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Promotion of V-P Oxide Catalyst for Butane Oxidation by Metal Additives

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Mixed oxide catalyst V-P-O for the butane oxidation to maleic anhydride was significantly promoted by the addition of some metal cations. In particular, the addition of a small amount of Bi (Bi/V=0.02) was the most effective. Over the Bi-added catalyst, the MA selectivity exceeded 70 mol% up to the butane conversion level of 88 mol%, attaining the maximum MA yield of 62 mol% at 395 °C.

The mixed oxide catalyst, V-P-O, containing a little excess phosphorus (P/V=1.05-1.20) has been solely employed in the industry for the synthesis of maleic anhydride (MA) from butane. Although many researchers[1-5] have ascribed its catalytic activity to the major crystalline phase of $(VO)_2P_2O_7$ included in it, the catalytic mechanism is still controversial. Our recent investigations[6,7] have shown that the surface of $(VO)_2P_2O_7$ tended to be covered with an amorphous layer having a composition of P/V=2. It has also been shown that the amorphous phase, when isolated, is as active as the unisolated catalysts for the butane oxidation. These findings has led us to propose that the catalytic activity of the catalyst is in fact provided with the amorphous layer covering $(VO)_2P_2O_7$ crystals. A remarkable fact about the catalyst is that the yield of MA remains still modest to date, not far exceeding 50 mol% in commercial production. A great deal of effort has been exerted to improve the MA yield. One such effort is to modify the catalyst with foreign additives. We have reported that, for the catalyst (P/V=1.1) prepared by a usual aqueous solution method,[8] the addition of Mg or Mn of the amount Mg/V or Mn/V =0.1 eventually increases the MA yield at the optimum temperature (maximum MA yield) to twice or more. These foreign additives are considered to be included in the surface amorphous layer. It is known that the catalyst prepared from an organic solution tends to show a larger specific activity for the butane oxidation mainly due to its larger specific surface area.[9] By use of this preparation method, we examined the effects of metal additives on the butane oxidation catalysis. As a result, significant promoting effects were observed with the addition of Mg, Mn, La, and Bi, and especially Bi brought about a maximum MA yield exceeding 60 mol%, as described below.

The V-P oxide catalyst (P/V=1) was prepared according to Trifiro et al.[9] The prescribed amount of V_2O_5 powder was mixed with an organic solution of benzyl alcohol (30 ml)-isobutyl alcohol (45 ml) and refluxed at 110 °C for 3 h. After standing at room temperature for 12 h under stirring, the solution was added with a prescribed amount of H_3PO_4 and again refluxed at 114 °C for 2 h to precipitate a precursor. The precursor was collected by filtration, dried at 150 °C for 24 h, and finally calcined at 400 °C for 1 h in air. Although the catalyst prepared in this way had a nominal composition of P/V=1, XPS measurements revealed that its surface was enriched in phosphorus, suggesting the formation of a surface amorphous layer similar to that mentioned above.

To prepare the metal added catalysts, an acetylacetonate of Mg, Mn, or La, or Bi chloride was added to the organic vanadium solution immediately after the addition of H_3PO_4, while the other procedures were kept the same. The amount of the metal (M) was set to M/V=0.1 (Mg, Mn) or 0.05 (La, Bi). The contents of Mg, Mn, and La in the prepared catalysts were confirmed to be close to the nominal compositions by means of X-ray fluorescence analyses. However, the content of Bi was found to be as low as Bi/V=0.02.

The oxidation of butane was carried out in a conventional fixed bed flow reactor at an atmospheric pressure in the temperature range 330-450 °C. The feed gas, 1.5 vol% butane diluted with air, was let to flow through the catalyst bed (1 g) at 40 $cm^3 \cdot min^{-1}$ ($SV=2400\ ml \cdot h^{-1} \cdot g^{-1}$-cat). The effluent was carried through a cold (ice) trap to remove MA. The trapped MA was intermittently (typically every 30 min) dissolved in water to be analyzed by titration with an aqueous NaOH solution. The remaining gaseous components (butane, CO, and CO_2) were analyzed by gas chromatography.

Figure 1 compares the catalytic performances of $VP_{1.0}$ and $VP_{1.0}Bi_{0.02}$ as a function of reaction temperature. The unmodified catalyst $VP_{1.0}$ showed butane conversions of 54-96 mol% and MA selectivities of 66-37 mol% in the temperature range of 380-450 °C, giving the maximum MA yield of 45 mol% at 430 °C. The modified catalyst $VP_{1.0}Bi_{0.02}$, on the other hand, was more active than $VP_{1.0}$ for the butane oxidation. In addition, MA selectivities exceeding 60 mol% were maintained up to the conversion level of 93 mol% at 405 °C. The maximum MA yield of 62 mol% was attained at 395 °C, with the MA selectivity of 70 mol% at the butane conversion of 88 mol%.

Table 1 summarizes some catalytic performances data of the modified and unmodified catalysts examined together with their specific surface areas (S.S.A). In accordance with the literature,[9] $VP_{1.0}$ catalyst prepared from the organic solution had large specific surface area (39 $m^2 \cdot g^{-1}$) than that prepared by the aqueous solution method (8.4 $m^2 \cdot g^{-1}$) and this brought about significant enhancements in butane conversion and MA yield. Compared with the unmodified catalyst, however, all the modified catalysts showed higher MA selectivities at high conversion levels and thus gave the maximum MA yields exceeding 50 mol%. Among the modified catalysts, $VP_{1.0}Bi_{0.02}$ gave the highest MA yield (62 mol%). The catalytic performance data of the modified catalysts can never be correlated simply with S.S.A. It appears that the metal cations added not only promote the specific activity for the butane oxidation but also maintain high MA

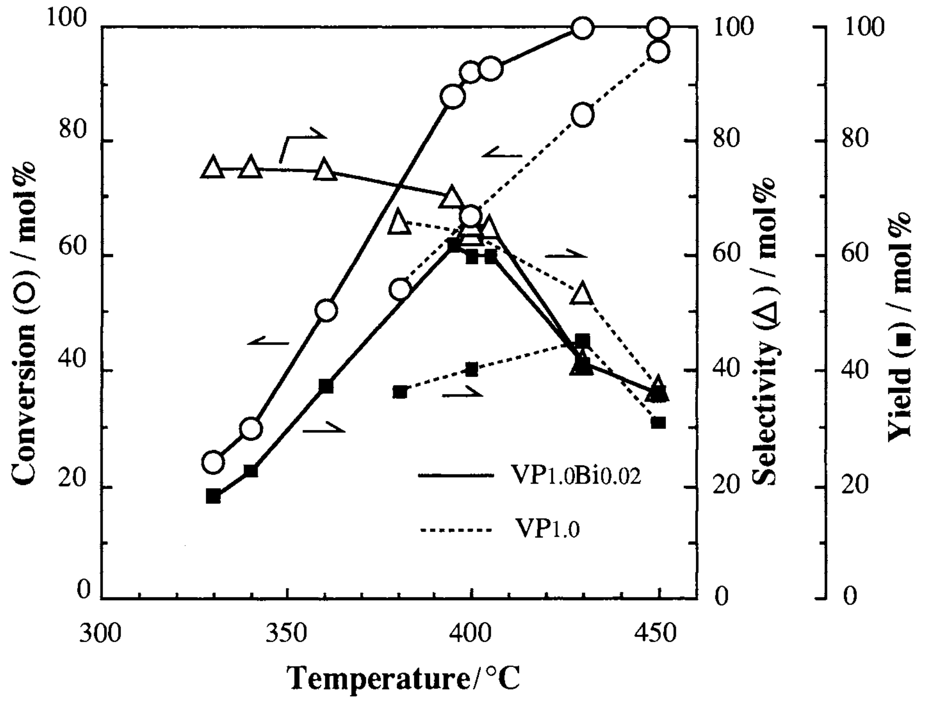


Fig. 1. Catalytic performances of $VP_{1.0}$ and $VP_{1.0}Bi_{0.02}$ as a function of reaction temperature.

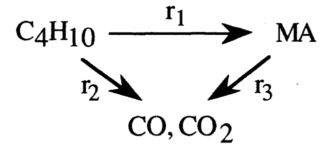
Table 1. Butane oxidation properties of modified and non-modified V-P-O catalysts

Catalyst	Temperature [a) /°C	Conversion / mol%	MA selectivity / mol%	MA yield / mol%	S.S.A. [b) / $m^2 \cdot g^{-1}$
$VP_{1.0}$	430	85	53	45	39
$VP_{1.0}Mn_{0.1}$(acac)	430	89	62	55	23
$VP_{1.0}Mg_{0.1}$(acac)	430	89	62	55	28
$VP_{1.0}La_{0.05}$(acac)	400	84	62	52	26
$VP_{1.0}Bi_{0.02}$(chloride)	395	88	70	62	43

a) Reaction temperature giving maximum MA yield. b) Specific surface area.

selectivities up to large conversion levels. The large surface area of $VP_{1.0}Bi_{0.02}$ (43 $m^2 \cdot g^{-1}$) may have resulted from the use of a chloride ($BiCl_3$) in the catalyst preparation.

Generally speaking, the partial oxidation of butane to MA (reaction 1) competes with the total oxidation to $CO+CO_2$ (reaction 2), while MA is further oxidized to $CO+CO_2$ (reaction 3), as shown in Scheme 1. Catalytic performances are influenced by the rates of the respective reactions (r_1, r_2, and r_3). To obtain high MA selectivities, the ratio r_1/r_2 should be large enough first of all. Similarly, r_3 should be suppressed sufficiently to obtain high MA yields. Figure 2 shows the correlations between MA selectivity and butane conversion observed over each catalyst at various temperatures, with MA yields being also scaled. The catalyst $VP_{1.0}$ showed the lowest MA selectivity at all conversions above 50 mol%, indicating that the metal additives are effective more or less to promote MA selectivities. It is seen that MA selectivities over $VP_{1.0}Bi_{0.02}$ are the highest and remains almost the same up to about 90 mol% conversion. This suggests that the addition of Bi is effective to increase r_1/r_2 while suppressing r_3. As we reported previously,[8) Mg seems to increase the ratio r_1/r_2 because it showed high MA selectivities at low conversion levels, while Mn does to suppress r_3. Over all the catalysts, however, MA selectivities fell very rapidly when conversion exceeded 90 mol%, presumably because of the formation of hot spots in the catalysts.



Scheme 1. Reaction routes in butane oxidation.

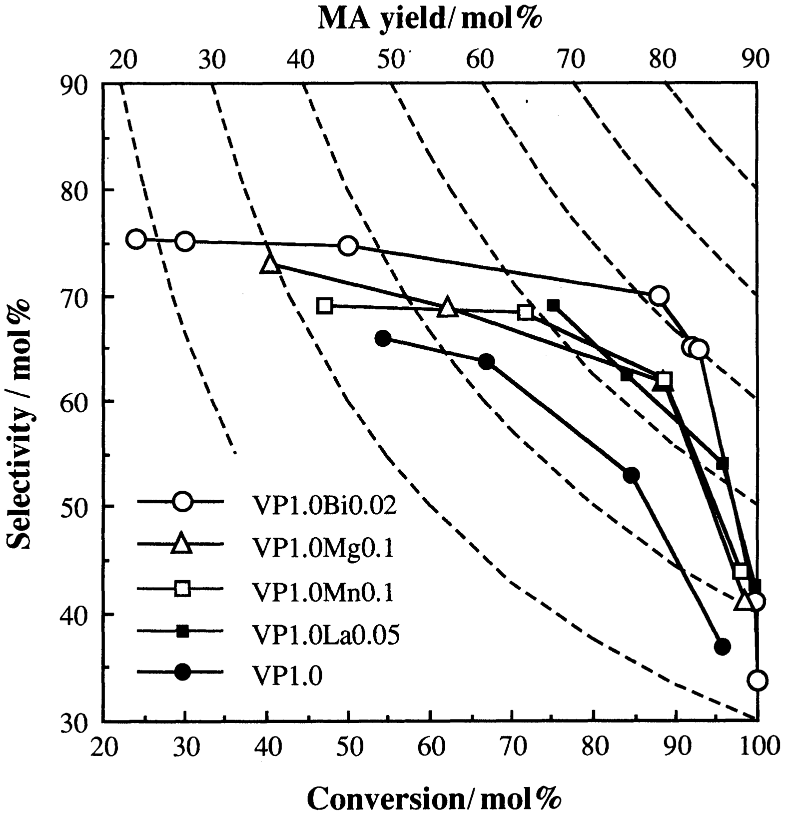


Fig. 2. Relationship between MA selectivity and butane conversion observed over modified and unmodified catalysts at various temperatures.

The XRD patterns of the catalysts showed no crystalline phases other than $(VO)_2P_2O_7$, as shown for some catalysts in Fig. 3. The modified catalysts showed no significant changes in diffraction angles from the unmodified catalyst. The metal additives seem to be present outside the lattice of $(VO)_2P_2O_7$ crystals. As revealed by XPS measurements, the surface P/V ratio of the unmodified catalyst was 1.6, suggesting the existence of a surface amorphous layer. Thus, the metal additives are likely to be included in the amorphous layer covering the $(VO)_2P_2O_7$ crystals. The (020) diffraction of $VP_{1.0}$ was noted to be rather broad. From such broadness of the diffraction line, the disorder of (020) plane of $(VO)_2P_2O_7$ phase has been assumed to be important for high MA selectivities.$^{9)}$ The modified catalysts, however, had considerably narrower diffraction lines, despite their better MA selectivities. This suggests that the proclaimed assumption can not always be verified.

In conclusion, the addition of some metal cations was effective to improve the catalytic properties of V-P-O catalyst for the oxidation of butane. Particularly effective was the addition of Bi, with which the maximum MA yield of 62 mol% was attained at 395 °C.

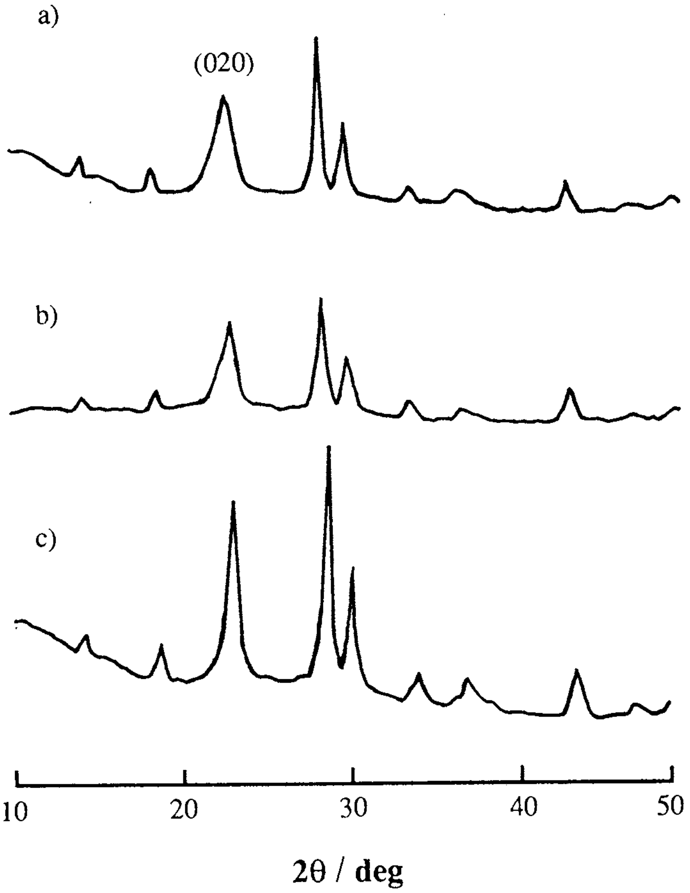


Fig. 3. X-Ray diffraction patterns of a) $VP_{1.0}$, b) $VP_{1.0}Bi_{0.02}$, c) $VP_{1.0}Mg_{0.1}$ after butane oxidation.

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