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The Important Step of the Selective Oxidation of n-Butane over $(VO)_2P_2O_7$

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Catalytic oxidations of n-butane, 1-butene, and 1,3-butadiene to maleic anhydride have been carried out over $(VO)_2P_2O_7$, α-$VOPO_4$, and β-$VOPO_4$, of which the surface and bulk structures were examined by XPS and XRD. It was concluded that the reason why $(VO)_2P_2O_7$ was much superior in the selective oxidation of butane was its very high selectivity in the step of the dehydrogenation of butane to butene.

Selective functionalization of alkanes is an important target from both industrial and fundamental viewpoints. V-P mixed oxides are effective catalysts for the process to produce maleic anhydride from n-butane and the process has already been industrialized, although further improvement is eagerly needed.1) Previous studies have indicated that $(VO)_2P_2O_7$ in which the oxidation state of V is +4 is the effective component of the catalysts for the reaction.2-5) We have attempted to prepare $(VO)_2P_2O_7$, α-$VOPO_4$, and β-$VOPO_4$ as pure as possible, and after it had been confirmed by XRD and XPS that there were no phase changes during the use for catalytic oxidation, we demonstrated that the pure $(VO)_2P_2O_7$ was much more efficient than the others and gave a high selectivity which was comparable with the best data claimed in patents by using mixed-phase catalysts.6)

However, it has not been clarified yet why and in which step $(VO)_2P_2O_7$ is effective. It is very probable that butane is initially dehydrogenated to butene and then oxidized to maleic anhydride by a scheme shown in Eq. 1.,7)

$$\begin{tikzcd}
\text{butane} \arrow[r, "1"] \arrow[d] & \text{butene} \arrow[r, "2"] \arrow[d] & \text{butadiene} \arrow[r, "3"] \arrow[d] & \text{furan} \arrow[r, "4"] \arrow[d] & \text{maleic anhydride} \arrow[d] \\
CO_x & CO_x & CO_x & CO_x & CO_x
\end{tikzcd} \qquad (1)$$

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where CO_x (CO and CO_2) may be produced from all reactants.

In the present study, we have attempted to determine in which step of Eq. 1 the $(VO)_2P_2O_7$ catalyst is effective. We compared rates and selectivities of butane, as well as those of intermediate butene and butadiene, over the three catalysts, and found that $(VO)_2P_2O_7$ was specifically selective in the dehydrogenation of butane to butene, i.e., the step 1 of Eq. 1.

$(VO)_2P_2O_7$ (11.4 $m^2 \cdot g^{-1}$), α-$VOPO_4$ (8.4 $m^2 \cdot g^{-1}$), and β-$VOPO_4$ (3.7 $m^2 \cdot g^{-1}$) were prepared according to the previous paper.[2)] These were confirmed by XRD and IR to be single crystalline phases, as in the previous paper.[2)] The oxidations of butane, 1-butene, and butadiene were carried out using a conventional fixed-bed flow reactor at an atmospheric pressure. The feed gas consisted of 1.5 vol% butane, 17 vol% oxygen and nitrogen (balance). The reaction temperature was 440 °C for butane and 360-440 °C for 1-butene and butadiene. The products were analyzed by gas chromatographs using a VZ-10 column for butane, butene, butadiene, and CO_2 and a Porapak QS for maleic anhydride, furan, and acetic acid. A Molecular Sieve 5A column was used for O_2 and CO.

Figure 1 shows the selectivity to maleic anhydride as a function of the conversion of butane or 1-butene over the three catalysts. As shown in Fig. 1a, the oxidation of butane over $(VO)_2P_2O_7$ yielded maleic anhydride selectively (the selectivity was comparable with or better than the best data in patents) in the wide range of the conversion. On the other hand, the selectivity was very low over α- and β-$VOPO_4$. In all catalysts, the products in butane oxidation were

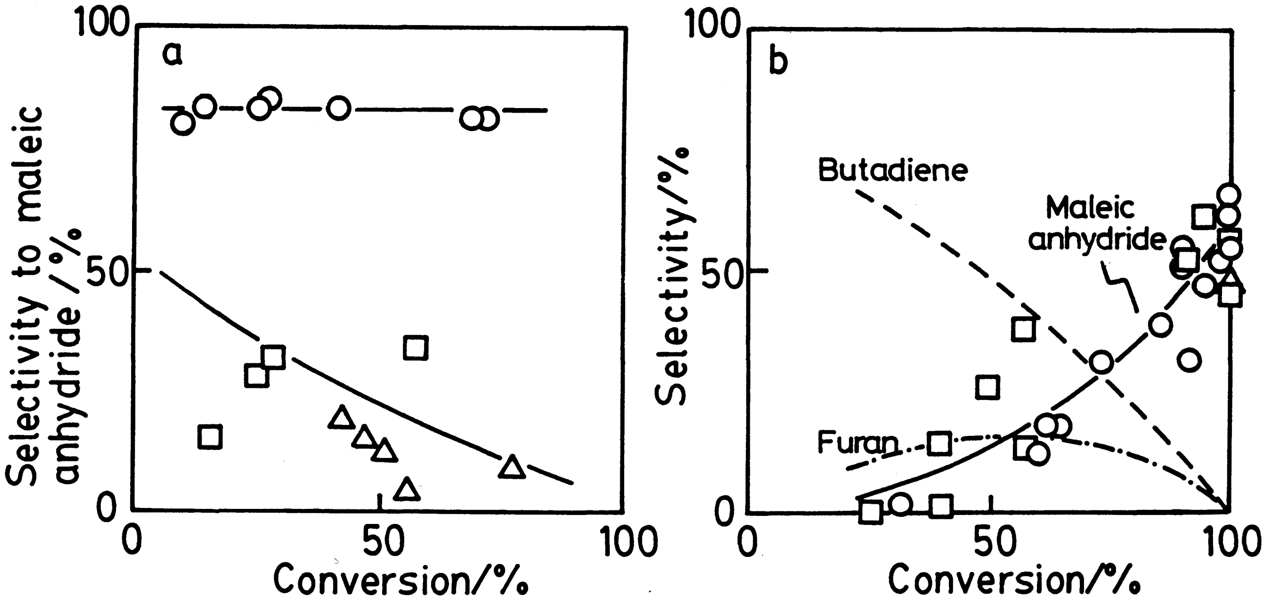

Fig. 1. Changes of the selectivity to maleic anhydride as a function of the conversion of oxidation of butane or 1-butene. (a) butane at 440 °C, (b) 1-butene at 360-440 °C (marks are for maleic anhydride).
○; $(VO)_2P_2O_7$, △; α-$VOPO_4$, □; β-$VOPO_4$

only maleic anhydride and CO_x. In the case of the oxidation of 1-butene (Fig. 1b), butadiene was the main product at the low conversions, and furan and maleic anhydride increased as the conversion increased. It is noted for the latter reaction that, although data are a little scattered, there were no significant differences among these catalysts in the selectivity-conversion correlation of these products. This is quite different from the result of the butane oxidation. Also in the oxidation of butadiene, the differences among the three catalysts were small.

Table 1. Catalytic Activity and Selectivity in Oxidation of Butane, 1-Butene, and Butadiene over Various V-P Oxides

Catalyst	Butane		1-Butene		Butadiene	
	A[a)]	S/%[b)]	A	S/%	A	S/%
$(VO)_2P_2O_7$	1	82	17	70	16	58
α-$VOPO_4$	3	14	65	81	56	75
β-$VOPO_4$	4	32	35	85	46	77

a) A: Reaction rate per unit surface area; 10^{-4} $mol \cdot m^{-2} \cdot h^{-1}$.

b) B: Selectivity to hydrocarbon products at about 50% conversion; on the basis of C_4.

The reaction was carried out at 440 °C and 1 atm (C_4-hydrocarbon; 1.5 vol%, O_2; 17 vol%, and N_2 balance).

Table 1 summarizes the catalytic activities and selectivities of the three catalysts for the oxidation of n-butane, 1-butene, and butadiene. There were only small differences in the relative rates of three hydrocarbons over each of the three catalysts. The reaction was 10-20 times faster for both butene and butadiene than for butane, indicating that the step 1 of Eq. 1 is the rate-determining step for the oxidation of butane over the three catalysts. The catalytic activities normalized to the surface area were similar for α- and β-$VOPO_4$, and they were three to four times those of $(VO)_2P_2O_7$ for the three hydrocarbons. As for the selectivity, the only difference among the catalysts is found in the selectivity of the oxidation of butane, as is already shown in Fig. 1. The selectivities of $(VO)_2P_2O_7$ for butene and butadiene were comparable with or a little lower than the others. Therefore, it may be concluded that $(VO)_2P_2O_7$ is superior in the selectivity of the step 1, that is, the dehydrogenation of butane to butene. Probably, the C-H dissociation of butane selectively proceeds on $(VO)_2P_2O_7$, while it does not on the others.

The changes in the bulk and surface structure of the catalysts under the working conditions were examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), in order to confirm the above conclusion. No changes were observed by XRD and XPS after use in the oxidation of butane for the three catalysts, as previously reported.[2,8] Even after use for butene oxidation, $(VO)_2P_2O_7$ showed no indication of change in the phase or in the oxidation state. This fact indicates that the V(IV) ions of $(VO)_2P_2O_7$ are stable and mostly present in the oxidation state of +4 under the reaction conditions. In the cases of α- and β-$VOPO_4$, decreases of the oxidation state in the surface layers were observed by XPS after use as reported in the literature;[8] from V(V) (518.5 eV) to mostly to V(IV) (517.6 eV) for β-$VOPO_4$ and from V(V) (518.6 eV) slightly to V(IV) (broader peak at 518.3 eV) for α-$VOPO_4$. XRD showed no changes in the bulk structure for α-$VOPO_4$ and change to a mixture of β-$VOPO_4$ and $(VO)_2P_2O_7$ for β-$VOPO_4$.

These XPS and XRD data would confirm the above conclusion. Since $(VO)_2P_2O_7$ exhibited no changes in the surface and bulk structure after its use as the catalyst for oxidations of butane and butene, the results for $(VO)_2P_2O_7$ are regarded to be its own characteristics. In α- and β-$VOPO_4$, reduction of the surface was observed after use for butene, although they showed no changes in the case of butane. So there is a possibility that butene formed in the oxidation of butane over α- and β-$VOPO_4$ was overoxidized due to their high oxidation states. This could be the reason of the low selectivity of $VOPO_4$ for butane. However, this possibility is less likely, since the three catalysts having different oxidation states showed a very similar selectivity for the oxidation of butene (Fig. 1). Therefore, the conclusion derived above can be rationalized.

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