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Porous manganese oxides materials: remarkably versatile redox catalysts

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Selective reduction and oxidation (redox) reactions are of great importance in production of numerous fine and pharmaceutical chemicals, environmental catalysis and abatement of organic pollutants in water. Noble metals such as Au, Pt, Re, Ru and Ir are often used as catalysts in redox reactions. However, considering the expensive cost and limited abundance of noble metals, it is of high interest to explore other transition metal catalysts. Manganese is second only to iron among the transition metals in its abundance in Earth's crust. Its similar to iron in physico-chemical properties and primarily occurs as manganese dioxide in a number of substantial deposits of mineral ores. Manganese oxides can be synthesized in a variety of different structural forms including porous molecular sieves and layered morphologies. Porous manganese oxide materials have received significant interest over past two decades, due to outstanding properties as versatile materials for potential applications in catalysis, membranes, fuel-cells, sensors and absorptive systems. The catalytic activity of porous manganese oxides can be further enhanced by tuning the structure and morphology, ion-exchanging with H⁺, doping with other metals and mixing with other metal oxides. Herein, we will demonstrate the versatility of porous manganese oxide materials based catalysts in a variety of selective redox processes such as liquid phase hydrogenation of various arenes, aldehydes and ketones, oxidation of alcohols, 5-hydroxymethyl furfural, exemplar environmental catalysis for instance oxidation of CO, CH₄, propane, and soot oxidation. We will attempt to establish rational design criteria by combining experimental data with adsorption isotherms, *in situ* operando spectroscopy techniques and computational simulations.

We have obtained 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. We were also able to achieve selective hydrogenation of halogenated arenes to corresponding reduced arenes without dehalogenation. 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 H₂ on OMS-2 was water assisted and occurred on the surface Mn of OMS-2(001) modified by an adsorbed H₂O molecule. 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. We have also shown that addition of CeO₂ to OMS-2 can significantly enhance the catalytic activity of diesel oxidation catalysts by lowering the T_{50%} conversion of CO and propane. We have also demonstrated tuning of OMS-2 structure and thermal phase transition can lead to superior catalytic activity in soot oxidation.

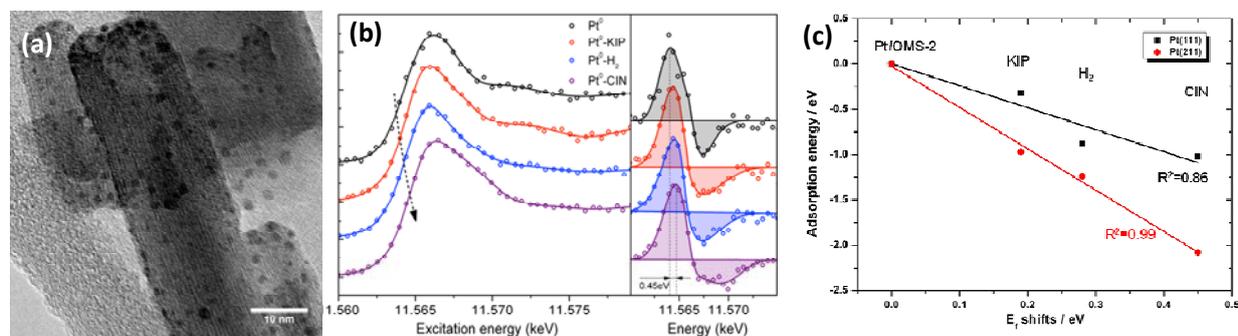


Figure 1. (a) HR-TEM image of 5 wt% Pt/OMS-2, (b) Pt L_{III} edge HERFD-XANES spectra of Pt/OMS-2 interacting with H₂, KIP and CIN and corresponding shifts in the Fermi energy (E_f). (c) Correlation between the experimentally measure shifts in the HERFD-XANES spectra and the calculated adsorption energies from DFT for the Pt(111) and Pt(211) surfaces.