Oxidative Dehydrogenation of Isobutyric Acid on V_2O_5–P_2O_5 Catalysts

MAMORU AI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

V_2O_5–P_2O_5 binary oxides were found to be effective for the synthesis of methacrylic acid (MAA) in the vapor-phase air oxidation of isobutyric acid (IBA), much like vanadium-containing heteropoly compounds. The products are MAA, acetone, propylene, and carbon oxides. With an increase in the content of phosphorus, the selectivity to acetone steadily decreases, while that to propylene increases. The selectivity to MAA passes through a maximum (50 to 60 mol%) at a P/V atomic ratio between 1.0 and 1.6, and it is little affected by the method of catalyst preparation. It was found that the selectivity is clearly related to the acid–base property of the catalyst. The oxidation activity attains a maximum at P/V = 1.0 to 1.6, and the activities of the V–P (1–1.6) catalysts are of the same order of magnitude as that of $H_5PMo_{10}V_2O_{40}$. The effects of reaction variables, such as oxygen concentration, IBA concentration, water vapor, and temperature, on activity and selectivity were studied for both the V_2O_5–P_2O_5 and $H_5PMo_{10}V_2O_{40}$ catalysts, and an attempt was made to clarify the difference in catalytic performance between V_2O_5–P_2O_5 and $H_5PMo_{10}V_2O_{40}$. © 1986 Academic Press, Inc.

INTRODUCTION

Heteropoly compounds, especially molybdovanadophosphoric acid ($H_{3+x}P$-$Mo_{12-x}V_xO_{40}$; $x = 1$–2) and its salts, have been found to be effective for the oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA); the effects of the catalyst components on the catalytic action and the mechanism of the reaction have also been studied (1–4). However, it is not yet clear why these catalysts exhibit a high selectivity to MAA.

In our previous studies (5, 6) we found that salts of molybdovanadophosphoric acid and composite heteropoly compounds, consisting of salts of molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and a vanadium promoter, are effective for the oxidation of *n*-butane to maleic anhydride, in which V_2O_5–P_2O_5-based catalysts have been known to exhibit a promising performance. In this connection, it has been proposed that the heteropoly compounds containing a vanadium component are similar to V_2O_5–P_2O_5 mixed oxides in their balance between acidic property and oxidizing function (6).

In line with this thought, it can be predicted that V_2O_5–P_2O_5 catalysts exhibit a performance comparable to that of the heteropoly compounds in the oxidative dehydrogenation of IBA to MAA.

In this study, we focused our attention on the formation of MAA from IBA with V_2O_5–P_2O_5 catalysts and attempted to clarify the effects of catalyst compositions and reaction variables and, further, the differences in the catalytic action between heteropoly compounds and V_2O_5–P_2O_5 mixed oxides.

EXPERIMENTAL

Catalysts

The V_2O_5–P_2O_5 catalysts are the same as those used in a previous study (7). Structures and surface areas have also been described in the previous study (7). The six methods of preparation are described below and summarized in Table 1. Method [A]:

401

TABLE 1

Preparation of V_2O_5-P_2O_5 Catalysts

Designator	Starting material		Reducing agent	Medium	Ref.
	Vandium	Phosphorus			
A	NH_4VO_3	85% H_3PO_4	none	H_2O	(8)
B	V_2O_5	$NH_4H_2PO_4$	oxalic acid	H_2O	(9)
C	V_2O_5	85% H_3PO_4	37% HCl	H_2O	(10)
D	V_2O_5	85% H_3PO_4	lactic acid	lactic acid	(11)
E	V_2O_5	$POCl_3$	$POCl_3$	THF[a]	(12)
F	V_2O_5	98% H_3PO_4	$C_6H_5CH_2OH$	isobutanol	(13)

[a] Tetrahydrofuran.

Method A. Catalysts were prepared from NH_4VO_3 and 85% H_3PO_4 without using a reducing agent, as described in Ref. (8).

Method B. Catalysts were prepared from V_2O_5 and $NH_4H_2PO_4$ by using oxalic acid, in the same manner as the VPb catalysts in Ref. (9).

Method C. Catalysts were prepared from V_2O_5 and 85% H_3PO_4 by using 37% HCl as a reducing agent, as described in Ref. (10).

Method D. Catalysts were prepared from V_2O_5 and 85% H_3PO_4 by using lactic acid, as described in Ref. (11).

Method E. Catalysts were prepared from V_2O_5 and $POCl_3$ by using tetrahydrofuran as the solvent, according to a patent. (12).

Method F. Catalysts were prepared from V_2O_5 and 98% H_3PO_4 by using a mixture of benzyl and isobutyl alcohols as a reducing solvent, according to a patent (13).

The V–Mo (8–2; atomic ratio) and V–Ti (4–6) oxide catalysts were prepared according to the following method. V_2O_5 was dissolved by using 37% HCl as a reducing agent. Then, either a solution of $(NH_4)_6Mo_7O_{24}$ or a gel of $Ti(OH)_4$ obtained by hydrolysis of $TiCl_4$ was added to the solution. The mixture was evaporated with stirring and dried in an oven at 130°C. The catalyst was calcined at 500°C for 6 h in a stream of air.

Molybdovanadophosphoric acid was prepared according to a method previously reported (14) and was supported on an equal weight of natural pumice between 10 and 20 in mesh size. Calcination was performed at 370°C for 6 h. The method of its preparation has also been described in the previous study (6).

Oxidation Procedures

Oxidation of IBA 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 was fed in from the top of the reactor, with IBA being introduced by means of a micro-liquid feeder. Unless otherwise indicated, the reaction conditions were fixed as follows: IBA concentration, 1.37 vol% in air; total flow rate, 400 ml (at 20°C)/min; amount of catalyst used, 10 g (V_2O_5-based oxides) and 20 g ($H_5PMo_{10}V_2O_{40}$). The effluent gas from the reactor was led into three chilled water scrubbers to recover the water-soluble compounds. At the end of 1 h, the content of the water scrubbers was collected (120 ml). Reaction products were analyzed on gas chromatographs; a 1-m column of molecular sieve 13X for CO; a 6-m column of propylene carbonate for CO_2 and propylene; a 1-m column of SP-1200 + H_3PO_4 at 130°C for acids; a 2-m column of PEG 20M at 100°C for aldehydes, ketones, and alcohols. Yield and selectivity of a particular product were defined as mole percentage yield and selectivity on a carbon-accounted-for basis.

RESULTS

Comparison of the Performance of Various Catalysts

Various catalysts were tested for the ability to form MAA from IBA under the conditions presented under Experimental.

$H_5PMo_{10}V_2O_{40}$. Since the performance of $H_5PMo_{10}V_2O_{40}$ had previously been studied, this catalyst was first studied as a reference. The products were MAA, acetone, propylene, and carbon oxides, as has previously been reported (2–4). The change in the selectivity to each product with an increase in the extent of reaction, a change attributable to the elevation of the reaction temperature, is shown in Fig. 1.

V_2O_5. The change in the selectivity obtained with a pure V_2O_5 catalyst is shown in Fig. 2. When the extent of reaction is low (less than 30%), the main products are acetone and MAA, and the selectivity to acetone, i.e., IBA → acetone + CO_x, is about 70 mol%. With an increase in the extent of the reaction, however, the selectivity to carbon oxides increases at the expense of a decrease in the selectivity to both acetone and MAA, indicating that carbon oxides are formed by the consecutive degradation of
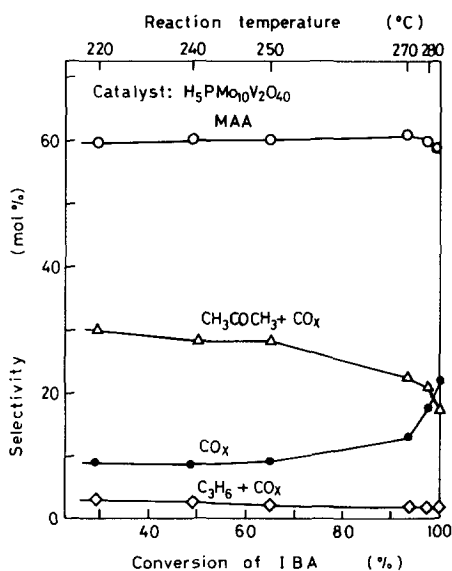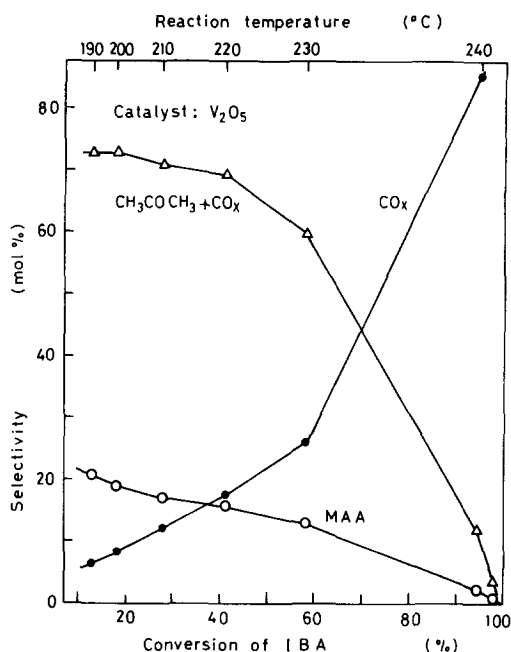
FIG. 2. Oxidation of IBA on the pure V_2O_5 catalyst.

acetone and MAA. It should be noted that propylene is not formed, in contrast to the case of $H_5PMo_{10}V_2O_{40}$.

V–Ti (4–6) oxide. Figure 3 shows the results obtained with a V–Ti (4–6) oxide catalyst. The profile of the product distribu-

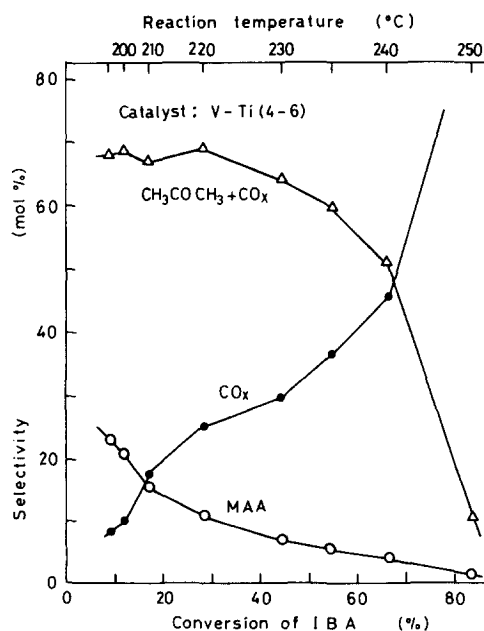FIG. 1. Oxidation of IBA on the $H_5PMo_{10}V_2O_{40}$ catalyst.

FIG. 3. Oxidation of IBA on the V–Ti (4–6) catalyst.

tion is similar to that obtained with the pure V_2O_5 catalyst, except that the selectivity to MAA decreases more greatly with an increase in the extent of the reaction.

V–Mo (8–2) oxide. The results are shown in Fig. 4. With the addition of MoO_3 to V_2O_5, the selectivity to MAA increases a little as opposed to that to acetone. It should also be noted that propylene is formed, though in a small amount.

V–P (1–1.6) oxide. Figure 5 shows the results obtained with a V–P (1–1.6) catalyst prepared by Method E. The selectivity to MAA is about 60 mol% when the extent of reaction is low (less than 30%). This value is comparable to that obtained with the $H_5PMo_{10}V_2O_{40}$ catalyst. However, the selectivity decreases slightly with an increase in the extent of reaction, while, on the contrary, the selectivity to propylene and that to carbon oxides increase. The formation of propylene is much greater than in the case of the $H_5PMo_{10}V_2O_{40}$ catalyst.

Effect of the Method of Preparing the V–P Oxide Catalyst

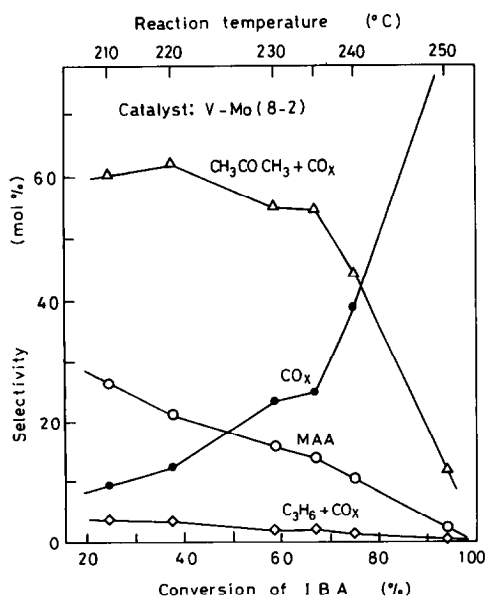It has been known that, in the oxidation of *n*-butane to maleic anhydride, the perfor-
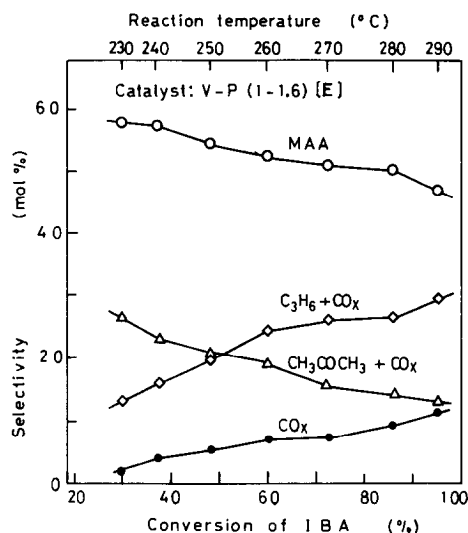

FIG. 5. Oxidation of IBA on the V–P (1–1.6) (E) catalyst.

mance of V–P oxide catalysts depends greatly on the method of preparation. Therefore, the effect of the method of preparation on catalytic activity and selectivity in the oxidation of IBA was examined.

The specific rates of MAA formation at 240°C, r_s (mol/h · m^2 of catalyst), were compared for catalysts prepared by the six methods described in Table 1. The results

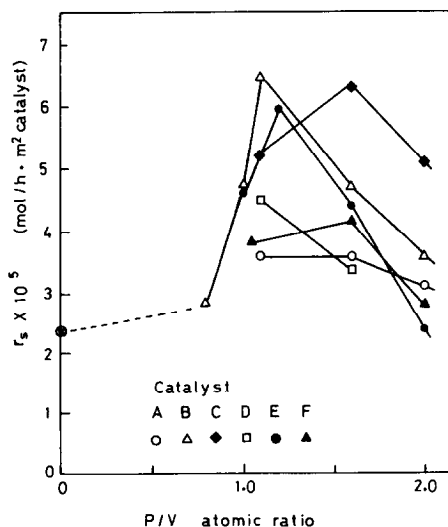FIG. 4. Oxidation of IBA on the V–Mo (8–2) catalyst.

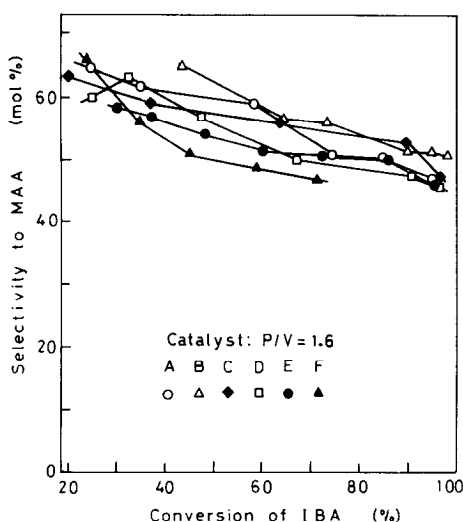FIG. 6. Comparison of the acitivities of V–P catalysts for formation of MAA from IBA.

FIG. 7. Comparison of the selectivities to MAA.

are shown in Fig. 6. The selectivities to MAA were also compared for the six P/V = 1.6 catalysts (Fig. 7). The effect of the method of preparation is relatively small; though, in all cases, the selectivity to MAA decreases slightly, from about 60 to 50 mol%, as the extent of reaction increases.

Effect of P/V Composition

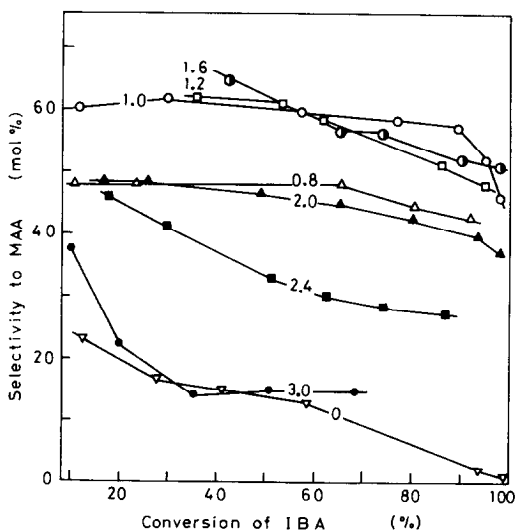As may be seen in Figs. 2 and 5, there exists a large difference in selectivity be-

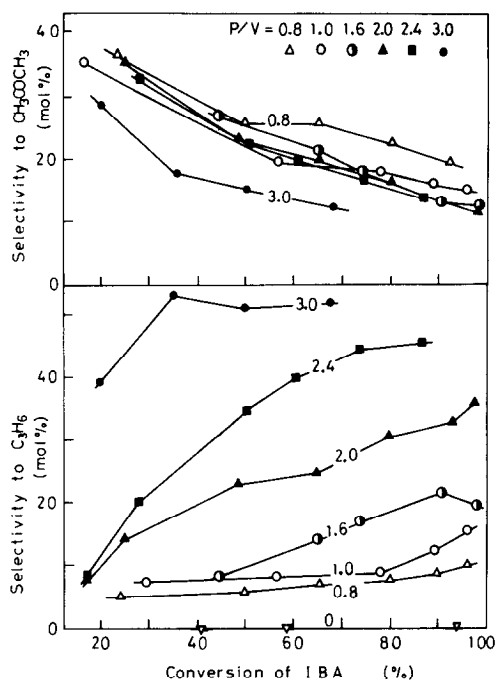FIG. 8. Effect of P/V composition on the selectivity to MAA. Number denotes P/V atomic ratio.

FIG. 9. Effect of P/V composition on the selectivity to acetone and to propylene. Number denotes P/V atomic ratio.

tween pure V_2O_5 and V–P (1–1.6) oxide. Therefore, the effect of P/V composition on catalytic action was studied. The effect on oxidation activity is shown in Fig. 6. The activity increases with the addition of phosphorus, passes through a broad maximum at P/V = 1.0 to 1.6, and then decreases with a further increase in phosphorus.

The effect on selectivity was studied by using a series of catalysts prepared by Method B, for the composition can be varied over a wide range by this method. Selectivities to MAA are compared in Fig. 8. The selectivity increases with phosphorus content, passes through a broad maximum at P/V = 1.0 to 1.6, and then decreases with a further increase in phosphorus.

The variation in the selectivity to propylene and that to acetone are shown in Fig. 9. With an increase in phosphorus content, the selectivity to propylene steadily increases, while that to acetone decreases, though the variation is small in the P/V range 1.0 to 2.4.

Similar results were obtained with the V–P oxide catalyst prepared by Method E.

Effects of Reaction Variables

Oxygen concentration. The reaction was conducted with the $H_5PMo_{10}V_2O_{40}$ and V–P (1–1.6) oxide (E) catalysts by changing the initial concentration of oxygen from 2.5 to 99 vol%, while fixing the other conditions as presented under Experimental. Overall consumption of IBA is plotted as a function of temperature in Fig. 10. The rate depends more greatly on the concentration of oxygen in the case of the V–P oxide than in the case of $H_5PMo_{10}V_2O_{40}$.

The effect on the selectivity was also studied for both the V–P (1–1.6) (E) oxide and $H_5PMo_{10}V_2O_{40}$ catalysts. Results obtained with the $H_5PMo_{10}V_2O_{40}$ catalyst are shown in Fig. 11. As the oxygen concentration decreases, the selectivity to MAA increases, but that to acetone decreases. The effect on the formation of propylene is not clear because the amount is small.

As for the V–P (1–1.6) oxide, the selectivities to each product were compared at a fixed level (50%) of IBA conversion. As may be seen in Fig. 12, the effect on the selectivity to MAA is the opposite of that in the case of the $H_5PMo_{10}V_2O_{40}$ catalyst; that is, the selectivity decreases as the oxygen concentration decreases. It should be noted

FIG. 11. Effect of oxygen concentration on selectivity. Number denotes initial concentration of oxygen (vol%).

that, with a decrease in oxygen concentration, the selectivity to propylene increases at the expense of a decrease in selectivity to both MAA and acetone.

IBA concentration. The reaction was conducted by changing the initial concentration of IBA from 0.33 to 2.4 vol% in air. The rate of consumption of IBA at 250°C is plotted as a function of IBA concentration
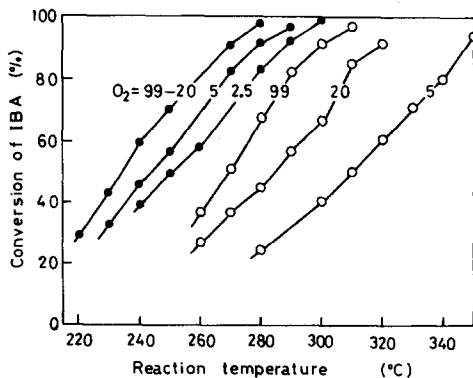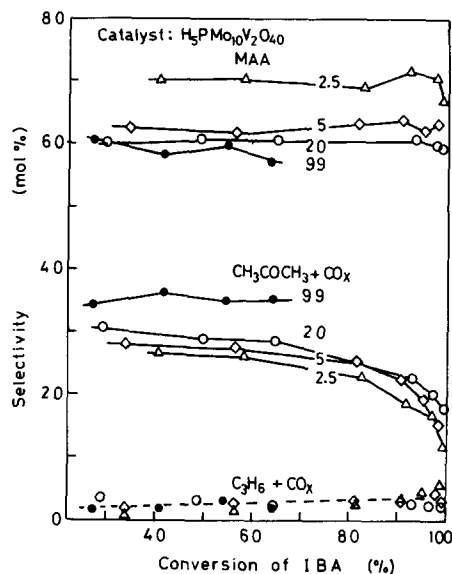

FIG. 10. Effect of concentration of oxygen on IBA conversion. Open circles, V–P (1–1.6) (E) catalyst (5 g); solid circles $H_5PMo_{10}V_2O_{40}$ catalyst (20 g). Number denotes initial concentration of oxygen (vol%).
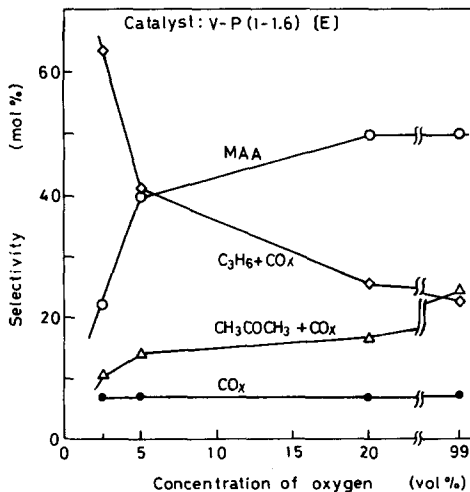

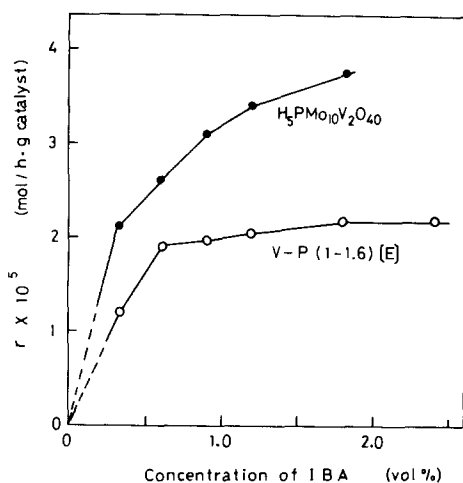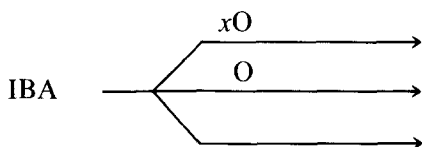FIG. 12. Effect of oxygen concentration on selectivity.

FIG. 13. Effect of IBA concentration on rate of IBA consumption.

in Fig. 13. In the case of the $H_5PMo_{10}V_2O_{40}$ catalyst, the rate increases steadily with concentration up to 1.8 vol%. On the other hand, in the case of the V–P (1–1.6) oxide, the rate increases with concentration up to 0.6 vol%, but it ceases to increase with further increases in the concentration.

Water vapor. The reaction was carried out in the presence of 16 vol% water vapor. Oxidation activity decreased by one-fourth, but the selectivity remained unchanged.

Reaction temperature. The effect of reaction temperature on selectivity was studied by comparing the selectivities at a fixed level (50%) of IBA conversion; the selectivity had been obtained by changing the amount of catalyst used from 1.6 to 30 g. Results are shown in Fig. 14. As the reaction temperature is elevated, the selectivity to MAA decreases, while that to propylene increases. The effect on selectivity to acetone and that to carbon oxides is small.

Stability of catalysts. The stability of the catalysts was checked. Figure 15 shows the yield of MAA at 260°C [V–P (1–1.6) (E) catalyst] and 240°C ($H_5PMo_{10}V_2O_{40}$ catalyst) as a function of elapsed time of reaction. The V–P oxide catalyst is much more stable than the $H_5PMo_{10}V_2O_{40}$ catalyst, and upon reaching steady state (after 1 h), no change was observed in the product distribution.

DISCUSSION

Selectivity

It is evident from the results that, on the V_2O_5-based catalysts, in a manner similar to that on heteropoly compound catalysts (*15*), the reaction of IBA proceeds by means of three parallel pathways:

(i)   acetone + CO_x + H_2O

(ii) MAA + H_2O

(iii) propylene + CO + H_2O

Reaction (i) is an oxidative C–C fission, Reaction (ii) is an oxidative dehydrogenation, and Reaction (iii) is an acid-catalyzed decomposition (*16*).

Taking into consideration the fact that basic sites act as oxidizing sites (*17*) and that the oxidative C–C fission is accelerated by the action of basic sites (*18*), it seems certain that the selectivity in the oxidation of IBA can be understood simply in terms of the acid–base property of the catalyst;

that is, Reaction (i) is accelerated mainly by the action of basic sites with an oxidizing function. Reaction (iii) is accelerated by the action of acidic sites, and Reaction (ii) is accelerated by the action of both acidic and basic sites with an intermediate strength.

In line with this thought, the performance of V_2O_5-based catalysts can be explained as follows. On pure V_2O_5 (Fig. 2), about 70% of the IBA is directed into Reaction (i) and the remainder into Reaction (ii), because
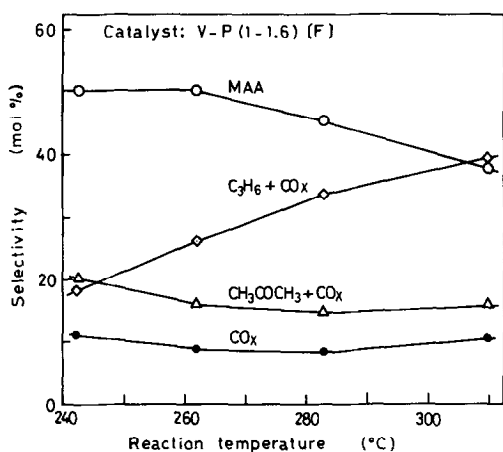
FIG. 14. Effect of reaction temperature on selectivity.

the action of basic sites with an oxidizing function is strong compared to the action of acidic sites.

Selectivity is scarcely affected by the addition to V_2O_5 of a more basic oxide such as TiO_2 (Fig. 3). Possibly, the balance between the oxidizing function and the acidic function is not modified.

Addition of an acidic oxide such as MoO_3 to V_2O_5 induces an increase in the selectivity to MAA and the formation of propylene at the expense of a decrease in the selectivity to acetone (Fig. 4). This may be caused by an enhancement of the acidic property by the addition of MoO_3 (19).

The variation in the selectivity is more noticeable in the case of the addition of phosphorus (Figs. 5, 8, and 9). It has been found in the previous study (7) that, with an increase in the content of phosphorus, the acidic property increases, while the basic property decreases. Accordingly, the selectivity to acetone decreases, and that to propylene increases, with the content of phosphorus (Fig. 9). As for the selectivity to MAA, it passes through a broad maximum at P/V = 1.0 to 1.6 (Fig. 8), indicating that the balance between the oxidizing function and the acidic function is fit for the oxidation of IBA to MAA at this P/V composition. It is interesting to note that this P/V composition is also proper for the oxidation of butene to maleic anhydride (7).

The selectivity to MAA is scarcely affected by the method of catalyst preparation (Fig. 7), much as in the case of the oxidation of butene to maleic anhydride, but not as in the case of the oxidation of n-butane to maleic anhydride (7). It can, therefore, be assumed that the presence of a specially strong-acid site is not needed for the formation of MAA, in contrast to the case of the oxidation of n-butane, because the affinity of IBA to catalyst is greater than that of paraffinic hydrocarbons.

A comparison of selectivities between the V–P (1–1.6) catalysts (Figs. 5 and 7) and the $H_5PMo_{10}V_2O_{40}$ catalyst (Fig. 1) reveals that the selectivity to MAA is on the same level, but that the amounts of by-products are clearly different; that is, the main by-product on $H_5PMo_{10}V_2O_{40}$ is acetone, while in the case of V–P oxide, the main by-product is propylene at a conversion of more than 50%. This suggests that the V–P (1–1.6) catalyst is more acidic and/ or less basic than the $H_5PMo_{10}V_2O_{40}$.

It is interesting to find that the effect of oxygen concentration on the selectivity to MAA is different between the V–P oxide and $H_5PMo_{10}V_2O_{40}$ (Figs. 12 and 11). Since MAA and acetone are both formed by oxidation reactions, while propylene is not formed by oxidation, it may be reasonable to say that, with an increase in oxygen concentration, the selectivity to MAA and that to acetone increase, while the selectivity to
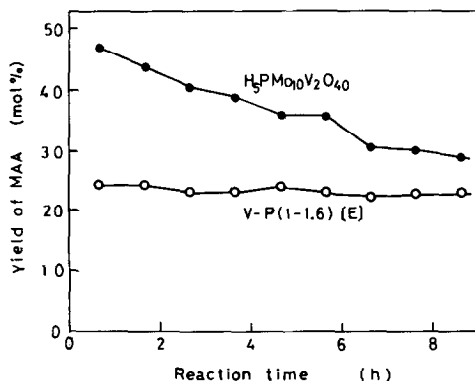

FIG. 15. Stability of catalytic activity.

propylene decreases (Fig. 12). However, in the case of $H_5PMo_{10}V_2O_{40}$, the situation is not the same, because a small amount of propylene is formed, regardless of the oxygen concentration (Fig. 11). With the increase in oxygen concentration, the selectivity to acetone increases at the expense of a decrease in selectivity to MAA. Thus, it may be concluded that, for the formation of MAA, a low oxygen concentration is favorable on the $H_5PMo_{10}V_2O_{40}$ catalyst, while a high oxygen concentration is favorable in the case of the V–P oxide, because the main by-product is propylene.

As may be seen in Figs. 5 and 9, the selectivity to propylene increases steadily with the extent of reaction. However, it is unlikely that propylene is formed by the subsequent reaction of acetone to MAA. In this connection, the results shown in Fig. 14 indicate that the selectivity is affected by the reaction temperature.

Oxidation Activity

As may be seen in Fig. 6, with an increase in the content of phosphorus, the activity for the formation of MAA passes through a maximum at $P/V = 1.0$ to 1.6. This trend of variation is similar to that observed in the activity for the acid-catalyzed reactions, but it is clearly different from that observed in the oxidation activity for *n*-butane and butene, where the activity sharply decreases with an increase in phosphorus content in a manner similar to the basic property of the catalyst (7). This suggests that activation of IBA on acidic sites is required for the formation of MAA and that the rate is not controlled by the oxidizing function of the basic sites (7).

The activity of V–P (1–1.6) catalysts is a little lower than that of $H_5PMo_{10}V_2O_{40}$ catalysts, but it is of the same order of magnitude (Fig. 13).

The effects of the reaction variables on the rate of V–P oxide and $H_5PMo_{10}V_2O_{40}$ catalysts differ somewhat. The rate on the V–P oxide is more dependent on oxygen concentration, and less dependent on IBA concentration, than the rate on H_5P-$Mo_{10}V_2O_{40}$ (Figs. 10 and 13). This finding also suggests that the reaction on V–P oxide is not controlled only by reduction of the catalyst by IBA, i.e., by the oxidizing function of the catalyst, unlike the case of $H_5PMo_{10}V_2O_{40}$ (4). It is assumed that the oxidizing function of basic sites on V_2O_5-based oxides is generally stronger than that on MoO_3-based catalysts, but that the V–P oxides are deficient in their basic property, because the amount of phosphorus is much greater than in the case of $H_5PMo_{10}V_2O_{40}$. Accordingly, the rate is controlled by the reoxidation of the catalyst, at least to a certain extent.

In conclusion, we would like to emphasize that the possession of two opposite properties of suitable strength, such as acidic sites and basic sites with an oxidizing function, is the most important factor enabling a catalyst to form MAA selectively in the oxidation of IBA, because the reaction is accompanied by two side reactions. However, it is still difficult to obtain detailed information about the proper strength.

REFERENCES

1. Mizutani, K., and Inoue, H., *Shokubai (Catalyst)* **14**, 183p (1972).
2. Otake, M., and Onoda, T., *Shokubai (Catalyst)* **18**, 169 (1976).
3. Otake, M., and Onoda, T., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 780. Kodansha, Tokyo/Elsevier, Amsterdam, 1981.
4. Akimoto, M., Ikeda, H., Okabe, A., and Echigoya, E., *J. Catal.* **89**, 196 (1984).
5. Ai, M., *J. Catal.* **85**, 324 (1984).
6. Ai, M., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. V. p. 475 (1984).
7. Ai, M., *Shokubai (Catalyst)* **27**, 428 (1985).
8. Ai, M., Boutry, P., and Montarnal, R., *Bull. Soc. Chim. Fr.*, 2775 (1970).
9. Bordes, E., and Courtine, P., *J. Catal.* **57**, 236 (1979).
10. Morselli, R. L., Trifiro, F., and Urban, L., *J. Catal.* **75**, 112 (1982).
11. Hodnett, B. K., Delmon, B., *J. Catal.*, **88**, 43 (1984).
12. Schneider R. A., Chevron Research Co., U.S. Patent 3,864,280 (1975).

13. Katsumoto, K., and Marquis, D. M. Chevron Research Co., U.S. Patent 4,132,670 (1979).

14. Tsigdinos, G. A., and Hallada, C. J., *Inorg. Chem.* **7**, 437 (1968).

15. Akimoto, M., Tsuchida, Y., Sato, K., and Echigoya, E., *J. Catal.* **72**, 83 (1981).

16. Otake, M., and Onoda, T., *J. Catal.* **38**, 494 (1975).

17. Ai, M., *J. Catal.* **54**, 223 (1978); "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 1060, Kodansha, Tokyo/Elsevier, Amsterdam, 1981.

18. Ai, M., "Proceedings, 9th Iberoamerican Symposium on Catalysis, Lisbon, 1984," Vol. II, p. 836 (1984); "Proceedings, 5th International Conference on the Chemistry and Uses of Molybdenum," Newcastle, 1985, *Polyhedron* (1986), in press.

19. Ai, M., and Suzuki, S., *Nippon Kagaku Kaishi* 260 (1973).