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Oxidation Activity and Acidity of MoO_3–P_2O_5 Catalysts

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The oxidations of 1-butene, butadiene, and acetic acid in a large excess of air were carried out over various Mo–P oxide catalysts with different P_2O_5 contents and at different calcination temperatures. The oxidation activities were compared with the dehydration activity for isopropyl alcohol, which was used as a measure of the acidity of the catalysts. The acidity of the catalysts increases with an increase in the P_2O_5 content and attains a maximum at about P/Mo = 0.1. With a further increase in P_2O_5, it decreases. P_2O_5 alone is completely inactive as a catalyst in the reactions. The acidity drops markedly with an increase in the calcination temperature. A good linear relationship is obtained between the dehydration activity and the oxidation activity for butene and butadiene, as well as the isomerization activity for butene. The activity per unit surface area for the oxidation of acetic acid is not affected by the P_2O_5 content. The results are discussed from the viewpoint of the acid–base nature of the reactants and the catalyst.

INTRODUCTION

In recent studies concerning oxidations on the MoO_3–Bi_2O_3–P_2O_5 catalyst system (*1–4*), the present authors have found that, with an increase in the Bi_2O_3 content, the acidity of the catalysts [which is indirectly measured by the activity in the dehydration of isopropyl alcohol (IPA) to propylene] increases at first, passes through a maximum at a Bi/Mo atomic ratio of 0.1, and then decreases to the value of the pure Bi_2O_3 catalyst, whose acidity is very low. In the presence of a large excess of oxygen, the activity for the oxidation and isomerization of such basic (electron-donating) compounds as olefins correlates fairly well with the acidity of the catalysts, and that for such electron-acceptor-type compounds as carboxylic acids sharply increases when the Bi_2O_3 content becomes more than Bi/Mo = 0.1. The findings on the activity and selectivity for the oxidation of some organic compounds under high oxygen concentration can be interpreted well in terms of the acid–base nature of the reactant and the catalyst.

The binary catalyst system of MoO_3–P_2O_5 is very effective for such partial oxidations as those of butadiene or crotonaldehyde to furan (*5*, *6*), of butadiene or butene to maleic anhydride (*1–4*, *7*), and of toluene to benzaldehyde (*8*, *9*); its catalytic specificity seems to be very different from that of the well-known Bi_2O_3–MoO_3 catalysts (Bi/Mo = 1–2) (*1–4*, *7*, *9–11*). Moreover, the activity has a fairly good thermal stability compared with pure MoO_3 or MoO_3-rich catalysts.

In the present work, attention is drawn to the MoO_3–P_2O_5 system. We have attempted to determine the role of P_2O_5 added to MoO_3 in the oxidation activity and to investigate the relationship between the oxidation and isomerization activities and the acidity of the catalyst.

It is hard to measure the acidity of catalysts by means of the conventional amine-titration method, for both the acidity and the surface area are very small, and, moreover, the catalysts have dark colors. However, it is well known that there are good correlations between the acidic properties and activities of catalysts for many acid-catalyzed reactions (*12*), so we have tried in this study to adopt the activity for the dehydration of IPA as a measure of the acidity of the catalysts.

EXPERIMENTAL METHODS

The vapor-phase oxidation of 1-butene, 1,3-butadiene, and acetic acid, and the dehydration of IPA, were carried out in an ordinary continuous-flow-type reaction system. The concentrations of the 1-butene, butadiene, and acetic acid were about 0.66, 0.66, and 1.5 mol % in air, respectively, and that of IPA was 1.65 mol % in air or nitrogen; the flow rate (at 25°C) was in the range of 1.5–2.0 liters/min; the amount of the catalyst used was 10–40 ml; the contact time, which is shown by the volume of the catalyst (ml) per total flow rate (ml/sec), was 0.4–1.6 sec. The reactor and the experimental and analytical procedures were the same as those employed in previous works (*1–9*).

The measurements were performed on two series of MoO_3–P_2O_5 catalysts. In Series A, the content of P_2O_5 was widely varied (P/Mo (atomic ratio) = 0, 0.013, 0.026, 0.05, 0.75, 0.10, 0.2, 0.3, ∞), keeping the calcination temperature at 520°C. In Series B, the calcination temperature was varied in the range 440–580°C, keeping the P/Mo atomic ratio at 0.1. The catalysts were both prepared as follows: the required quantities of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_3PO_4 were dissolved in hot water, after which pumice (10–20 mesh) was added; the solution was then evaporated with constant stirring, and finally dried in an oven at 130°C. The amount of pumice was 500 ml (about 150 g)/g atom of molybdenum and phosphorus. The catalysts were calcined for 5 hr in a stream of air. The packing density of the catalysts was about 0.75 g/ml in the P/Mo range of 0–0.3. The surface area of these catalysts was determined by the BET method, using nitrogen at −195°C.

RESULTS

A. Performance on Series A Catalysts

In this section, the measurements were performed over a series of MoO_3–P_2O_5 catalysts with different P/Mo ratios.

1. Dehydration of IPA (Acidity Measurement)

A gaseous mixture of IPA with air or nitrogen was passed through a bed of the catalyst at the contact time of 0.8 sec in the temperature range of 140–220°C. Apart from propylene, only diisopropyl ether and acetone were found in the product. Representative results of these experiments are listed in Table 1. The ether is produced to a significant extent with respect to propylene in the case of the nitrogen atmosphere, especially at low temperature, but only to a very little extent in air. On the other hand, the formation of acetone is very small in nitrogen, but much more appreciable in air, though propylene is the main product. No loss of activity was observed within 4–5 hr, even in the nitrogen atmosphere.

The value of the conversion to propylene at 185°C is plotted as a function of the P/Mo ratio in Fig. 1. With an increase in the P_2O_5 content, the conversion of IPA to propylene in an air atmosphere increases at first, passes through a maximum at the P/Mo atomic ratio of 0.1, and then decreases. The pure P_2O_5 catalyst prepared by the same procedure as the MoO_3–P_2O_5 catalysts is completely inactive under the conditions examined. The dehydration of IPA is markedly influenced by the reaction medium, either air or nitrogen, presumably due to the fact that the oxidation state of the metal oxides is changed with the reaction medium, which affects strongly the acidic nature of the catalyst. Therefore, it is not reasonable to correlate the dehydration activity measured in a nitrogen atmosphere with the other activities measured in air.

The dependence of the dehydration reaction on the IPA concentration was studied in an air atmosphere in order to evaluate the rate constant (k_D), which is more

TABLE 1
PRODUCT DISTRIBUTIONS IN THE REACTION OF IPA OVER MoO_3–P_2O_5 CATALYSTS[a]

Catalyst (atomic ratio):		P/Mo = 0.026			P/Mo = 0.10			P/Mo = 0.20		
Reaction temp (°C):		159	185	200	155	185	196	164	185	198
A. In nitrogen atmosphere										
Conv to (mol %)	C_3H_6	44	98	100	5.0	50	74	3.8	17	35
	$C_3H_7OC_3H_7$	19	2.0	0	10	7.0	5.0	3.3	7.0	3.3
	CH_3COCH_3	0	0	0	0.2	0.5	0.9	0.3	0.7	1.0
B. In air atmosphere										
Conv to (mol %)	C_3H_6	3.0	22	58	5.0	50	82	4.1	18	41
	$C_3H_7OC_3H_7$	0	1.0	0.2	0.8	0.7	0.4	0.3	0.6	0.3
	CH_3COCH_3	1.0	3.0	6.0	0.9	3.0	4.0	1.0	2.7	4.0

[a] IPA = 1.65 mol %; total flow rate = 1.5 l/min; catalyst = 20 ml.

adequate than the value of conversion as a measure of the dehydration activity of the catalysts. The relation between the IPA concentration in the charge and the propylene concentration in the produced gas is shown in Fig. 2. To find the reaction order in IPA (n), the trial-and-error treatment was undertaken, using the data of Fig. 2 and the ordinary kinetic equation: $C_0^{1-n} - C^{1-n} = (1 - n)k_Dt$, where C_0 and C are the reactant concentrations in the charge and the effluent gas, respectively, and where t is the contact time. The value of n was found to equal 0.2. This value of n was used in calculating k_D from the data in Fig. 1. The values of k_D at 185°C are plotted as a function of the P/Mo ratio on the right side in Fig. 1.

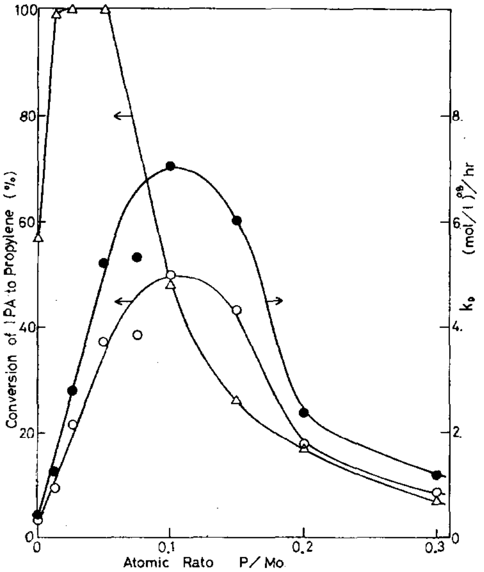

FIG. 1. Dehydration activity for IPA as a function of the phosphorus content: temp = 185°C, IPA concentration = 1.65 mol %, catalyst = 20 ml, total flow rate = 1.5 liters/min (contact time = 0.8 sec), (○) IPA conversion in air, (△) in nitrogen, (●) 0.2 order rate constant in air (k_D).

2. Oxidation of Butene

The oxidation of 1-butene was performed in the presence of excess air in the temperature range of 360–520°C under the

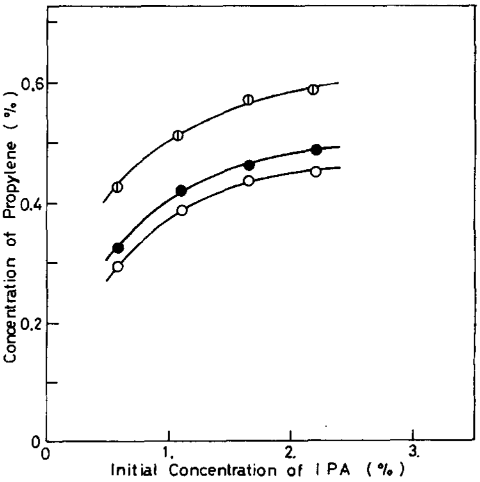

FIG. 2. Dependence of propylene formation on the initial concentration of IPA: (○) P/Mo = 0.013, T = 217°C, (⦶) P/Mo = 0.10, T = 180°C, (●) P/Mo = 0.3, T = 205°C in air; other conditions as in Fig. 1.

TABLE 2

Experimental Results of Butene Oxidation Over MoO_3–P_2O_5 Catalysts[a]

	Oxidation		Isomerization			
			Conv of 1-C_4H_8 to			
Catalyst composition P/Mo	Total conv of C_4H_8 (mol %)	Conv to C_4H_6 (mol %)	*cis*-2-C_4H_8 (mol %)	*trans*-2-C_4H_8 (mol %)	(*cis* + *trans*)/(1 + *cis* + *trans*)	$\frac{trans}{cis}$
0.	3.2	1.0	4.8	6.2	0.112	1.28
0.013	4.1	1.15	8.9	10.9	0.204	1.23
0.026	5.1	1.51	11.4	13.2	0.257	1.16
0.05	6.8	2.0	16.8	18.4	0.375	1.10
0.075	8.2	2.3	19.0	20.0	0.42	1.05
0.10	9.5	2.5	19.2	19.8	0.43	1.04
0.15	6.3	1.8	16.6	18.2	0.37	1.10
0.20	4.1	1.1	11.4	13.2	0.254	1.16
0.3	3.0	0.8	7.5	9.4	0.168	1.25

[a] Feed gas = 1-C_4H_8 0.66% in air; temperature = 420°C; total flow rate = 1.5 liters/min; catalyst = 10 ml.

conditions as described in the experimental section. Since oxygen is in a large excess, the oxidation of olefins over these catalysts proceeds by a series of parallel-consecutive paths and produces various intermediates whose amounts vary as the reaction advances. It is therefore hard to obtain the catalytic activity for the partial oxidation separately from that for the complete combustion. Table 2 shows comparative data obtained at 420°C and Table 3 shows some information about the selectivity of the catalyst. The selectivity of the catalyst is not appreciably modified by the P_2O_5 content. CO_2 and CO are the main products at high conversion of butene. In this study, as a measure of the oxidation activity for butene, the total consumption of butene (conversion to its isomers is not included) is adopted for convenience.

The total conversion of butene to products at 420°C is plotted as a function of the P/Mo ratio in Fig. 3. As the total conversion of butene is in the neighborhood of a 0.8 order in olefin concentration (2), the rate constants of the oxidation are calculated and plotted on the right side in Fig. 3.

Similarly to the dehydration activity, the oxidation activity of butene (k_O) increases with the P_2O_5 content and attains a maximum at P/Mo = 0.1.

3. Isomerization of Butene

The oxidation of butene is always accompanied by its isomerization. It is hard to evaluate the isomerization rate accurately due to the simultaneous oxidation of the isomers produced. The value of [*cis*-2-C_4H_8 + *trans*-2-C_4H_8]/[*cis*-2-C_4H_8 + *trans*-2-C_4H_8 + 1-C_4H_8] was adopted

TABLE 3

Selectivity of MoO_3–P_2O_5 Catalyst in Oxidation of Butene[a]

Catalyst composition P/Mo	Temp (°C)	Total conv of C_4H_8 (%)	Selectivity to (mol %)			
			MA[b]	C_4H_6	CO_2	CO
0.026	500	82	14	7	30	15
0.10	470	80	15	6	27	15
0.20	520	80	14	7	30	17

[a] Feed gas = 1-C_4H_8 0.66% in air; total flow rate = 1.5 liters/min; catalyst = 40 ml.

[b] MA = maleic anhydride.

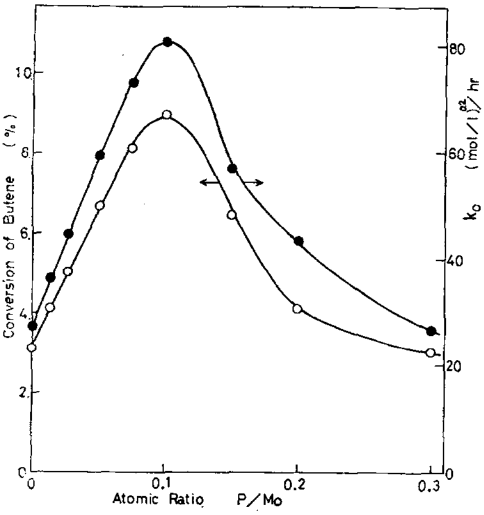

FIG. 3. Oxidation activity for butene as a function of the phosphorus content: temp = 420°C, 1-butene = 0.66 mol % in air, contact time = 0.4 sec, (○) conversion, (●) 0.8 order rate constant (k_0).

as a measure of the isomerization activity. The data at 250 and 420°C are plotted against the P/Mo ratio in Fig. 4. At thermodynamic equilibrium at 250 and 420°C, the values are about 0.84 and 0.80, respectively. The characters of the curves (Fig. 4) are almost the same as those of the oxidation (Fig. 3) and dehydration (Fig. 1) curves.

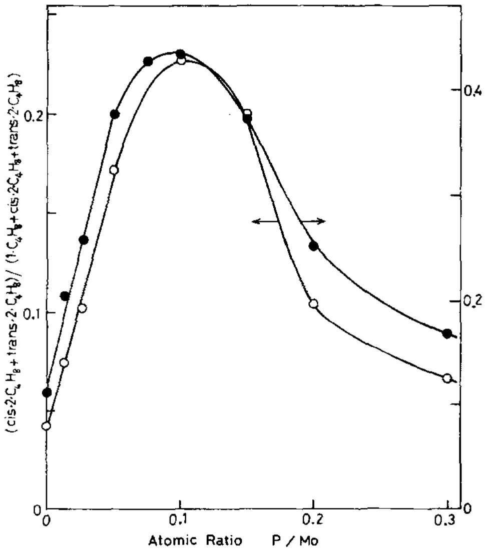

FIG. 4. Isomerization activity for 1-butene as a function of the phosphorus content: 1-butene = 0.66% in air, contact time = 0.4 sec, (○) T = 250°C, (●) T = 420°C.

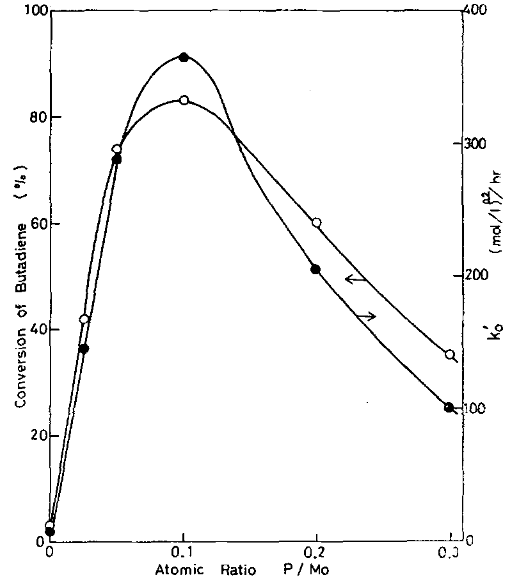

FIG. 5. Oxidation activity for butadiene as a function of the phosphorus content: temp = 420°C, catalyst = 40 ml, total flow rate = 2.0 liters/min (contact time = 1.2 sec), (○) conversion, (●) 0.8 order rate constant (k'_0).

4. *Oxidation of Butadiene*

The oxidation of butadiene was also carried out in a manner similar to that of

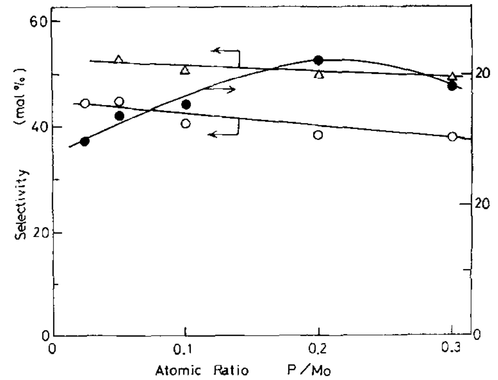

FIG. 6. Variation of the selectivity of butadiene to furan and maleic anhydride with the P_2O_5 content: catalyst = 40 ml, total flow rate = 2.0 l/min, temp = 390–470°C, (○) maleic anhydride, (●) furan at conversion of 60%, (△) maleic anhydride at conversion of 80%.

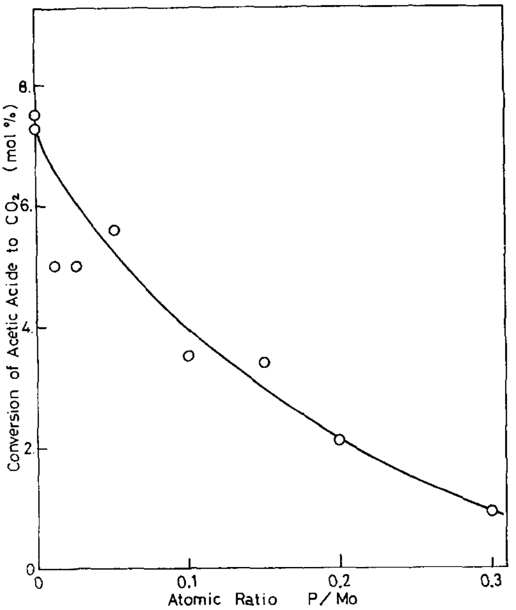

Fig. 7. Oxidation activity for acetic acid as a function of the phosphorus content: temp = 420°C, acetic acid = 1.5 mol % in air, contact time = 0.8 sec.

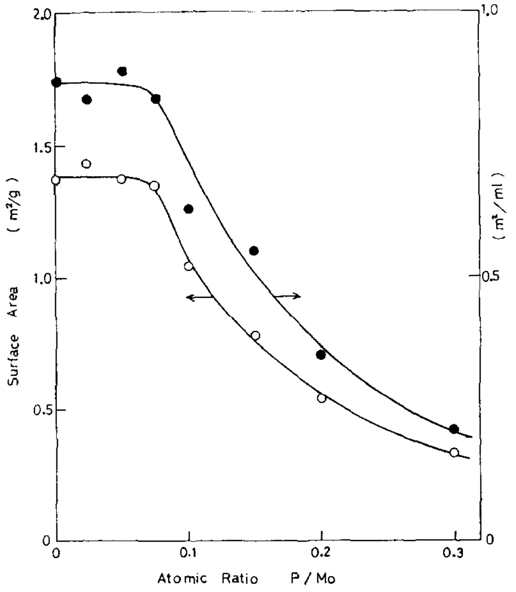

Fig. 8. Effect of the P_2O_5 content on the surface area: (○) m^2/g, (●) m^2/ml.

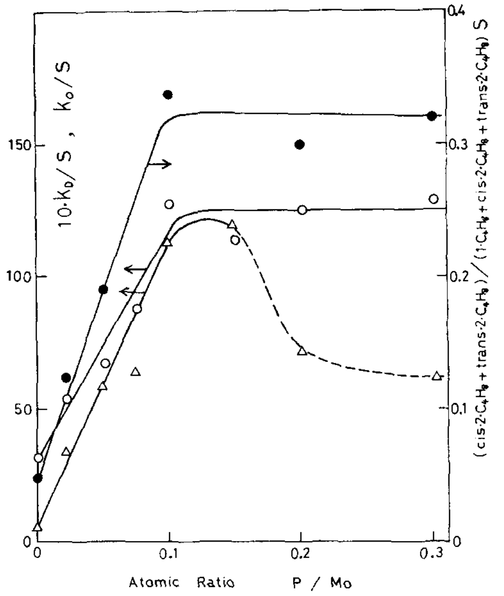

Fig. 9. Activities per unit surface area versus content of P_2O_5: (△) $10 \cdot k_D/S$ (IPA dehydration), (○) k_o/S (butene oxidation), (●) (isomerization of butene at 250°C), $S = m^2/ml$.

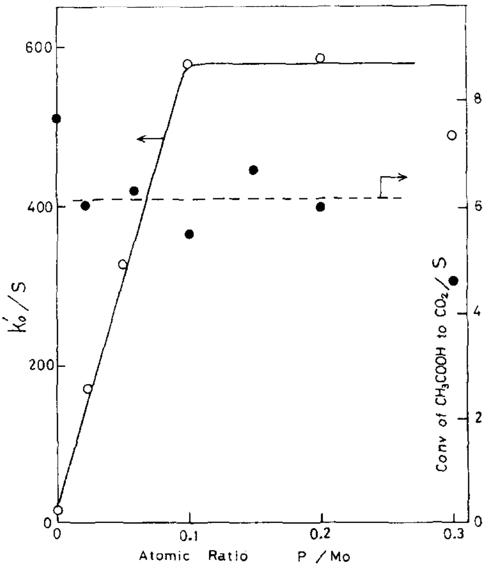

Fig. 10. Activities per unit surface area versus content of P_2O_5: (○) k'_o/S (butadiene oxidation), (●) conversion of acetic acid to CO_2/S, $S = m^2/ml$.

butene. Figure 5 gives the dependence of the total butadiene conversion (total butadiene consumption) and the rate constant of the oxidation at 420°C on the P_2O_5 content. The rate constant (k'_O) was calculated by assuming that the reaction is of 0.8 order in butadiene (*2*). The features of the curves were the same as those of the curves obtained in the butene oxidation.

Figure 6 gives information about the products (*6*). The effect of the P_2O_5 content on the selectivity to maleic anhydride was small, while the formation of furan gave a maximum at the P/Mo atomic ratio of about 0.2–0.3.

5. Oxidation of Acetic Acid to CO_2

Contrary to such olefins as butene and butadiene, which are basic because of their double bonds, carboxylic acids are considered to interact less easily with the catalyst as the activity increases (*1–4*).

The oxidation of acetic acid was carried out, and the conversion of acetic acid to CO_2 was adopted as a measure of the activity for the reaction, because CO_2 was the main product. Figure 7 shows the conversion of acetic acid as a function of the P/Mo ratio. The oxidation activity for acetic acid decreases steadily with an increase in the P/Mo ratio. The shape of the curve is quite different from that of the oxidation of olefins.

6. Surface Area

The effect of the P_2O_5 content on the surface area of the MoO_3–P_2O_5 catalysts was examined (Fig. 8). The surface area remains unchanged at a low P_2O_5 content ($P/Mo < 0.1$); however, it decreases with a further increase in P_2O_5 content ($P/Mo > 0.1$).

7. Catalytic Activities per Unit Surface Area

The influence of the P_2O_5 content on the catalytic activities per unit surface area is shown in Figs. 9 and 10. For the reactions of IPA, butene, and butadiene these activities vary in a similar way; they increase linearly with P_2O_5 content up to about $P/Mo = 0.1$ and remain almost unchanged with a further increase in P_2O_5 content, except in the case of the IPA dehydration in which the activity per unit surface area decreases, to some extent, with the P_2O_5 content. However, the activity for the oxidation of acetic acid remains almost unchanged over the whole range of P/Mo.

B. Performance on Series B Catalysts

Another series of experiments was performed using MoO_3–P_2O_5 ($P/Mo = 0.1$) catalysts with different calcination temperatures in the 440–580°C range; the conditions and procedure for each reaction were the same as those described in the preceding section.

1. Dehydration of IPA (Acidity Measurement)

The value of the conversion of IPA to propylene and the rate constant for the 0.2 order reaction (k_D) at 185°C are plotted as a function of the calcination temperature in Fig. 11. The catalytic activity for the dehydration of IPA decreases almost linearly with the calcination temperature.

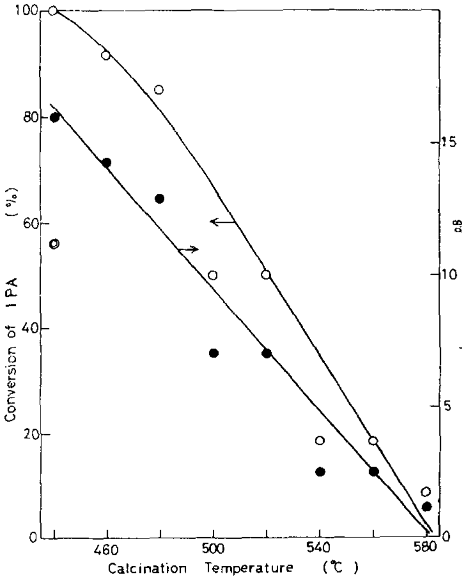

FIG. 11. Dependence of the dehydration activity for IPA on the calcination temperature: $P/Mo = 0.1$, reaction temp = 185°C, IPA = 1.65 mol % in air, contact time = 0.8 and 0.4 sec, (○) conversion (contact time = 0.8 sec), (◎) (0.4 sec), (●) 0.2 order rate constant (k_D).

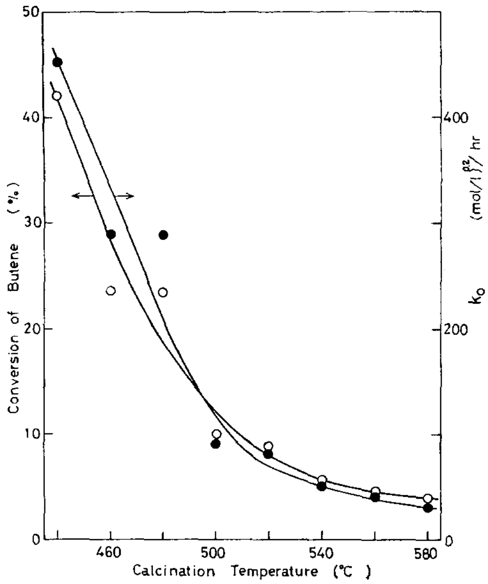

FIG. 12. Dependence of the oxidation activity for butene on the calcination temperature: P/Mo = 0.1, T = 420°C, 1-butene = 0.66 mol % in air, contact time = 0.8 sec, (○) conversion, (●) 0.8 order rate constant (k_0).

2. Oxidation of Butene

The value of the total conversion of butene and the 0.8 order rate constant (k_0) at 420°C are shown against the calcination temperature in Fig. 12. The catalytic activity for butene oxidation decreases sharply with the calcination temperature.

3. Isomerization of Butene

The value of [*cis*-2-C_4H_8 + *trans*-2-C_4H_8] / [1-C_4H_8 + *cis*-2-C_4H_8 + *trans*-2-C_4H_8] at 250 and 420°C is plotted against the calcination temperature in Fig. 13. The catalytic activity for butene isomerization also decreases almost linearly with the calcination temperature.

4. Surface Area

The effect of the calcination temperature on the surface area was examined (Fig. 14). On increasing the calcination temperature, the surface area declined sharply in the temperature range below about 500°C, and less markedly above 500°C.

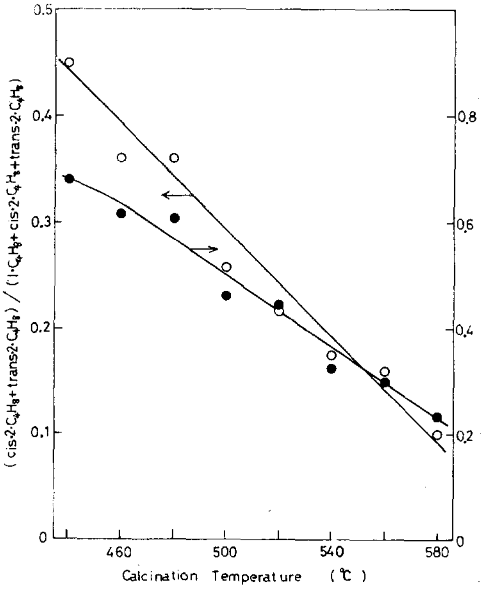

FIG. 13. Dependence of the isomerization activity for 1-butene on the calcination temperature: 1-butene = 0.66 mol % in air, contact time = 0.4 sec, (○) T = 250°C, (●) T = 420°C.

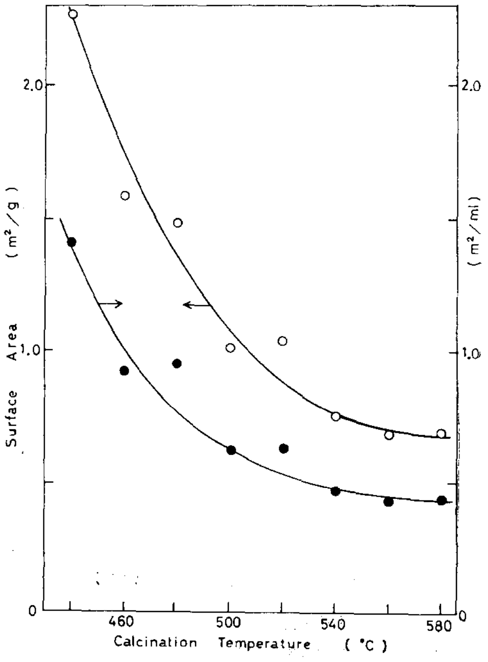

FIG. 14. Effect of the calcination temperature on the surface area: (○) m^2/g, (●) m^2/ml.

5. *Catalytic Activities per Unit Surface Area*

The IPA dehydration activity per unit surface area decreases almost linearly with the calcination temperature; however, the activity per unit surface area for butene oxidation falls sharply at 480–500°C (Fig. 15).

DISCUSSION

Assuming that the dehydration activity really represents the acidity of catalysts, the results show that the acidity of the catalysts rises upon the addition of a small amount of P_2O_5 to MoO_3, passes through a peak at about $P/Mo = 0.1$, and then decreases sharply upon any further addition (Fig. 1). It is considered from Figs. 8 and 9 that the rise in the acidity at the low P_2O_5 content ($P/Mo < 0.1$) is attributable to a rise in the acidity per unit surface area, and that the sharp fall at the high P_2O_5 content ($P/Mo > 0.1$) is caused mainly by the decrease in the surface area and only partly by a fall in the acidity per unit surface area.

The acidity of the pure P_2O_5 catalyst, without MoO_3, was quite low. This suggests that the acidic nature of the MoO_3–P_2O_5 system does not arise from the phosphorus component alone, but from a new acidic site generated by the combination of molybdenum and phosphorus components. Probably, the formation is optimal at the P/Mo ratio of 0.1. The decrease of the acidity caused by the use of a high calcination temperature seems to result from decreases both in the acidity per unit surface area and in the surface area itself (Figs. 14 and 15).

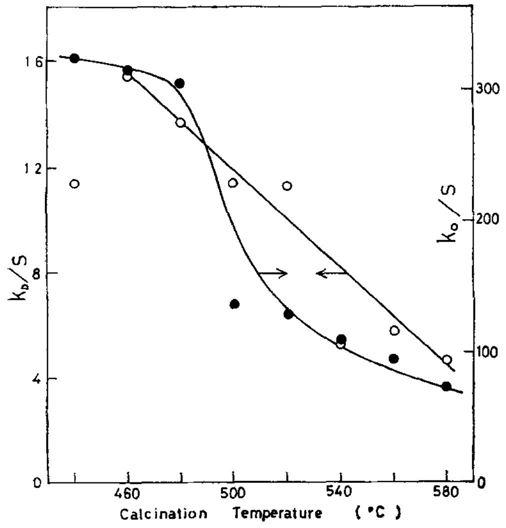

FIG. 15. Activities per unit surface area versus calcination temperature: (○) k_D/S (IPA dehydration), (●) k_O/S (butene oxidation), S = surface area (m^2/ml).

If the acidic site of the catalyst plays a main role in the oxidation and isomerization of olefins, the existence of a proportional relationship between these activities and the acidity must be expected. The character of the curves in Fig. 1 obtained in an air atmosphere is quite similar to those in the olefin oxidation and isomerization shown in Figs. 3, 4, and 5 and the character of the curves in Fig. 11 is also similar to those in Figs. 12 and 13. The dependence of the oxidation and isomerization activities for butene on the dehydration activity for IPA is shown in Figs. 16 and 17. A good linear relationship was obtained among these activities, except in the case of the oxidation in which catalyst modification has been effected by changing the calcination temperature (Fig. 17). A good linear relationship was also found for the dependence of butadiene oxidation on IPA dehydration activity. These results indicate that the oxidation activity for olefins as well as the isomerization activity correlates fairly well with the acid property of the catalysts.

The rapid drops in the oxidation activity for butene with an increase in the calcination temperature (Fig. 12, 15, and 17) is explained by assuming that the higher the acid strength of a site, the more easily it is destroyed, that is, the site of strong acid strength which is effective in the oxidation is destroyed selectively.

The activity for the oxidation of acetic acid decreases steadily with the P_2O_5 content, but the value of the activity per unit surface area remains unchanged (Fig. 7 and 10). This character is completely different from that for the oxidation of

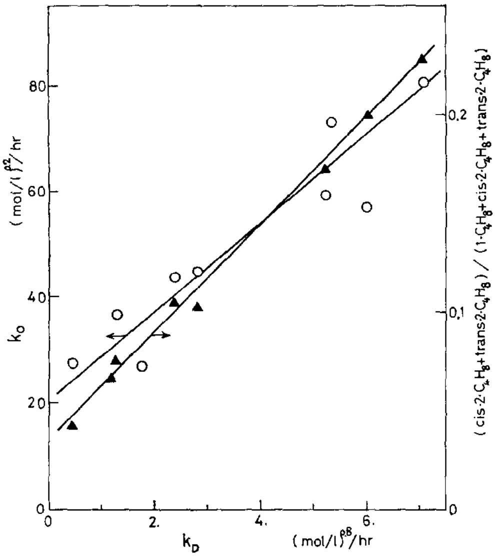

FIG. 16. Oxidation and isomerization activities for butene versus dehydration activity for IPA. The variation in these activities has been effected by changing the phosphorus content (isomerization at 250°C).

olefins. This can be also explained by assuming that acidic compounds are catalyzed at a different site of catalyst from the acidic site which is effective in the oxidation and isomerization of such basic compounds as olefins. This site may be one having a basic nature, whose amount is not presumably changed with the P_2O_5 content, although proof concerning the basic site is required to clarify this point.

In summary we can say that the amount of P_2O_5 and the calcination temperature greatly affect the acidities of the catalyst systems and that the catalytic activities for oxidation and isomerization are correlated well with the acidity of the catalysts.

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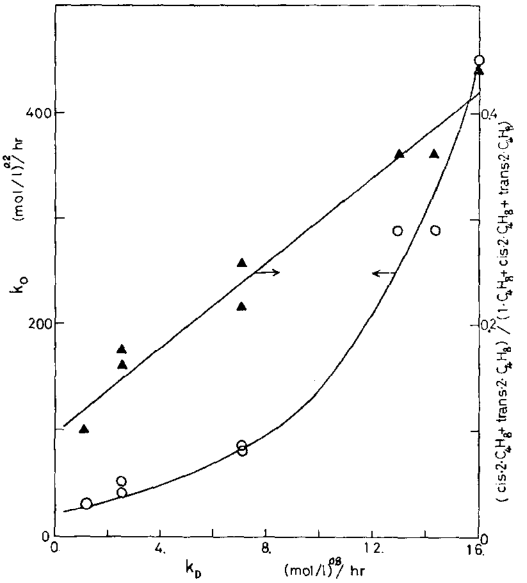

FIG. 17. Oxidation and isomerization activities for butene versus dehydration activity for IPA. The variation in these activities has been effected by changing the calcination temperature (isomerization at 250°C).

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