Localization of Surface V=O Species on a Specific Crystal Plane of $(VO)_2P_2O_7$

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The surface concentration of the V=O species of $(VO)_2P_2O_7$ catalysts was revealed to be proportional to the exposure of the (020) plane, indicating that the surface V=O species are localized on the (020) plane.

$(VO)_2P_2O_7$ is an active and selective catalyst for the oxidation of *n*-butane to maleic anhydride (MA), and many papers have been devoted to relating its selectivity to structural factors. Some authors claimed that the selectivity for MA depends on the exposure of a specific crystal plane, *i.e.* the (020) plane.[1–4] Low selectivity for the other planes has been confirmed through the selective coating of the (020) plane with a silica over-layer.[4] Another structural factor suggested is the presence of specific surface oxo-species. Centi *et al.* claimed that surface V=O species are responsible for allylic oxidation and ring insertion of oxygen.[5] The present study aims to clarify the relation between the (020) plane and the surface V=O species of $(VO)_2P_2O_7$ for the elucidation of an effective structure for the selective oxidation.

Two series of $(VO)_2P_2O_7$ catalysts having various P/V ratios (P/V = 0.95–1.08) were prepared by (*a*) refluxing an *iso*-butyl alcohol and benzyl alcohol solution of V_2O_5 and H_3PO_4[6] (VPO-OR) and by (*b*) evaporating an aqueous solution of V_2O_5, 85% H_3PO_4 and $NH_2OH{\cdot}HCl$[7] (VPO-AQ) followed by calcination in flowing 1.5% *n*-butane–air at 823 K for 3 h. The surface area of these series was around 14 $m^2\ g^{-1}$ (VPO-OR) and 8 $m^2\ g^{-1}$ (VPO-AQ), respectively. Scanning electron micrographs (SEM) were measured with a Hitachi S-800S instrument. The number of surface V=O species was determined by using the NARP (nitric oxide-ammonia rectangular pulse) technique[8] modified for $(VO)_2P_2O_7$ catalysts.[6]

According to SEM micrographs, both VPO-AQ and VPO-OR catalysts consisted of plate-like crystallites, though the crystallites of VPO-AQ were larger and thinner than those of VPO-OR. For example, the crystallites of VPO-AQ (P/V = 1.00) were 800 ± 300 nm in length and 35 ± 20 nm thick, while those of VPO-OR (P/V = 1.04) were 450 ± 200 nm in length and 100 ± 30 nm thick. On the basis of the observed length and thickness of each crystallite, the ratio of the basal plane to the whole surface area, *i.e.* the exposure of basal plane, was calculated. VPO-AQ has a higher exposure of the basal plane than VPO-OR: the exposure was 90 ± 3% for VPO-AQ (P/V = 1.00) and 65 ± 6% for VPO-OR (P/V = 1.04). The average exposure of the basal plane of VPO-AQ catalysts ranged from 75 to 90% depending on the P/V ratio, while that of VPO-OR catalysts ranged from 60 to 70%. The exposure of the basal plane was proportional to the relative intensity of the (020) line with respect to the major peaks in the XRD pattern, *i.e.* $I_{020}/(I_{020}+I_{204}+I_{302})$, indicating the basal plane can be attributed to the (020) plane of $(VO)_2P_2O_7$. This result agreed well with the fact that $(VO)_2P_2O_7$ has a layer-type structure with a major development of the basal (020) plane.[4,9,10]

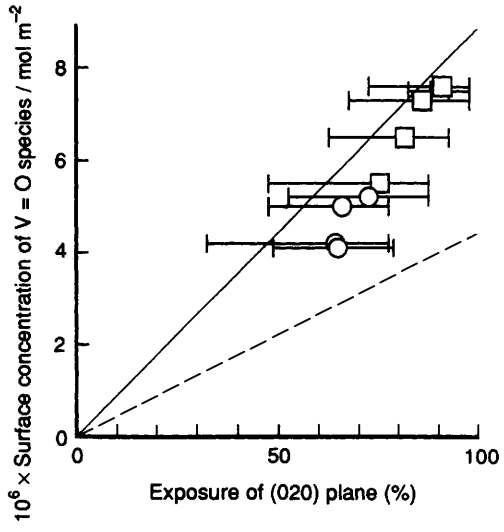

Fig. 1 Surface concentration of V=O species with exposure of the (020) plane of VPO-AQ (□) and VPO-OR (○) catalysts. Solid and broken lines represent the surface concentration of vanadium ions and exposed V=O species on the (020) plane.

The number of surface V=O species measured by the NARP technique also varied with the preparation method and the P/V ratio. On average, VPO-AQ has more of the surface V=O species. Fig. 1 shows the relation between the exposure of the (020) plane determined from SEM micrographs and the surface concentration of V=O species. Error bars represent the distribution of the exposure of the (020) plane. As shown in Fig. 1, the surface concentration of V=O species increases in proportion to the exposure of the (020) plane, irrespective of the method of preparation. This correlation suggests that the surface V=O species are localized on the (020) plane.

The localization of the V=O species on the (020) plane is supported by the agreement between the correlation in Fig. 1 and the crystal structure of $(VO)_2P_2O_7$. From the crystal structure, the concentration of vanadium ions per unit area of the (020) plane is 8.4×10^{-6} mol m^{-2} (020), which is twice the concentration of exposed V=O bonds.[9] This is because vanadyl pseudo-octahedra have a *trans*-configuration.[4,9,10] Solid and broken lines in Fig. 1 represent the respective surface concentrations, of vanadium ions and exposed V=O species on the (020) plane. As shown, the surface concentration of the V=O species measured by the NARP technique is very close to that of surface vanadium ions. This result indicates that the configuration of the V=O double bonds in the top layer changes from *trans* to *cis* to expose the V=O double bond. Such a rearrangement of the surface layer is quite possible, because $(VO)_2P_2O_7$ is easily transformed to other phases having various configurations of vanadyl octahedra, such as β-$VOPO_4$, δ-$VOPO_4$, γ-$VOPO_4$, β′-phase *etc.*[1–3,9]

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References

1 I. Matsuura and M. Yamazaki, *New Developments in Selective Oxidation*, ed. G. Centi and F. Trifiro, Elsevier, Amsterdam, 1990, p. 563.
2 E. Bordes, *Catal. Today*, 1993, **16**, 21.
3 Y. Zhang, R. Sneede and J. C. Volta, *Catal. Today*, 1993, **16**, 31.
4 K. Inumaru, T. Okuhara and M. Misono, *Chem. Lett.*, 1992, 1955.
5 G. Centi, F. Trifiro, G. Busca, J. R. Ebner and J. T. Gleaves, *Proc. 9th Int. Congr. Catal.*, 1988, **4**, 1538.
6 D. Ye, A. Satsuma, T. Hattori and Y. Murakami, *Appl. Catal.*, 1991, **69**, L1; D. Ye, A. Satsuma, A. Hattori, T. Hattori and Y. Murakami, *Catal. Today*, 1993, **16**, 113.

7 T. Shimoda, T. Okuhara and M. Misono, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2163.
8 A. Miyamoto, Y. Yamazaki, M. Inomata and Y. Murakami, *J. Phys. Chem.*, 1981, **85**, 2366; 2372.
9 E. Bordes, P. Courtine and J. W. Johnson, *J. Solid State Chem.*, 1984, **55**, 270.
10 G. Busca, F. Cavani, G. Centi and F. Trifiro, *J. Catal.*, 1986, **99**, 400.