



Dehydrogenation of C4 hydrocarbons using vanadium based catalysts

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Scientific Background and Aims

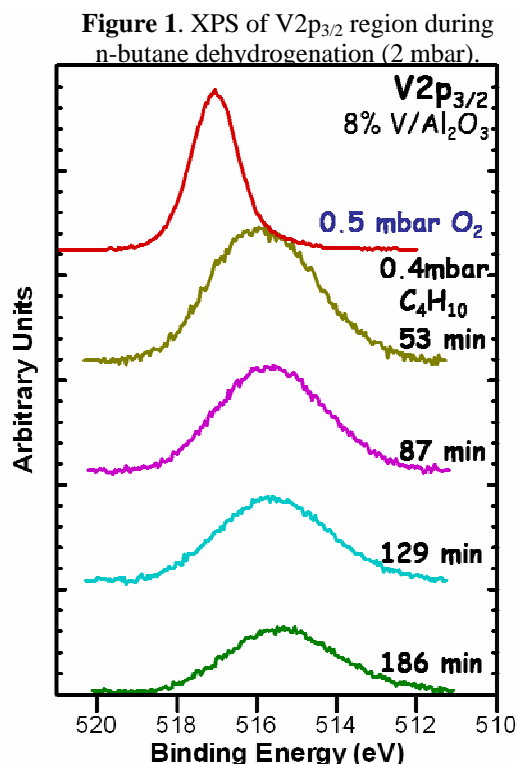
Dehydrogenation of n-butane to butene and butadiene is a highly interesting commercial process due to increasing demand for unsaturated hydrocarbons for industrial applications. Many commercial processes for the dehydrogenation of light alkanes use catalysts containing chromia or platinum supported on alumina. The dehydrogenation of alkanes is an endothermic process, which requires high reaction temperatures and low pressures. Unfortunately at higher temperatures light alkanes are produced and coke formation is encouraged causing catalyst deactivation. Oxygen treatment can be used to regenerate the catalyst, hence prolonging the life-time of the catalyst.

This study forms part of the ATHENA project one of the goals of which is to investigate selective gas-phase alkane dehydrogenation. As part of an international collaboration our aim is to utilise the techniques of high pressure *in-situ* XPS and NEXAFS to investigate the electronic structure of the vanadium species under reaction conditions. The techniques are used to gain a better understanding of alumina-supported V_xO_y based catalysts through investigation of their structure-reactivity relationships. In addition, *ex-situ* experiments (typically at 100 mbar pressure) were used to examine the differences in the reaction products and final state catalyst at increased pressure. By performing the experiments in an adjoining reaction chamber, the sample could be transferred under reaction gas atmosphere.

Results and Discussion

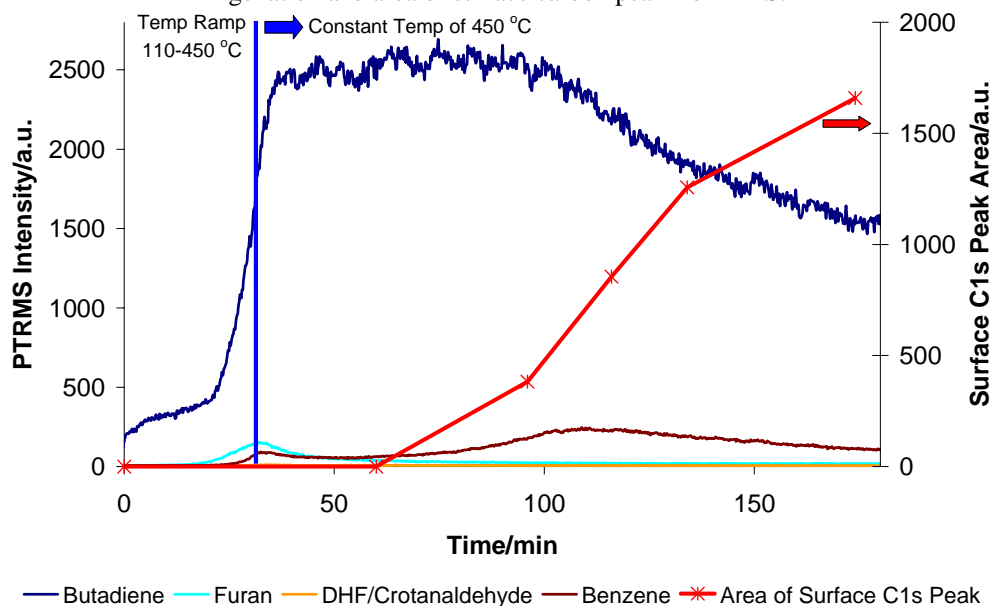
The electronic structure of vanadia/alumina catalysts was examined during the dehydrogenation of n-butane. High-pressure measurements were made possible due to a specially designed, differentially pumped, electrostatic lens system. Hence spectra could be measured while the cell

pressure was maintained at 2 mbar. The reaction products were detected using a Proton Transfer Reaction Mass Spectrometer (PTRMS). An 8% V/alumina catalyst was examined both *in-* and *ex-situ* for the n-butane dehydrogenation reaction at partial pressures of 0.4 and 100 mbar of butane respectively.



After an initial treatment in oxygen, the 8% V/alumina catalyst contained predominantly V_2O_5 crystallites. This is in agreement with literature, as at vanadium loadings above one monolayer of V on alumina crystalline V_2O_5 is expected to be the major species^{1,2,3}. However,

Figure 2. PTRMS reaction profile for 8% V/alumina during n-butane dehydrogenation and area of surface carbon peak from XPS.



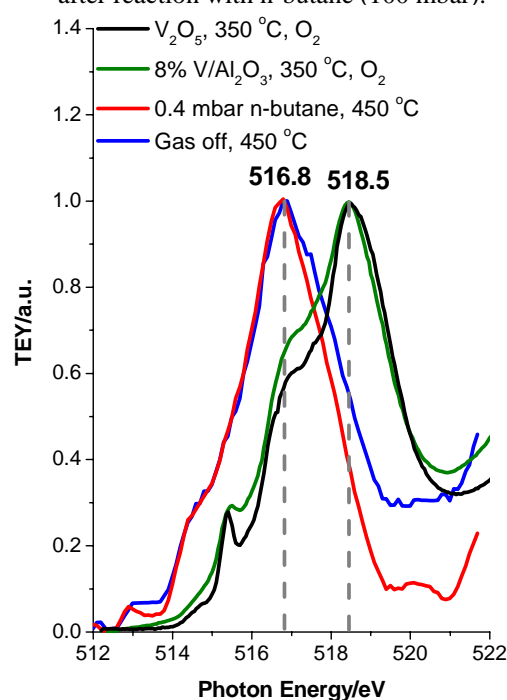
immediately after introduction of butane gas NEXAFS (not shown) reveals that the V_2O_5 structure is lost. This effect is confirmed by the XP spectra, which show a reduction of the vanadium species coupled with a decrease in intensity during the reaction (figure 1). The initial reduction may be due to removal of oxygen from the catalyst in the form of oxygenated products. Furan and dihydrofuran/crotonaldehyde) were observed as the catalyst was heated to reaction temperature. After 87 mins there is a further shift in binding energy and a reduction in intensity. The shift to lower binding energy suggests a decrease in the vanadium oxidation state. This correlates with the formation of a surface carbon species, which is the main source of deactivation for dehydrogenation catalysts.

Figure 2 shows the trends of the reaction products: butadiene, furan, DHF/crotonaldehyde and benzene (butene not shown). There is a steep increase in the surface carbon content, which correlates with a maximum in benzene formation and is proportional to the decrease in butadiene formation. The carbon was identified as chain/graphitic carbon.

Therefore investigation of the surface species under reaction conditions has identified two stages. During reaction the vanadium species is reduced to contain a mixture of V^{5+} and V^{4+} . At this point the catalyst is active and shows only slow deactivation. The second step is the deposition of carbon on the surface, which leads to further deactivation. This deactivation is mainly due to carbon laydown, which blocks the active vanadium sites.

As with the *in-situ* experiment, the *ex-situ* reaction showed formation of oxygenated products during heating in n-butane. Due to the higher partial pressure of n-butane, the catalyst rapidly deactivated over a period of only 30

Figure 3. NEXAFS VL_3 edge before and after reaction with n-butane (100 mbar).



minutes. A steep decline in activity was detected where benzene production reached a maximum. Hence it is likely that this point coincided with the formation of surface carbon, similarly to the *in-situ* reaction. Once transferred to the measurement cell, NEXAFS (figure 3) showed a great reduction in the vanadium species and XPS indicated high surface carbon content. The total percentage of elemental carbon detected on the catalyst surface was 46 %. The ratio of vanadium to aluminium decreased on comparison of pre-

and post-reaction catalysts, suggesting that carbon laydown occurs preferentially on the vanadium.

Acknowledgements

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