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Oxidation Behavior of Vanadyl Pyrophosphate as a n-Butane Oxidation Catalyst

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$(VO)_2P_2O_7$ is oxidized to β-$VOPO_4$ via β'-phase (d = 4.87, 4.23, 3.19, 2.64 Å) which was probably a phosphate such as $VPO_{4.75}$ containing vanadium in the average oxidation state of + 4.5. However, when excess phosphorus is present in $(VO)_2P_2O_7$, oxidation stops at the stage of β'-phase. This suggests that the new phase, β'-$VPO_{4.75}$, is a selective catalyst for n-butane oxidation to maleic anhydride.

Vanadium-phosphorus oxides are effective catalysts for the synthesis of maleic anhydride by the direct oxidation of n-butane. Many patents[1)] and other publications[2-6)] state that highly selective and active catalysts for n-butane oxidation to maleic anhydride can be obtained at a P/V atomic ratio in the range from 1.0 to 1.2. Chevron[1a)] stated in his patent that vanadium-phosphorus oxide called B-phase, $(VO_2)_2(P_2O_5)_{1.2}$ is a particularly active catalyst; however, the XRD values presented in his patent are essentially the same as those of $(VO)_2P_2O_7$. Recently, Misono et al.[7)] prepared pure $(VO)_2P_2O_7$ and reported this as the active species of the catalyst for the synthesis of maleic anhydride by the direct oxidation of n-butane.

This communication reports new findings on the relationship between the oxidation behavior of vanadyl pyrophosphates prepared with different P/V atomic ratios and their catalytic activities for the oxidation of n-butane into maleic anhydride.

Catalysts with P/V atomic ratios ranging from 0.95 to 1.20 were used in this study and they were prepared as follows. Ten grams of vanadium pentoxide were added to 100 ml of isobutyl alcohol and hydrogen chloride gas was introduced into this mixture for five minutes with stirring. The orange vanadium pentoxide was reduced to a brown organic vanadyl compound with the formula $(CH_3)_2CH_2O(VO)OCH_2(CH_3)_2$. To the resulting solution, a given amount of orthophosphoric anhydride was added and the mixture was heated under reflux at 120 °C for 2 h. The green solution obtained was transferred to a crucible, and heated at 150 °C for 1 h, then at 200 °C for 1 h, and finally at 250 °C for 4 h to dryness. The solid thus obtained was further calcined at 350 °C for 4 h to give a catalyst precursor.

Catalytic tests were carried out in a tubular flow reactor with 3 g of catalyst at different flow rates by passing artificial air containing 1.5 vol% of n-butane. Table 1 shows the results obtained when about 75% of n-butane

Table 1. Catalytic Activity for n-Butane Oxidation to Maleic Anhydride

Catalyst P/V	W/F g h mol^{-1}	C_4H_{10}-Conv. %	MAA-Select. %	MAA-Yield wt%
0.95	20	72	56	68.1
1.00	46	75	62	78.6
1.05	78	74	71	88.8
1.10	92	76	78	100.2
1.20	107	72	78	94.9

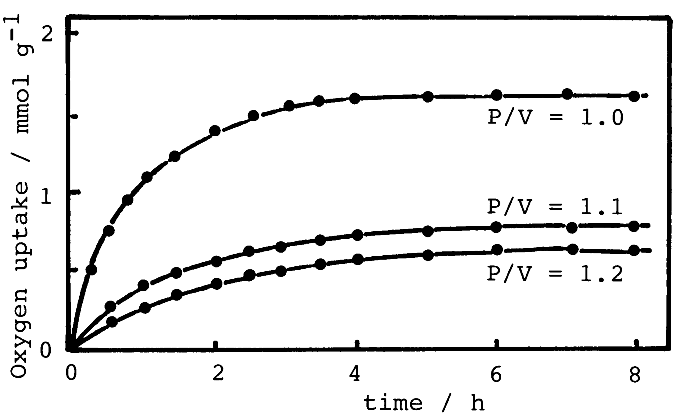

Fig. 1. Rate of oxygen uptake in the used catalyst at 550 °C.

was oxidized in reactions conducted at 420 °C at different flow rates. Catalytic activity decreased with increasing P/V atomic ratio, while selectivity to maleic anhydride increased with P/V atomic ratio until a plateau of 78% was reached at a P/V atomic ratio of 1.1. After the reaction, the catalyst was immediately removed and subjected to XRD measurement. Only peaks corresponding to $(VO)_2P_2O_7$ could be observed for each catalyst. Catalyst surface area range from 10 to 13 m^2 g^{-1}.

Each catalyst, recognized as $(VO)_2P_2O_7$ by XRD analysis, was oxidized at 550 °C in an ordinary constant-volume gas adsorption apparatus. The amount of oxygen uptake by 1 g of catalyst with the passage of time are shown in Fig. 1. From the quantity of uptaken oxygen, it was apparent that the catalyst of P/V = 1.0 could be completely oxidized to VPO_5 (the oxidation state of V was +5). In the case of the catalysts with P/V = 1.1 and 1.2, the oxidation ceased when the oxygen uptake was reached to half of the uptaken oxygen by $(VO)_2P_2O_7$. The average oxidation state of vanadium in the catalysts is about + 4.5.

While conducting the oxygen-uptake experiment, the catalysts were subjected to XRD measurement at 550 °C in an oxygen gas atmosphere using in-situ XRD apparatus. The results are shown in Fig. 2 and 3. In the case of the catalyst with P/V = 1.0, the peak for $(VO)_2P_2O_7$ (d = 3.88, 3.14, 3.00 Å) attenuated with time, and unknown peaks (d = 4.87, 4.23, 3.19 Å) and the peaks for β-$VOPO_4$ (d = 4.62, 4.23, 3.19 Å) appeared. By further oxidation the peaks for $(VO)_2P_2O_7$ and

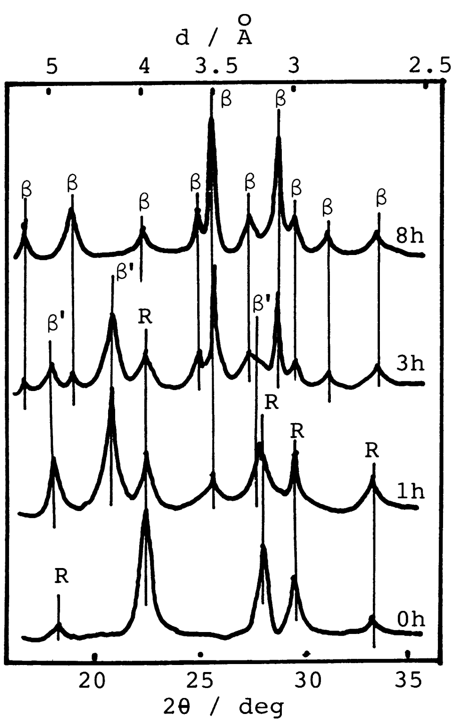

Fig. 2. Variation of XRD patterns of catalyst of P/V = 1.0 in an oxygen atmosphere at 550 °C.
R: $(VO)_2P_2O_7$, β: β-$VOPO_4$, β': β'-phase.

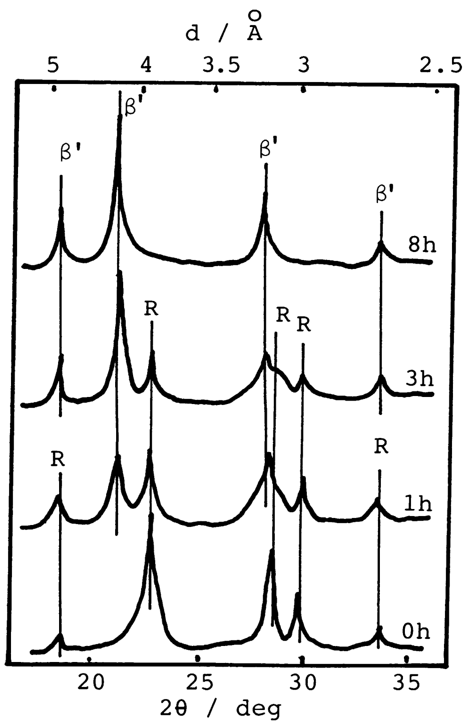

Fig. 3. Variation of XRD patterns of catalyst of P/V = 1.1 in an oxygen atmosphere at 550 °C.
R: $(VO)_2P_2O_7$, β': β'-phase.

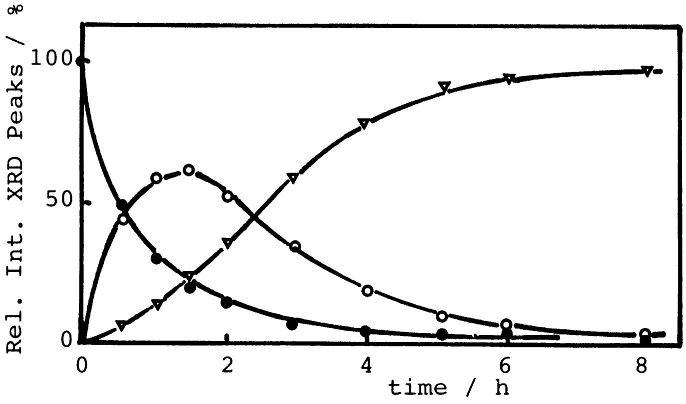

Fig. 4. Change of phase composition with oxidation time on catalyst of P/V = 1.0.
●: $(VO)_2P_2O_7$, ○: β'-phase,
▼: β-$VOPO_4$.

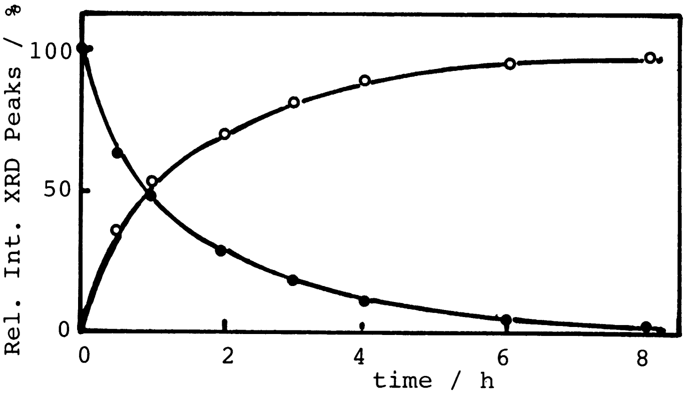

Fig. 5. Change of phase composition with oxidation time on catalyst of P/V = 1.1.
●: $(VO)_2P_2O_7$, ○: β'-phase.

unknown peaks disappeared, leaving only those corresponding to β-$VOPO_4$. In the case of the catalyst with P/V = 1.10, the peaks for $(VO)_2P_2O_7$ attenuated and those for the unknown peaks increased with time, finally leaving only the unknown peaks after 8 h. No peaks corresponding to β-$VOPO_4$ appeared in this case. The new XRD pattern (d/Å: 4.87(38), 4.23(100), 3.19(40), 2.64(23). 2.44(11), 2.10(6), 1.84 (7) relative intensity in parentheses) was different from either α-, α'-$VOPO_4$ or β*-phase, found by Hodnett et al.[8] In this paper we call this new phase β'-phase.

In Fig. 4 the principal peaks associated with each of these three phases, i.e. d = 3.88 for $(VO)_2P_2O_7$, d = 3.40 for β-$VOPO_4$ and d = 4.23 for β'-phase are plotted as a function of time for the catalyst of P/V = 1.0. These data show $(VO)_2P_2O_7$ is oxidized to β-$VOPO_4$ via β'-phase. The result for the catalyst of P/V = 1.10 is presented in Fig. 5. Stabilization of β'-phase by excess phosphorus may be noted. That β'-phase was observed in an oxidation experiment clearly indicates to be a phosphate such as $VPO_{4.75}$ containing vanadium in the average oxidation state of +4.5.

In conclusion, $(VO)_2P_2O_7$ is oxidized to β-$VOPO_4$ via β'-phase, but the oxidation ceases at the stage of β'-phase if excess phosphorus is present in $(VO)_2P_2O_7$. Thus, oxidation of n-butane to maleic anhydride by this type of catalyst may proceed by a redox reaction between $(VO)_2P_2O_7$ and $VPO_{4.75}$ (β'-phase).

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