A Transmission EXAFS Study of V_2O_5–TiO_2 Selective Oxidation Catalysts: Evidence that the Active Phase is Disordered

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Extended *X*-ray absorption fine structure (EXAFS) studies beyond the vanadium K-edge of supported V_2O_5 catalysts show that the catalytically active surface phase supported on anatase is not in epitactic registry with the TiO_2 but is in a state of structural disorder.

Supported V_2O_5 catalysts are of considerable commercial importance since they exhibit high activity and selectivity in the oxidative conversions of hydrocarbons: *e.g.* phthalic anhydride, the precursor of anthraquinone and several useful esters, is formed from *o*-xylene in high yield at modest temperatures on the catalyst provided that vanadium oxide is laid down in thin layers upon a TiO_2 (anatase) support.[1] Doubt exists as to the mechanisms of this reaction, but in most formulations to date it has been either tacitly assumed or explicitly stated that there is a close, epitactic match between the (010) planes of V_2O_5 and the predominant growth planes of the anatase substratum.[2,3] Our EXAFS results, summarized below, cannot be interpreted on this basis; and they suggest other attributes which this active, supported catalyst (and others possibly) possess.

By employing $VOCl_3$ which reacts with hydroxy groups on the exposed anatase faces, it is possible to lay down in coherent contact with this support close to monolayer amounts of V_2O_5. Using finely divided anatase (150 $m^2\ g^{-1}$) prepared by hydrolysis of titanium(IV) butoxide, the concentration of the vanadium which constitutes a monolayer could be increased so that 7 mole % of V_2O_5 was attained. This is sufficient to enable conventional transmission measurement to be made for the *X*-ray absorption coefficient. The measurements were recorded using the Daresbury (S.E.R.C.) facility. As vanadium and titanium are adjacent elements in the periodic table some fine-structure from the Ti K-edge propagates under the V K-edge, and this contribution was subtracted. To eliminate dis-

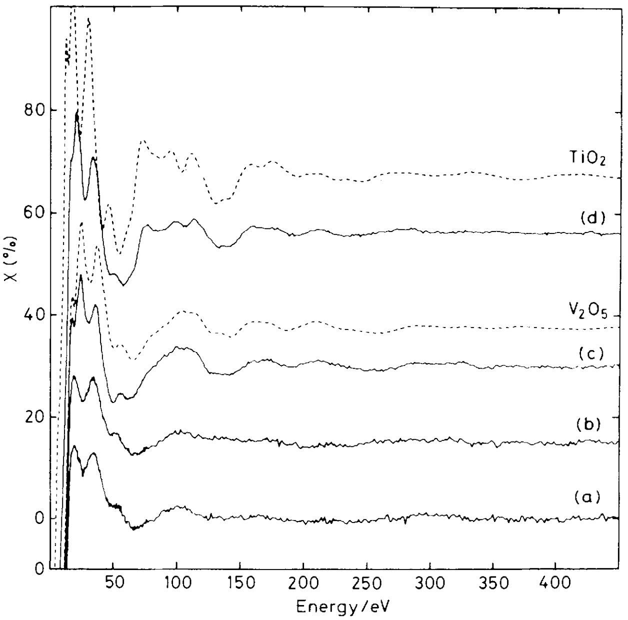

Figure 1. EXAFS spectra for the vanadium-edge of the V_2O_5 monolayer on TiO_2 after 5 h heat treatment at various temperatures: (a) 70 °C, (b) 350 °C, (c) 600 °C, (d) 650 °C. 'V_2O_5' and 'TiO_2' are EXAFS spectra of crystalline V_2O_5 and TiO_2 (rutile), respectively.

tortions from the finite energy resolution of the monochromator, sample thickness absorption products were kept small (μ_x *ca.* 1). The energy scale was calibrated by reference to a well defined pre-edge feature of vanadium at 5469.5 eV.

Figure 1 shows the EXAFS spectrum beyond the K-edge of vanadium for a catalyst prepared as described above but after 5 h heat treatment at the temperatures indicated. EXAFS spectra of crystalline V_2O_5 and rutile (TiO_2) are also shown.

The lack of fine structure, apparent in the EXAFS spectrum of the vanadium oxide phase in the catalytically active, supported material (curves a and b), is due to disorder together with a beat phenomenon. Our full paper will discuss the evidence for the occurrence of a surface species in which vanadium has two terminal and two bridging bonds to oxygen. The variance of the V–O bond length is larger (of the order of 3 to 4 × 10^{-3} Å^2) than that found in the VO_4^{3-} ion. No V–V scattering was observed, and this implies a very large variance in the V–V distance. The existence of two short (1.65 ± 0.05 Å) and two long (1.90 ± 0.05 Å) surface V–O bonds of magnitude comparable with those expected of terminal and bridging V–O bonds, respectively, in chain vanadates,[4] could be deduced from our results.

This condition is retained after heating to *ca.* 400 °C. On further heating (to *ca.* 600 °C, curve c) it is known from *X*-ray diffraction and microcalorimetric measurements that the finely dispersed anatase sinters and the vanadium oxide is liberated. Clearly the jettisoned oxide is, from its EXAFS spectrum, indistinguishable from crystalline V_2O_5. Upon further heating (to 650 °C) some oxygen is expelled and a solid-solution, $Ti_{(1-x)}V_xO_4$, possessing a rutile structure, forms. Significantly the EXAFS spectrum beyond the vanadium K-edge for this phase closely mirrors that of the titanium K-edge of pure rutile, a fact which confirms the identification of the phase and the expected similarity in phase factors between Ti and V. Accurate measurement of mass loss accompanying expulsion of oxygen on heating confirmed that the vanadium was in the v oxidation state.

X-Ray absorption near-edge structure measurements reinforce the picture that emerges from the EXAFS measurements: that the catalytically active monolayer 'vanadium oxide' species is disordered.

The principal feature of this work is the evidence that the arrangement of fundamental, structural units in the catalytically active surface phase is not translationally ordered and epitactic. It also raises the possibility, to be explored in later work, as to whether one of the main functions of an efficient support is to engender a sufficiently disordered local structure possessing a range of interatomic distances and/or large vibrational amplitudes.

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