by other neutron spectroscopies; and 2) to analyse the INS data with the assistance of DFT calculations. The other half of the project will be conducted at UniTO and will imply the use of FT-IR spectroscopy, H₂ adsorption and HR-TEM measurements, to complement the INS results.

In particular, the PhD student will:

- o be involved in all the stages of the project, and actively take part to the frequent meeting with Chimet S.p.A.;
- o be responsible for the preparation and execution of research proposals to perform neutron or X-ray experiments following the results of precedent measurements;
- o analyse the INS data with the help of DFT calculations carried out under the supervision of the ILL supervisor;
- o perform FT-IR experiments (also under realistic reaction conditions) and H₂ adsorption measurements under the supervision of the UniTO Thesis supervisor;
- o participate to HR-TEM measurements on a selection of catalysts investigated by the other techniques;
- o have access to our national and international collaboration network to perform experiments with complementary techniques, such as e.g. XPS;
- o collaborate closely with another PhD student in our group who is also working in the frame of the collaboration with Chimet S.p.A., and is in charge of the development of a DRIFT set-up in operando and of the performance of catalytic tests with the Catlab micro-reactor;
- o other academic-related activities