Low Temperature Oxygen Chemisorption: A Facile Technique for Characterization of Vanadium Oxide Catalysts Supported on Anatase and Rutile Polymorphs of TiO$_2$

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Oxygen chemisorption at $-78\,°C$ has been determined on the reduced surface of vanadium oxide catalysts supported on anatase and rutile modifications of TiO$_2$; a correlation is found between oxygen chemisorption capacities with the activity of the catalysts for vapour-phase oxidation of methanol to formaldehyde.

Low temperature oxygen chemisorption (LTOC) has received increased attention recently, as a surface-specific probe for characterization of supported molybdena,[1—4] vanadia,[5—7] and tungsten sulphide[8—10] catalysts. This technique allows active phase dispersion in supported catalysts to be determined quantitatively. Attempts have been made to correlate oxygen chemisorption capacities of the catalysts with their activities for hydrodesulphurisation (HDS) reactions. However, only scant information has been reported using supported vanadia catalysts. The present work was undertaken with a view to investigate the differences in the dispersion of vanadium oxide supported on anatase and rutile separately and their performance towards oxidation of methanol to formaldehyde.

A series of V$_2$O$_5$ catalysts with V$_2$O$_5$ loadings ranging from 2 to 14% by weight supported on anatase (surface area 92 m^2 g^{-1}) and rutile (surface area 33 m^2 g^{-1}) were prepared by impregnation of an aqueous solution containing NH$_4$VO$_3$. The catalysts were subsequently dried and calcined at 500 °C for 6 h. Oxygen chemisorption experiments were performed using a static high vacuum system followed by the method of Parekh and Weller.[1] The details of experimental procedure are described elsewhere.[5] A flow microreactor interfaced with a gas chromatograph and operating under normal atmospheric pressure was used for the vapour-phase oxidation of methanol at 150 °C. The feed gas (air) was passed through two saturators containing methanol. The main reaction product, *i.e.*, formaldehyde, was analysed by a column containing 10% Carbowax 20M on Chromosorb. Traces of dimethyl ether were also found in anatase supported catalysts owing to the dehydration of methanol. Pure supports were found to be inactive under these experimental conditions.
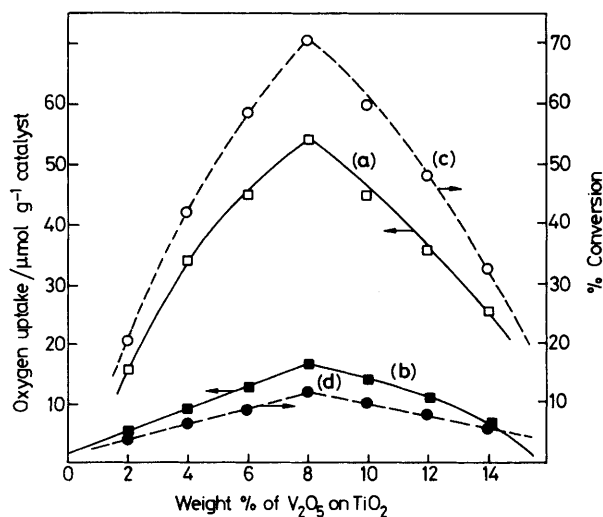
Results of oxygen chemisorption capacities of various catalysts are plotted as a function of V$_2$O$_5$ content in Figure 1, which shows that the oxygen uptake capacity increases with V$_2$O$_5$ content up to 8% w/w of V$_2$O$_5$ on TiO$_2$ and decreases at higher loadings. This behaviour is attributed to the formation of a monolayer of vanadium oxide with a high degree of dispersion on anatase and rutile surfaces. Evidence for this observation is provided by X-ray diffraction results of these catalysts wherein the most intense X-ray diffraction (XRD) line due to V$_2$O$_5$ corresponds to the (001) plane and was observed from 8 wt.% V$_2$O$_5$ onwards, in both anatase and rutile supported catalysts. The intensity of these lines increases gradually as a function of the V$_2$O$_5$ content in the catalyst. The absence of XRD lines due to V$_2$O$_5$ below 8 wt.% (within the monolayer) on both anatase and rutile indicates that the vanadium oxide is present in a highly dispersed amorphous state on TiO$_2$. Beyond the monolayer level (8% w/w of V$_2$O$_5$) the gradual decrease of oxygen uptake with an increase in vanadia content is due to the formation of a crystalline vanadia phase. Consequently, not all the active vanadium oxide phase is available for titration with oxygen chemisorption. In both anatase and rutile, irrespective of their crystallographic structures, the maximium oxygen uptake is observed at 8% w/w of V$_2$O$_5$. The oxygen chemisorption capacities of vanadia supported on anatase are higher ($\sim$3—4 times) than the corresponding rutile supported ones, suggest-
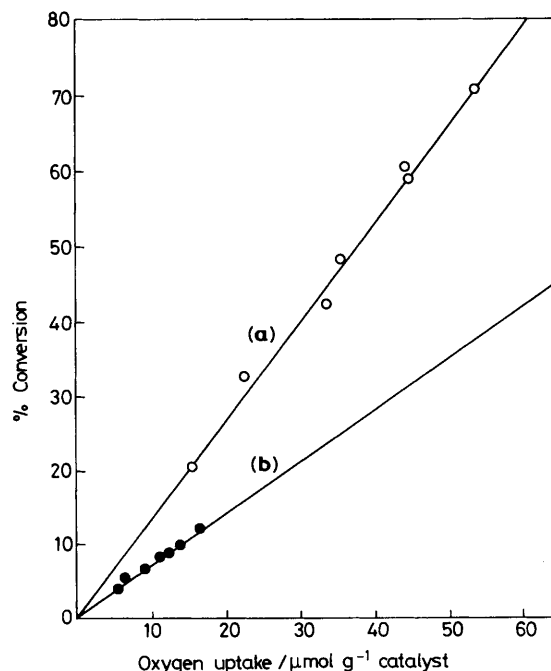

Figure 1. Oxygen uptake as a function of V$_2$O$_5$ loading and conversion to formaldehyde as a function of V$_2$O$_5$ loading of various catalysts: (a) □ V$_2$O$_5$/TiO$_2$ (anatase); (b) ■ V$_2$O$_5$/TiO$_2$ (rutile); (c) ○ V$_2$O$_5$/TiO$_2$ (anatase); (d) ● V$_2$O$_5$/TiO$_2$ (rutile).

Figure 2. Conversion to formaldehyde as a function of oxygen uptake for various catalysts: (a) ○ V$_2$O$_5$/TiO$_2$ (anatase); (b) ● V$_2$O$_5$/TiO$_2$ (rutile).

ing a better dispersion of vanadia on anatase than on rutile. The dispersion of vanadia ('O'/V_2O_4) calculated from oxygen chemisorption of monolayer catalysts (corresponds to 8 wt.% of V_2O_5) of anatase and rutile was 28.4 and 8.1% respectively. The poor dispersion of vanadia on rutile might be due to the presence of larger crystallites of V_2O_5 on rutile surface than on anatase. Oxygen chemisorbs selectively at low temperature ($-78\,°C$) on co-ordinatively unsaturated sites (CUS) generated upon reduction. These CUS are located on the highly dispersed vanadia phase which is formed at low vanadia loadings and remains as a 'patchy-monolayer' on the TiO_2 surface.

The percentage conversion of methanol to formaldehyde during partial oxidation of methanol, which is plotted as a function of vanadia content and oxygen uptake by various catalysts in Figure 1, increases with V_2O_5 content up to a certain level (8% w/w; corresponds to monolayer) and decreases at higher V_2O_5 content. The results suggest that the V_2O_5 phase attaining the monolayer capacity is more highly active than the other catalysts. The activities on anatase supported catalysts are very high and about six times greater than those for the rutile supported ones. The variation of oxygen uptake with the percentage conversion of methanol to formaldehyde is shown in Figure 2. The results clearly demonstrate that the percentage conversion to formaldehyde is directly proportional to the amount of oxygen chemisorbed at $-78\,°C$ by the pre-reduced catalysts. The linear correlation suggests strongly that the catalytic functionality of the dispersed vanadia phase on TiO_2 responsible for the selective oxidation of methanol to formaldehyde is located on the 'patchy monolayer' phase and that this functionality can be titrated by the LTOC technique.

Thus LTOC is found to be a valuable method for characterization of vanadium oxide catalysts supported on anatase and rutile modifications of TiO_2.

References

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