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Manyar, H. (2017). *Catalysis by Design: Understanding Catalyst structure-activity relationship at molecular level from fundamental and applied perspectives*. Abstract from International Conference on Sustainable Development of Energy and Environment, Pune, India.

**Document Version:**  
Peer reviewed version

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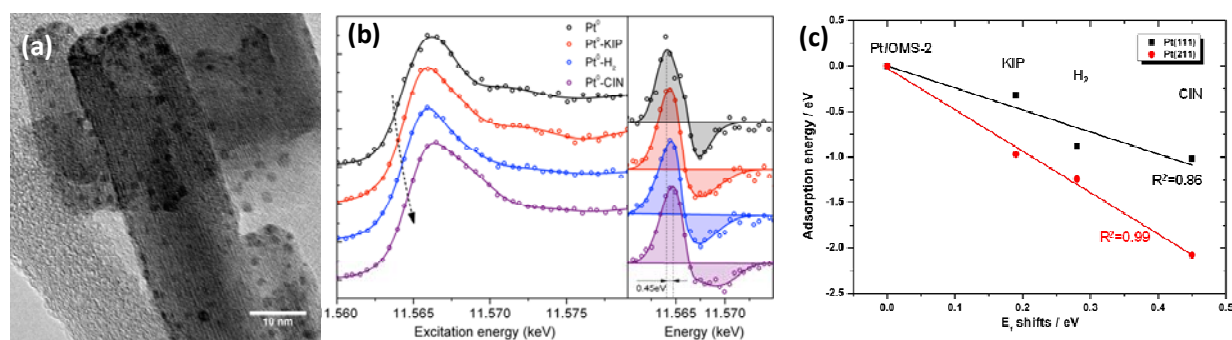
# Catalysis by Design: Understanding Catalyst structure-activity relationship at molecular level from fundamental and applied perspectives

Haresh G. Manyar\*

*CentACat, School of Chemistry & Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK.*

(\*) [h.manyar@qub.ac.uk](mailto:h.manyar@qub.ac.uk)

Catalysis is an enabling technology, playing a key role in sustainable, environmentally benign manufacture of chemicals with ~90% of chemical processes and ~35% of world's GDP relying on catalysis. It is possible to design new and improved catalysts to enhance activity and product selectivity by using multi-disciplinary approach. By understanding the mechanistic interactions at molecular level, by combining reaction kinetics, in situ spectroscopy and molecular modelling. Herein, we will establish rational design criteria by using selective chemical processes and catalysts such as hydrogenation of various arenes, aldehydes and ketones. We aim to understand molecular interactions at the catalyst active site using multidisciplinary approach based on computational simulations, *in situ* operando spectroscopy techniques and experimental adsorption isotherms. The insights obtained from theory and experiments were combined to establish rational design criteria for development of new catalysts. We have obtained new insights into control of selectivity of either C=C or C=O double bond using ketoisophorone and cinnamaldehyde as the exemplar molecules using manganese oxide octahedral molecular sieves (OMS-2) and Pt/OMS-2 catalysts [1,2]. We were also able to achieve selective hydrogenation of halogenated arenes to corresponding reduced arenes without dehalogenation [3]. High selectivities for reduction of C=C, 97% selectivity to levodione at 100% conversion were achieved by using OMS-2 and platinum supported on OMS-2 catalysts. In the case of cinnamaldehyde hydrogenation using Pt/OMS-2, reduction of C=O double bond was favoured forming cinnamyl alcohol with 80% selectivity at 96% conversion. Density functional theory (DFT) calculations showed the dissociation of H<sub>2</sub> on OMS-2 was water assisted and occurred on the surface Mn of OMS-2(001) modified by an adsorbed H<sub>2</sub>O molecule. For the first time, an *in situ* study on the interaction of molecules with a supported metal catalyst in a pressurized reactor by means of X-ray absorption spectroscopy (XAS). This approach to the best of our knowledge has never been used to evaluate the influence of adsorbed molecules on the electronic structure of the active site in the liquid phase. The change in the Pt electronic structure following the adsorption of ketoisophorone and cinnamaldehyde was followed by *in situ* XANES. Excellent agreement is found between the HERFD-XANES shifts observed in Figure 1b and the adsorption energies calculated by DFT as shown in Fig. 1c on both the Pt(111) and Pt(211) surfaces and provides insight into the reaction selectivity. The relative adsorption strengths of ketoisophorone and cinnamaldehyde on the OMS-2 support compared with the Pt was found to determine the product selectivity. This demonstrates, for the first time, that, the combination of state-of-the-art spectroscopy (HERFD-XANES) and theoretical calculations is a powerful and versatile tool to reveal differences in adsorption behaviour for reactants in the liquid phase under reaction conditions. Direct hydrodeoxygenation of plant oils and fatty acids into renewable biofuels and alcohols is an attractive alternative to transesterification of triglycerides (FAMES). Understanding the reaction mechanisms in carboxylic acid and amide hydrogenations allowed us to design new catalyst structures based on synergistic effects of bimetallic sites in close proximity to perform such demanding hydrogenations (industrially 100-200 bar H<sub>2</sub> pressures, 200-300 °C) under mild conditions (5-30 bar H<sub>2</sub> pressures, 60-130 °C). It was possible to tune product selectivity to either hydrocarbons or long chain alcohols.



**Figure 1.** (a) HR-TEM image of 5 wt% Pt/OMS-2, (b) Pt L<sub>III</sub> edge HERFD-XANES spectra of Pt/OMS-2 interacting with H<sub>2</sub>, KIP and CIN and corresponding shifts in the Fermi energy ( $E_f$ ). (c) Correlation between the experimentally measure shifts in the HERFD-XANES spectra and the calculated adsorption energies from DFT for the Pt(111) and Pt(211) surfaces.

## References

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