

## Structure Sensitivity of the Catalytic Oxidation of n-Butane to Maleic Anhydride

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Disorder along the (020) cleavage plane of the  $(VO)_2P_2O_7$  catalyst considerably enhances the activity of the selective oxidation of n-butane to maleic anhydride.

Vanadium-phosphorus oxides with a P:V atomic ratio close to 1.0 are the catalysts most commonly utilized for the selective oxidation of n-butane to maleic anhydride.<sup>1</sup> The active phase in the oxidation of n-butane and but-1-ene is a vanadyl pyrophosphate  $[(VO)_2P_2O_7]$ ,<sup>2-5</sup> but the activity depends on the method of preparation of the active phase (in aqueous or organic media).<sup>4,5</sup> The oxidation of but-1-ene on active phases prepared by different methods<sup>6</sup> showed no great differences in activity, but in the selective oxidation of n-butane,<sup>5,7-9</sup> only the active phase prepared by reduction of  $V_2O_5$  or  $VOPO_4$  in an organic medium (such as isobutyl alcohol) shows high activity.

We report here the relationship between the activity of two phases of  $(VO)_2P_2O_7$  in n-butane and but-1-ene activation and the modification of the crystalline structure as shown by X-ray diffraction analysis.

Catalyst (a) was prepared in an aqueous medium by the reduction of  $V_2O_5$  with 37% HCl, the addition of orthophosphoric acid, concentration of the solution, and subsequent addition of water to obtain a blue precipitate which was removed from the solution by filtration. The precipitate was dried in an oven at 130 °C (24 h) and calcined for 3 h at 420 °C first in air and then for an additional 3 h in a mixture of 1% n-butane and air. The final catalyst had a surface area of 6 m<sup>2</sup>/g and a P:V ratio of 1.05.

Catalyst (b) was prepared in an organic medium by the reduction of  $V_2O_5$  with isobutyl alcohol, addition of ortho-

phosphoric acid and subsequent filtration of the slurry. The powder was dried for 24 h in an oven at 130 °C and then calcined in the same manner as catalyst (a). The final catalyst had a surface area of 27 m<sup>2</sup>/g and a P:V ratio of 1.02.

The catalytic tests were performed in an isothermal

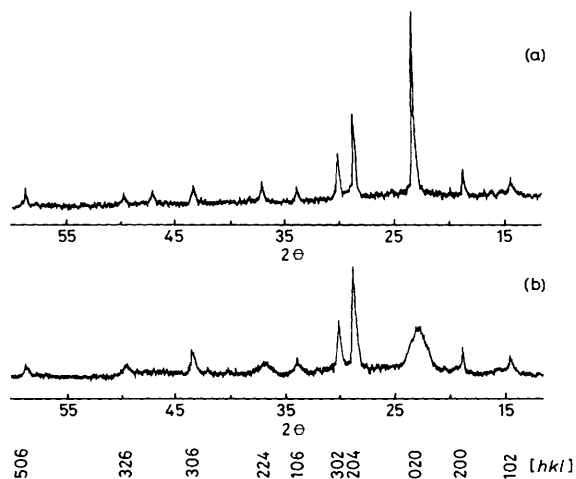
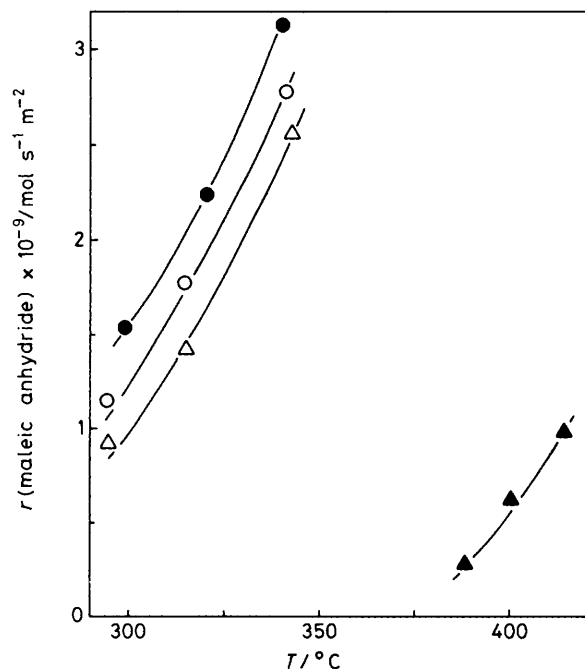


Figure 1. X-Ray diffraction patterns of  $(VO)_2P_2O_7$ , Cu- $K_\alpha$  radiation, (after the catalytic tests) prepared according to methods (a) and (b).

stacked-pellet flow reactor<sup>7,9</sup> using a mixture of 0.63% vol. hydrocarbon, 10.2% vol. oxygen, and 89.2% vol. nitrogen. In all cases, 1 g of catalyst was used. The amount of maleic anhydride formed was determined by absorption in water and titration with 0.1 M NaOH. The amount of maleic anhydride was also determined by g.c. using a Poropak QS column and a flame ionization detector. The feed composition was determined by g.c.

The X-ray diffraction patterns (X.R.D.) of the two catalysts after catalysis are shown in Figure 1. No variation in the X.R.D. patterns are observed before and after the catalytic



**Figure 2.** Specific rate (per m<sup>2</sup> surface area of catalyst) of maleic anhydride formation from n-butane (filled symbols) and but-1-ene (open symbols) as a function of the reaction temperature. Catalyst (a): (● ○); catalyst (b): (▲ △).

tests. The X.R.D. patterns correspond well to those of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>;<sup>2,10</sup> however, in catalyst (b) considerable disorder is present along the (020) cleavage plane of the crystalline structure. In contrast, in catalyst (a) a crystalline (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> structure is present and, in agreement with data reported in the literature,<sup>2,10</sup> the diffraction line corresponding to the (020) plane is the most intense.

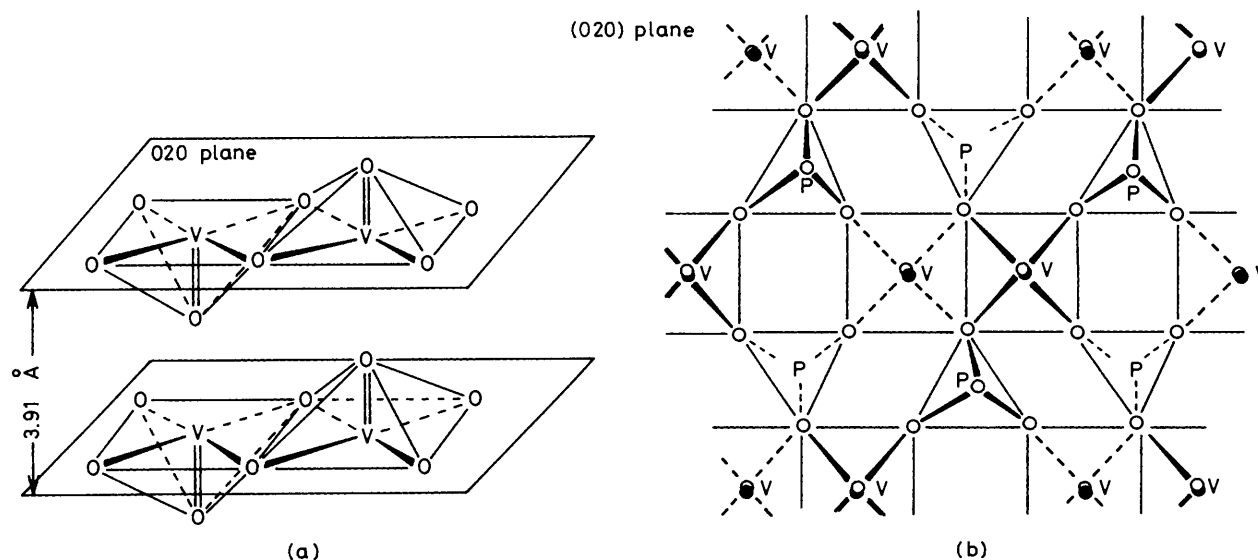
Figure 2 shows the specific rates of maleic anhydride formation (per m<sup>2</sup> surface area of catalyst) from n-butane and but-1-ene on the two catalysts. Although the two catalysts show similar rates of maleic anhydride formation from but-1-ene, there is a considerable difference in activity for n-butane oxidation. Thus, n-butane oxidation is a 'structure sensitive reaction'.

Previously<sup>11</sup> we have suggested that the mechanism of oxidation of n-butane to maleic anhydride passes through an initial stage of dehydrogenation to butene. This suggests that the difference in activity of the two catalysts is related to the first step in the activation of n-butane, in agreement with the rate limiting step in the kinetics of n-butane oxidation.<sup>7</sup>

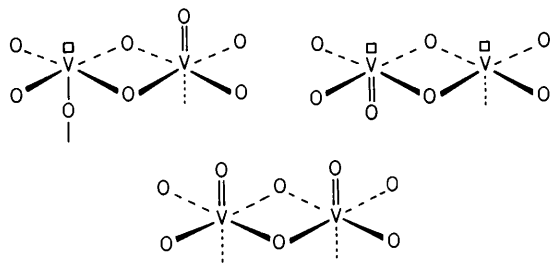
These results indicate that disorder along the (020) cleavage plane of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> increased the number of active sites for n-butane activation but did not modify the nature of the active centres for the subsequent oxidation of but-1-ene to maleic anhydride.

The structure of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> consists of chains of V polyhedra linked by pyrophosphate groups in a three-dimensional skeleton. The structure contains vanadyl phosphate layers perpendicular to the *c* axis,<sup>10</sup> with a surface arrangement as shown in Figure 3.

The presence of two neighbouring vanadium atoms, one with a vacancy in the co-ordination sphere and the other with double bonded oxygen suggests an allylic activation of but-1-ene. However X-ray diffraction patterns indicate that only in catalyst (b), the one able to activate n-butane, the distance associated with the (020) plane is not well-defined, but varies within a range of distances. We suggest that disorder in this plane may derive from defects in the structure, possibilities for which are shown in Figure 4. The disorder along the (020) plane can derive from lack of an oxygen atom, from inversion from a *trans* to a *cis* vanadyl position, or from the modification of the V–O bond strength. Whatever the



**Figure 3.** Idealized (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> structure: (a) only vanadyl groups; (b) projection along the (020) plane.



**Figure 4.** Possible local structural modifications of the  $(VO)_2P_2O_7$  structure.

cause, the defective structure leads to the formation of a highly reactive pair of vanadium ions, capable of activating the alkane *via* co-ordinative attack. The V-V distance (*ca.* 3.33 Å) corresponds well to the distance required to interact with the hydrogen atoms linked to the C-1 and C-3 atoms of n-butane.

In conclusion, we think that in order to activate n-butane selectively the presence of suitable neighbouring sites is necessary for simultaneous interaction: a centre able to abstract a hydrogen atom and a centre able to accommodate the excess electrons from the alkane.

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