

Advances in Selective Hydrogenation of α,β -unsaturated Aldehydes and Ketones using porous Manganese Oxide (OMS-2) and Platinum supported OMS-2 Catalysts

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Introduction

Selective hydrogenation of α,β -unsaturated aldehydes and ketones is of great importance in fine chemical industry. In this study, 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 5 wt% Pt/OMS-2 catalysts. For the first time, OMS-2 has been shown to be an efficient and selective hydrogenation catalyst. High selectivities for either the C=C or C=O double bond at ~100% conversion were achieved by using OMS-2 and platinum supported on OMS-2 catalysts [1,2]. 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 theoretically calculated activation barrier was in good agreement with the experimentally determined value for the hydrogenation reactions. A significant increase in the rate of reaction was observed in the presence of Pt due to the enhancement of H₂ dissociative adsorption and subsequent reaction on the Pt or spillover of the hydrogen to the OMS-2 support. For the first time, an *in situ* study on the interaction of molecules with a supported metal catalyst in liquid phase in a pressurized reactor by means of X-ray absorption spectroscopy (XAS) was performed. 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. The resulting shift in the Pt Fermi energy is in good agreement with the molecule adsorption energy trends calculated by DFT 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.

Materials and Methods

OMS-2 and 5 wt% Pt/OMS-2 catalysts were synthesized at QUB and the HRTEM image of the catalyst is shown in Figure 1a. Hydrogenations were carried out in a 100 cm³ Autoclave Engineers pressure reactor. *In situ* liquid phase XANES was performed in a homemade stainless steel autoclave reactor with a polyether ether ketone (PEEK) window. The Pt L_{III} edge was monitored using High Energy Resolution Fluorescence Detector (HERFD) at the SuperXAS beamline of the Swiss Light Source (SLS).

Results and Discussion

In the hydrogenation of ketoisophorone using OMS-2 catalyst at 373 K and a hydrogen pressure of 1 MPa, the reaction was completed in less than 4 h, with >97%

selectivity to levodione. In the case of cinnamaldehyde hydrogenation using 5wt% Pt/OMS-2, reduction of C=O double bond was favored forming cinnamyl alcohol with 80% selectivity at 96% conversion. DFT was used to examine the mechanism for H₂ dissociation as well as the adsorption strength of ketoisophorone and cinnamaldehyde on OMS-2 and Pt. The adsorption of ketoisophorone on Pt was found to be much weaker than that on OMS-2, indicating that most of the ketoisophorone adsorbs on the OMS-2 sites even in the presence of Pt. This result is consistent with the fact that the selectivities for ketoisophorone hydrogenation are similar using both OMS-2 and Pt/OMS-2. In contrast, cinnamaldehyde adsorbs more strongly on Pt compared with OMS-2. In this case, when the catalyst contains Pt, preferential adsorption and reaction takes place on the Pt and thus contrasting selectivities are observed using Pt/OMS-2, i.e. the reaction favors cinnamyl alcohol formation whilst the OMS-2 favours hydrocinnamaldehyde formation. To probe these differences experimentally, Pt L_{III}-edge HERFD-XANES was measured in the liquid phase experiments. Figure 1b shows the resulting data and the Fermi energy level shifts observed. Excellent agreement is found between the HERFD-XANES shifts observed and the adsorption energies calculated by DFT as shown in Figure 1c on both the Pt(111) and Pt(211) surfaces.

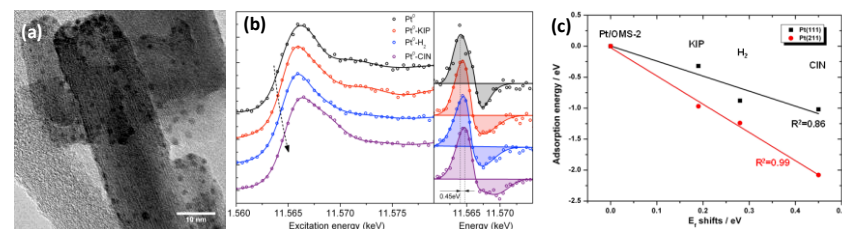


Figure 1 (a) HR-TEM image of 5 wt% Pt/OMS-2, (b) Pt L_{III} edge HERFD-XANES spectra of Pt/OMS-2 interacting with H₂, KIP and CIN and corresponding shifts in the Fermi energy (E_f). (c) Correlation between the experimentally measure shifts in the HERFD-XANES spectra and the calculated adsorption energies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

Significance

OMS-2 has been shown to be an efficient and selective hydrogenation catalyst. DFT calculations showed the dissociation of H₂ on OMS-2 was water assisted. This demonstrates, for the first time, that, the combination of state-of-the-art spectroscopy (HERFD-XANES) and theoretical calculations is a powerful tool to reveal differences in adsorption behavior of reactants in the liquid phase under reaction conditions and relate this to product selectivity. This strategy can be implemented for the study of other liquid phase catalytic processes.

References

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