



Dehydrogenation and Oxidative Dehydrogenation of *n*-Butane using Vanadium Based Catalysts: an in situ XPS study

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Scientific Background and Aims

Catalytic dehydrogenation of light alkanes is a valuable reaction for the production of essential building blocks required for industrial applications. One reaction of particular interest is the dehydrogenation of *n*-butane to form butenes and butadiene, which are precursors for the manufacture of synthetic rubber. Currently many commercial processes for the dehydrogenation of light alkanes contain chromia or platinum supported on alumina. The process is endothermic, requiring high reaction temperatures and low pressures. Unfortunately at higher temperatures cracking can occur and formation of coke or carbonaceous deposits is enhanced, resulting in catalyst deactivation. Hence oxygen regeneration steps are required to remove carbon deposits from the catalyst surface. Research continues in this area as it is important to understand the nature of the active species and causes of deactivation in order to develop future catalysts.

Vanadia-containing catalysts have been shown to be active as selective dehydrogenation or oxidative dehydrogenation catalysts [1, 2]. In the current study, we selected V_xO_y /alumina catalysts with a range of vanadium loadings and used surface sensitive techniques to develop links between surface structure and catalytic activity.

Results and Discussion

The surface electronic structure of V_xO_y /alumina catalysts (1-8 wt% V) was investigated using high pressure in situ XPS. Typically the catalyst surface was examined under either a dehydrogenation (0.4 mbar *n*-butane) or oxidative dehydrogenation (0.4 mbar 1-2 % oxygen in *n*-butane) atmosphere. The reaction products were monitored concurrently by proton transfer reaction mass spectrometry (PTRMS).

In an oxygen atmosphere, the XP spectrum (figure 1) shows that vanadium is in the +5 oxidation state. Comparison of the NEXAF spectrum (figure 2) of the oxygen

treated catalyst suggests the presence of polymeric and dimeric vanadates, which is in good agreement with literature for V_xO_y /alumina catalysts [3]. Dehydrogenation and oxidative dehydrogenation (ODH) of *n*-butane were investigated over the 3.5% V/alumina catalyst. For both reactions, the catalysts were found to be active and the major products formed were butene and butadiene. On addition of oxygen (1-2 %) to the feed, the product selectivity changed and formation of oxygenated side-products, such as furan and dihydrofuran, increased. The change of feed to include oxygen also caused a decrease in formation of benzene which has been associated with catalyst deactivation.

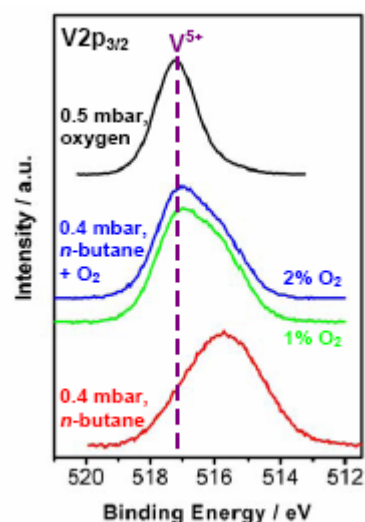


Figure 1: $V2p_{3/2}$ XPS of 3.5% V/alumina under varying reaction conditions.

Vanadium XP (figure 1) and NEXAF (figure 2) spectra measured during the reactions confirm that addition of oxygen to the reaction mixture helps to maintain a V^{5+} species. In particular the $V2p$ XPS (figure 1) shows marked differences in the oxidation state of the vanadium species under varying reaction conditions. Pure *n*-butane as the reactant shows an increase in reduction with an average oxidation state of vanadium less than 4. Ideally, the oxygen

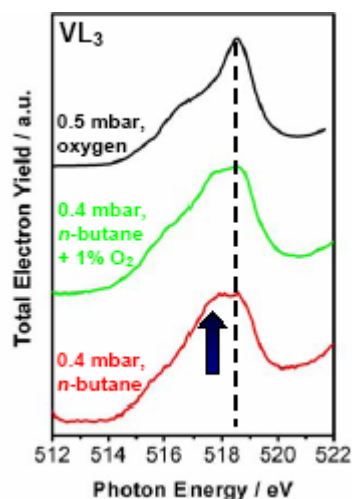


Figure 2: VL₃ NEXAFS of 3.5% V/alumina under varying reaction conditions.

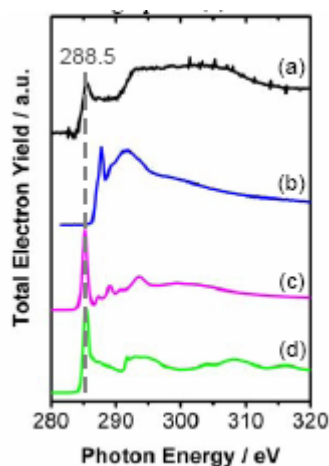


Figure 3: C K-edge NEXAFS of post-reaction 3.5% V/alumina (a) and reference spectra of n-butane [4] (b), benzene [4] (c) and graphite (d)

content of the feed could be optimised to reduce formation of oxygenated side products while maintaining a higher vanadium oxidation state.

Finally, the 1, 3.5 and 8 % V/alumina catalysts were examined ex situ after deactivation under ‘real’ dehydrogenation conditions (1 bar *n*-butane, 723 K). V2p XPS showed a main peak at 515.9 eV, indicating that mainly V³⁺ species were present. Hence the vanadium was greatly reduced during the deactivation process. The carbon K-edge absorption spectrum for the 3.5% V/alumina (figure 3a) and 8% V/alumina are similar, the predominant feature at 288.5 eV shows the presence of unsaturated hydrocarbons when compared with reference compounds (figure 3). Due to the absence of higher energy features, it is unlikely that the carbon species is solely graphite. The carbon NEXAFS of 1% V/alumina (not shown) was similar to that of a styrene reference [5].

This is in agreement with Raman spectroscopy studies [6] which suggest that polystyrene is an intermediate in the formation of carbon deposits during dehydrogenation over V_xO_y/alumina catalysts.

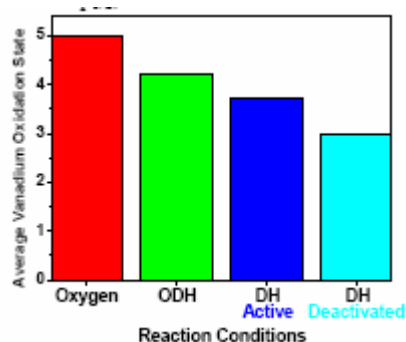


Figure 4: Average vanadium oxidation state, calculated by deconvolution of V2p_{3/2}, under reaction conditions.

By combining the results of the in- and ex-situ experiments, a general trend relating vanadium oxidation state to catalytic activity under different reaction conditions can be observed (figure 4). Under dehydrogenation conditions (*n*-butane, 723 K) the vanadium oxidation state decreases with time on stream. After this initial change carbon was deposited on the catalyst surface, causing deactivation of the catalyst. Hence, the investigations suggest that maintenance of a higher oxidation state of vanadium is a crucial step in preventing catalyst deactivation.

Conclusions

In the final analysis, high pressure in situ XPS and NEXAFS were shown to be useful analytical techniques for the investigation of V_xO_y/alumina surfaces under reaction conditions. The benefit of oxidative dehydrogenation was to maintain a higher oxidation state of vanadium; however more oxygenated side-products were produced. Links between the electronic structure of vanadium and catalytic activity were successfully established.

Acknowledgements

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