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Oxidation of Methacrolein to Methacrylic Acid on V_2O_5–P_2O_5-Based Catalysts

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The vapor-phase oxidation of methacrolein to methacrylic acid was studied with V_2O_5–P_2O_5 and V_2O_5–P_2O_5-based catalysts. The highest selectivity among the V_2O_5–P_2O_5 catalysts was obtained with a P/V atomic ratio from 1.06 to 1.2, while the oxidation activity decreased steadily with an increase in the phosphorus content. The oxidation activity of the P/V = 1.06 catalyst was lower than that of such heteropoly-compound catalysts as $H_3PMo_{12}O_{40}$, $Cs_2HPMo_{12}O_{40}$, $H_5PMo_{10}V_2O_{40}$, and $Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$. However, the selectivity of the P/V = 1.06 was the same as that of the heteropoly-compound catalysts. As for the third components added to the P/V = 1.15 oxide, TeO_2 was the only oxide which could improve the selectivity. It was also found that the addition of a small amount of $H_3PMo_{12}O_{40}$ and its salts to the P/V = 1.15 oxide enhances the oxidation activity to the same level as that of the heteropoly-compound catalysts and, moreover, also improves the selectivity. The highest selectivity was obtained by the addition of $Zr_{3/4}PMo_{12}O_{40}$ with an Mo/V atomic ratio of 0.1. The oxidation rate on the P/V = 1.06 catalyst increased almost linearly with the oxygen concentration in the feed gas, while the rate on the heteropoly-compound catalysts was less dependent on the oxygen concentration. In contrast with the heteropoly-compound catalysts, the best performance with the V_2O_5–P_2O_5 and V_2O_5–P_2O_5-based catalysts was obtained in the presence of a high oxygen concentration.

INTRODUCTION

Methacrylic acid (MAA), a raw material of so-called organic glass, was recently produced by a two-step oxidation of isobutene: oxidation of isobutene to methacrolein (MAL) and that of MAL to MAA. The second step is performed mostly with heteropoly-compound catalysts containing a vanadium component (*1–3*). In addition to a great number of patents, a few scientific studies have also been reported on the catalytic behavior of molybdovanadophosphoric acid [$H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 1–2)] and its salts (*4–6*). It is recognized that the effective catalytic performance of a heteropoly compound is to be ascribed to its eminent acidic property as well as its redox property (*4, 7*). Further, it is also known that such a heteropoly compound is decomposed at around 400°C and loses its catalytic activity (*4, 7, 8*).

On the other hand, the V_2O_5–P_2O_5 (P/V atomic ratio = 1.0 to 1.2) system is a unique catalyst possessing a surprisingly high selectivity in the oxidation of butane to maleic anhydride; moreover, it is sufficiently stable at around 400°C.

It has been found in our previous studies that the heteropoly compounds containing a vanadium component are effective as catalysts for the oxidation of butane to maleic anhydride, much like the V_2O_5–P_2O_5 catalysts (*9, 10*). Conversely, it has also been found that V_2O_5–P_2O_5-based catalysts are effective for the oxidative dehydrogenation of isobutyric acid to MAA, much like the heteropoly-compound catalysts (*11*). In this connection, it has been proposed that the heteropoly compounds containing a vanadium component are similar to V_2O_5–P_2O_5-based mixed oxides in their balance between acidic property and oxidizing function (*10, 12*).

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Accordingly, it can be predicted that V_2O_5–P_2O_5-based catalysts exhibit a performance comparable to that of a heteropoly-compound catalyst in the oxidation of MAL to MAA.

In this study, we attempted to ascertain the catalytic performance of V_2O_5–P_2O_5-based oxides in the oxidation of MAL to MAA and, further, to clarify the differences in the catalytic action between V_2O_5–P_2O_5-based oxides and heteropoly compounds.

EXPERIMENTAL

Reaction Procedures

Oxidation of MAL was conducted in a continuous-flow reaction system. The reactor was made of a steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. Air or a mixture of oxygen and nitrogen was fed in from the top of the reactor with a fixed rate of 300 ml (at 20°C)/min; MAL and water were introduced into a preheating section of the reactor by means of two micro-liquid-feeders (injection syringe pumps). Unless otherwise indicated, the reaction conditions were fixed as follows: feed rate of MAL/steam/air, 16.3/328/750 mmol/h; composition of MAL/steam/air, 1.5/30.0/68.5 mol%; amount of catalyst used, 50 ml; space velocity, about 525 h^{-1}. The other procedures were the same as those described in the previous study (*11*). The fresh and pure MAL monomer was donated by Mitsubishi Rayon Co.

Catalysts

12-Molybdophosphoric acid [$H_3PMo_{12}O_{40}$] was from Kanto Chem, Co., and 12-molybdovanadophosphoric acid [$H_5PMo_{10}V_2O_{40}$] was prepared according to the method previously reported (*13*). The cesium salts, $Cs_2HPMo_{12}O_{40}$ and $Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$, were prepared according to the principle reported (*14*). All were supported on an equal weight of natural pumice with a mesh size between 10 and 20. Calcination was performed at 370°C for 6 h in a stream of air.

The V_2O_5–P_2O_5 catalysts with P/V atomic ratio = 0.9, 1.06, 1.2, and 1.6 and the V_2O_5–P_2O_5–M_nO_m catalysts with M/P/V atomic ratio = 0.15/1.15/1, where M = Zr, Te, Nb, and Co, are the same as those used in the previous study (*15*). The X-ray diffraction patterns showed that the P/V = 1.06 and 1.2 catalysts consist of vanadyl pyrophosphate [$(VO)_2P_2O_7$] (*16, 17*).

The P/V oxides incorporated with a small amount (Mo/V = 0.1) of heteropoly compounds, [V_2O_5 + 1.15 P_2O_5 + 1/60 $M^{n+}_{3/n}PMo_{12}O_{40}$], where M = H^+, Cs_+, NH_4^+, Bi^{3+}, and Zr^{4+}, were prepared according to the method described in the previous study (*15*).

Surface areas were measured by the BET method using nitrogen at −196°C.

RESULTS

Performance of Heteropoly-Compound Catalysts

Since the performance of heteropoly-compound catalysts had previously been studied, this study was begun by using these catalysts as references. The reaction was conducted first with the $H_5PMo_{10}V_2O_{40}$ catalyst under the reaction conditions described under Experimental and in the temperature range from 280 to 360°C. The main products were MAA, acetic acid (AcOH), and carbon oxides (CO_x), plus a small amount of acetone. The change in the selectivities to each product with an increase in the extent of the reaction, a change attributable to the elevation of the reaction temperature, is shown in Fig. 1.

As the reaction proceeds, the selectivities to acetic acid and carbon oxides increase at the expense of the selectivity to MAA. The results are substantially in agreement with those reported in the earlier study (*6*) and patent (*18*).

The reaction was also conducted with other heteropoly compounds. The MAL conversion at a fixed temperature of 320°C, as an index of the oxidation activity, and the selectivities to MAA at different extents

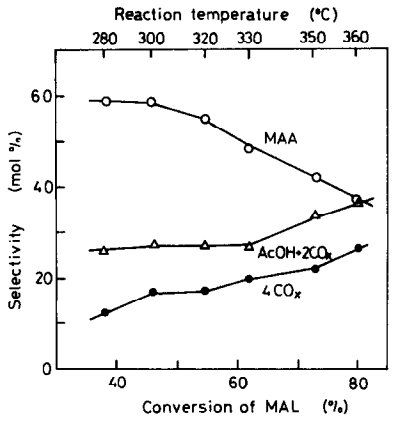

FIG. 1. Oxidation of MAL on the $H_5PMo_{10}V_2O_{40}$ catalyst.

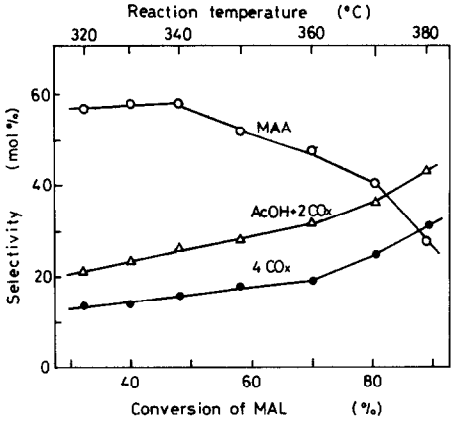

FIG. 3. Oxidation of MAL on the P/V = 1.06 catalyst.

of the reaction were measured for each catalyst. The results are shown in Fig. 2, together with the surface areas. No marked difference was observed in the selectivity to MAA, although the cesium-salt catalysts were a little more active than the free-acid catalysts.

Performance of V_2O_5/P_2O_5 Catalysts

The performances of a series of V_2O_5–P_2O_5 catalysts with different P/V compositions were studied. Figure 3 shows the selectivities of the P/V = 1.06 catalyst for each product as a function of the extent of the reaction. As an index of the oxidation activity, the MAL conversion at 320°C was compared with those obtained with the heteropoly-compound catalysts in Fig. 2. It is clear that the P/V = 1.06 catalyst is markedly less active than the heteropoly-compound catalysts. However, as may be seen in Figs. 1 to 3, the selectivity of the P/V = 1.06 catalyst is substantially the same as that obtained with heteropoly compounds.

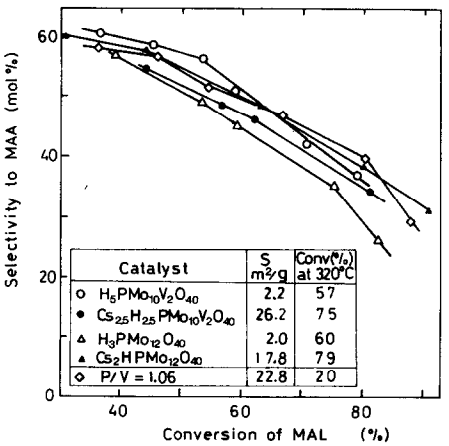

FIG. 2. Oxidation of MAL on the heteropoly-compound catalysts.

The selectivities to MAA obtained from the catalysts with four different P/V compositions are plotted as a function of the extent of the reaction in Fig. 4. As indices of the oxidation activity, the MAL conversions at 340°C obtained from each catalyst are also listed in Fig. 4, together with the surface areas. The oxidation activity decreases steadily with an increase in the phosphorus content, much as in the cases of the oxidation of butane (*19*), butene (*19, 20*), and acrolein (*21*). The highest selectivity to MAA was obtained with the P/V = 1.06 to 1.2 catalysts, as in the cases of the oxidation of butane (*19*) and acrolein (*21*).

Effects of the Third Components Added to V_2O_5–P_2O_5

In order to improve the performance of the V_2O_5–P_2O_5 catalysts, a small amount

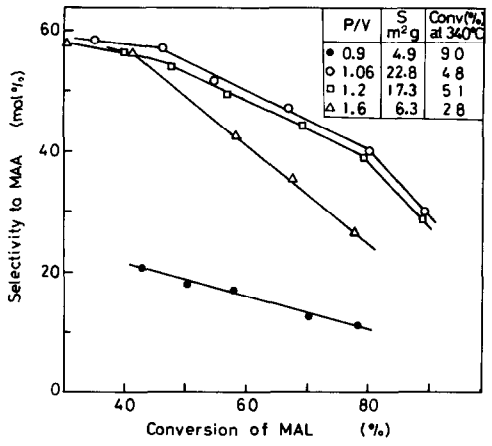

FIG. 4. Oxidation of MAL on the P/V catalysts with different compositions.

(M/V atomic ratio = 0.1) of a third metal oxide (M_nO_m), such as TeO_2, Co_3O_4, Nb_2O_5, or ZrO_2, was added to the P/V = 1.15 oxide. The catalysts thus obtained were also tested for the ability to form MAA.

The selectivities of each catalyst to form MAA are plotted as a function of the extent of the reaction in Fig. 5. As indices of the oxidation activity, the MAL conversions at 340°C are also listed together with the surface areas in Fig. 5. TeO_2 was found to be the only oxide which can improve the selectivity, much as in the cases of the oxidation of propylene (*15*) and propane (*22*) to form acrylic acid.

Effect of Heteropoly Compounds Added to V_2O_5–P_2O_5

A small amount (Mo/V atomic ratio = 0.1) of a heteropoly compound, such as $H_3PMo_{12}O_{40}$ or its salt of NH_4^+, Cs^+, Bi^{3+}, or Zr^{4+}, was added to the P/V = 1.15 oxide, and the effect of the additives on the performance was studied.

The selectivities of each catalyst to form MAA are plotted in Fig. 6, together with the MAL conversions at 320°C and the surface areas. It is clear that the addition of heteropoly compounds to the P/V = 1.15 oxide enhances the oxidation activity to the same level as that of the heteropoly compounds and, moreover, also improves the selectivity to a certain extent. The best results in the selectivity were obtained with the addition of $Zr_{3/4}PMo_{12}O_{40}$ and the next best results were obtained with that of $(NH_4)_3PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$.

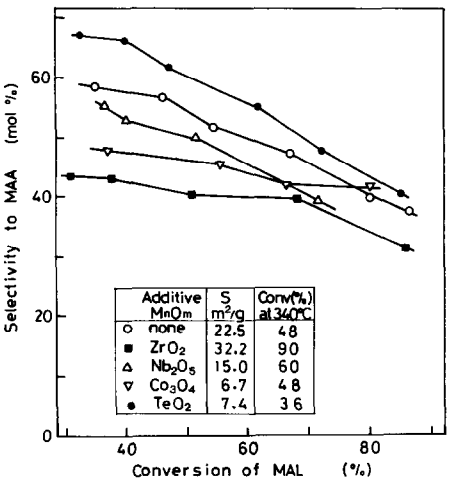

FIG. 5. Oxidation of MAL on the P/V = 1.15 catalysts incorporated with a small amount (M/V = 0.1) of third metal oxide (M_nO_m).

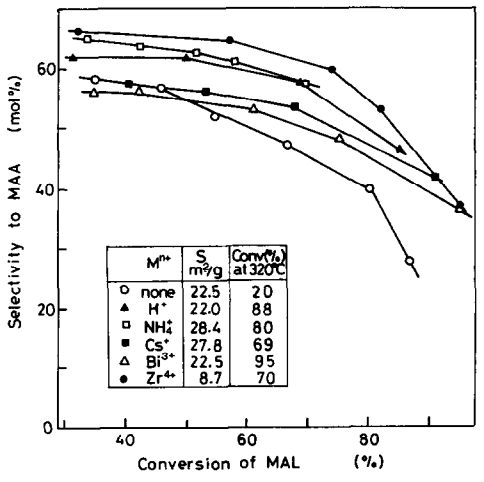

FIG. 6. Oxidation of MAL on the P/V = 1.15 catalysts incorporated with a small amount (Mo/V = 0.1) of heteropoly compound. Catalyst: V_2O_5 + 1.15 P_2O_5 + 1/60 $M^{n+}_{3/n}$ $PMo_{12}O_{40}$.

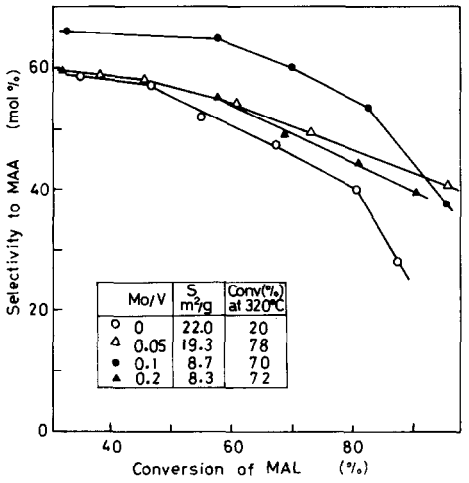

FIG. 7. Oxidation of MAL on the P/V = 1.15 catalysts incorporated with different amounts of $Zr_{3/4}PMo_{12}O_{40}$.

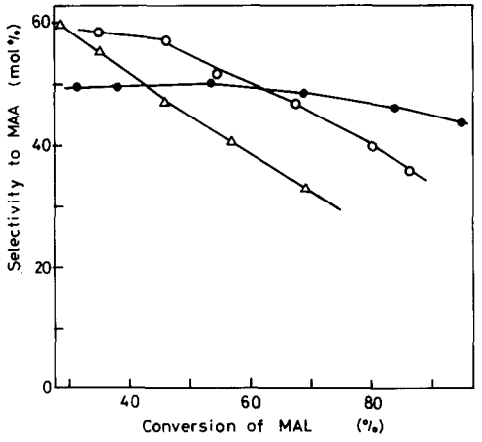

FIG. 8. Effect of the oxygen concentration on the selectivity of the P/V = 1.06 catalyst. MAL concentration: 1.5 mol%. Oxygen concentration: (△) 2.8, (○) 13.7, (●) 34 mol%.

Effect of the Amount of $Zr_{3/4}PMo_{12}O_{40}$ Added to V_2O_5–P_2O_5

Different amounts of $Zr_{3/4}PMo_{12}O_{40}$ were added to the P/V = 1.15 oxide, and the effects of the amount on the catalytic performance were studied. Figure 7 shows the selectivities to MAA and the MAL conversions at 320°C obtained from the catalysts with the Mo/V atomic ratios of 0, 0.05, 0.1, and 0.2. It was found that the oxidation activity is enhanced markedly by the addition of a very small amount (Mo/V = 0.05) and that the best results are obtained with the Mo/V = 0.1 catalyst.

Effect of the Oxygen Concentration on the Selectivity

The effect of the oxygen concentration on the selectivity to MAA was studied for the P/V = 1.06 and [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalysts. The reaction was conducted by changing the initial concentration of oxygen from 2.8 to 34 mol%, while fixing the other conditions as presented under Experimental. Figure 8 shows the selectivities of the P/V = 1.06 catalyst as a function of the extent of the reaction.

With the oxygen concentration of 2.8 mol%, the selectivity to MAA decreases markedly as the extent of the reaction increases. However, in the presence of a large excess of oxygen, the selectivity decreases much more dully with an increase in the extent of the reaction. It is, therefore, concluded that the presence of a large excess of oxygen is favorable in the case of the V_2O_5–P_2O_5 catalysts.

Figure 9 shows the results obtained with

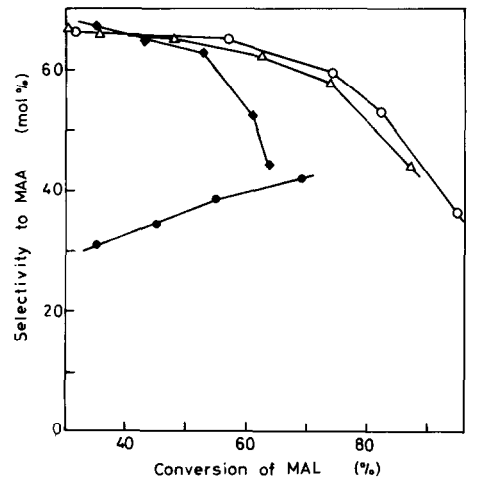

FIG. 9. Effect of the oxygen concentration on the selectivity of the [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalyst. MAL concentration: 1.5 mol%. Oxygen concentration: (◆) 1.4, (△) 2.8, (○) 13.7, (●) 34 mol%.

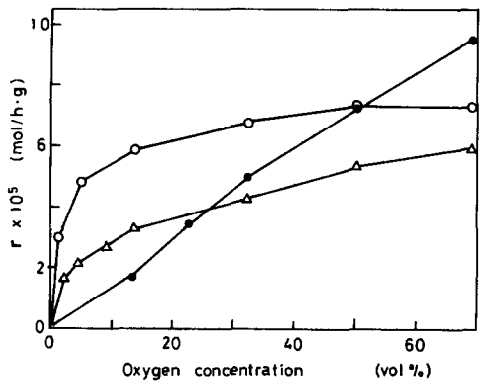

FIG. 10. Effect of the oxygen concentration on the rate of MAL oxidation. MAL concentration: 1.5 mol%. Catalyst and reaction temperature: (●) P/V = 1.06, 300°C; (○) $H_5PMo_{10}V_2O_{40}$, 280°C; (△) V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$, 280°C.

the [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalyst. The best results are obtained with an oxygen concentration from 2.8 to 13.7 mol%.

Effect of the Concentrations of Oxygen and Methacrolein on the Rate

It was found that the activity of the P/V = 1.06 catalyst for the oxidation of MAL is markedly lower than that of the heteropoly-compound catalysts and that the addition of a small amount of a heteropoly compound to the P/V oxide enhances the activity to the same level as that of the heteropoly-compound catalysts. In order to clarify the function of the heteropoly compounds added to the P/V oxide, the variation in the oxidation rate depending on the variation in the concentrations of both oxygen and MAL was studied for the P/V = 1.06, $H_5PMo_{10}V_2O_{40}$, and [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalysts.

The rates of MAA formation at different initial concentrations of oxygen were measured for each catalyst; the reaction temperatures were adjusted so that the MAA yield did not exceed 10 mol%. The results are shown in Fig. 10.

At a low oxygen concentration, the rate on the P/V = 1.06 catalyst is low, but it increases almost linearly with the oxygen, even at high concentration levels of 69 mol%. On the other hand, the rate on the $H_5PMo_{10}V_2O_{40}$ catalyst increases sharply in the presence of a small amount (2 mol%) of oxygen, but with a further increase in the oxygen concentration, it increases more dully, until it eventually ceases to increase at all. Similar results have been observed in the oxidation of isobutyric acid (*11*). The features of the curve obtained with the [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalyst are similar to those of the curve obtained with the $H_5PMo_{10}V_2O_{40}$ catalyst.

The effect of the MAL concentration on the rate was then studied. The results are shown in Fig. 11. The rate on the P/V = 1.06 catalyst is almost independent of the MAL concentration in the range from 0.38 to 2.25 mol%, while the rates on the $H_5PMo_{10}V_2O_{40}$ and [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalyst increase with an increase in the MAL concentration up to 2.25 mol%.

DISCUSSION

The results shown in Figs. 10 and 11 indicate that the character of the reaction on the P/V = 1.06 catalyst is completely different from that on the heteropoly-compound

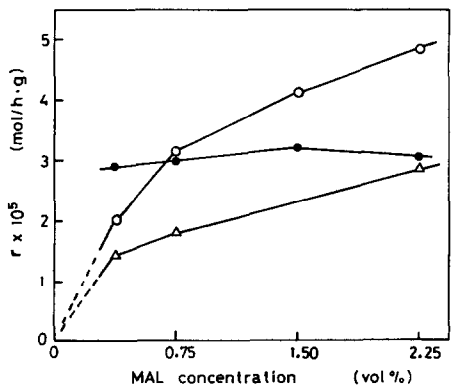

FIG. 11. Effect of the MAL concentration on the rate of MAL oxidation. Oxygen concentration: 13.7 mol%. Catalyst and reaction temperature: (●) P/V = 1.06, 310°C; (○) $H_5PMo_{10}V_2O_{40}$, 280°C; (△) V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$, 280°C.

catalysts. This leads us to the consideration that heteropoly compounds possess an enhanced redox property; as a result, their reoxidizing function is sufficiently strong, even at a relatively low temperature (*23*). Accordingly, the oxidation rate on these compounds is controlled by the activation or the reaction of MAL on the surface rather than by the reoxidation of a reduced catalyst by gaseous oxygen. On the other hand, the P/V = 1.06 oxide, in which the content of phosphorus is much greater than that in the heteropoly compounds, is deficient in the basic sites which attract gaseous oxygen and which serve to reoxidize the reduced active sites (*24*). Accordingly, the oxidation on the P/V oxide is controlled by the reoxidation of reduced active sites by gaseous oxygen.

Accordingly, it is assumed that a small amount of a heteropoly compound added to the P/V oxide serves to enhance the reoxidizing function.

With regard to the selectivity, the P/V = 1.06 and 1.2 catalysts exhibit substantially the same performance as the heteropoly-compound catalysts, much as in the case of the oxidation of isobutyric acid to MAA (*11*). However, as may be seen in Figs. 8 and 9, the highest selectivity on the P/V catalyst is obtained with an oxygen concentration from 13.7 to 34 mol% (at the MAL concentration of 1.5 mol%), while the highest selectivity on the [V_2O_5 + 1.15 P_2O_5 + 1/60 $Zr_{3/4}PMo_{12}O_{40}$] catalyst is achieved with an oxygen concentration from 2.8 to 13.7 mol%. Further, a survey of the patents reveals that the oxygen/MAL molar ratio used in a reaction on heteropoly-compound catalysts is usually 2, suggesting that the presence of a large excess of oxygen is not desirable in the case of heteropoly-compound catalysts.

This difference may also be ascribed to the difference in the reoxidizing function between the P/V oxide and the heteropoly compounds. In the case of the P/V catalyst, when the oxygen concentration is low, an elevated temperature is required to achieve an appreciable level of MAL conversion; this results in an increase in the consecutive oxidation of MAA. The possession of a sufficient oxidation activity may be essential for the P/V catalyst to achieve a high selectivity to MAA. Accordingly, the presence of a high oxygen concentration is desirable.

On the other hand, in the case of the heteropoly-compound catalysts, the reaction can proceed to an appreciable level even with a low oxygen concentration. Possibly, the consecutive oxidation of MAA is preferentially promoted with a higher oxygen concentration. This may be the reason why the presence of a low oxygen concentration is used.

As for the consecutive oxidation of MAA, this reaction may be promoted by the basic sites (*23*). As mentioned above, the heteropoly compounds seem to be more basic than the P/V = 1.06 oxide, because the content of phosphorus in heteropoly compounds is lower than that in the P/V = 1.06 oxide. As a result, heteropoly-compound catalysts promote the consecutive oxidation of MAA more strongly than the P/V = 1.06 catalyst does. Accordingly, the low selectivity of the P/V = 0.9 oxide and the P/V = 1.15 oxide incorporated with a basic oxide, such as ZrO_2 and Co_3O_4, can be understood. In this connection, it is assumed that the TeO_2 added to the P/V oxide plays a role in suppressing the basic sites.

As mentioned above, the possession of a sufficient oxidation activity may be essential for the P/V catalysts to achieve a good selectivity. Accordingly, the effect of heteropoly compounds added to the P/V oxide in the selectivity can also be understood; the addition of heteropoly compounds induces a large increase in the oxidation activity (Fig. 6), this results in an increase in the selectivity at high conversion levels. The low selectivity of the P/V = 1.6 catalyst (Fig. 4) may also be ascribed to its low oxidation activity.

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