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Oxidation Activity and Acid–Base Properties of 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

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The acidic and basic properties and the oxidation activity for *n*-butane and 1-butene were studied for V_2O_5–P_2O_5 catalysts prepared by six methods. The acidity increases and the basicity decreases with an increase in the phosphorus content. The catalytic activity for two acid-catalyzed reactions revealed that, in the cases of certain catalysts, a marked generation of strong-acid sites occurs at P/V atomic ratio = 1.0, while in the cases of the other catalysts, few or no strong-acid sites are generated. The oxidation activity for both *n*-butane and 1-butene decreases greatly with the phosphorus content, much as the catalytic activity does for a base-catalyzed reaction such as the dehydrogenation of ethanol, indicating that the activity is governed by basic or oxidizing sites, rather than by the acidic sites, not as in the cases of many other V_2O_5-based catalysts. The selectivity to maleic anhydride from 1-butene is not affected by the method of preparation and steadily increases with the phosphorus content up to P/V = 1.6. However, in the case of the oxidation of *n*-butane, the selectivity is greatly affected by the method of preparation and the composition. It is considered that the high selectivity is related to the generation of strong-acid sites. © 1986 Academic Press, Inc.

INTRODUCTION

Maleic anhydride has traditionally been produced by the air oxidation of benzene. In recent years, though, as a more economic route, the oxidation of butene with V_2O_5–P_2O_5-based catalysts has been proposed (*1*). In addition to a great number of patents, scientific studies have also been reported on the oxidation of butene to maleic anhydride and the V_2O_5–P_2O_5 binary system (*2–9*).

The V_2O_5–P_2O_5-type catalysts seemed unsuitable for use in the oxidation of paraffinic hydrocarbons because of their low oxidation activity. However, more recently, increasing attention has been given to the improvement of the V_2O_5–P_2O_5 catalysts so as to achieve a satisfactory performance even in the oxidation of paraffinic hydrocarbons (*10, 11*).

A survey of the recent literature indicates that the performance of V_2O_5–P_2O_5 catalysts in the oxidation of *n*-butane to maleic anhydride is greatly dependent on their method of preparation. However, it also seems interesting to note that catalysts with a higher phosphorus composition, P/V atomic ratio = ca. 1.6, are usually employed for the oxidation of butene, while lower-phosphorus-content catalysts, P/V = 1.0 to 1.2, have been proposed as being effective for use in the oxidation of *n*-butane (*11*).

The structure of the V_2O_5–P_2O_5 binary system has been studied relatively well, and several phases, such as $(VO)_2P_2O_7$ (*6, 8, 9*), α-$VOPO_4$ (*11*), and β^*-phase (*12*), have been proposed as the active phase. We may be sure that the catalytic action is connected with the presence of a certain special phase. However, it has not yet fully explained why these phases exhibit a desirable catalytic action.

It is considered that such chemical properties as redox and acid–base properties are more directly responsible for the catalytic action (*13*) and that these properties are enhanced or modified by the addition of phosphorus.

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TABLE 1

Preparation of V_2O_5–P_2O_5 Catalysts

Designator	Starting materials		Reducing agent	Medium	Ref.
	Vanadium	Phosphorus			
A	NH_4VO_3	85% H_3PO_4	None	H_2O	*2, 3, 8*
B	V_2O_5	$NH_4H_2PO_4$	Oxalic acid	H_2O	*8*
C	V_2O_5	85% H_3PO_4	37% HCl	H_2O	*9*
D	V_2O_5	85% H_3PO_4	Lactic acid	Lactic acid	*12*
E	V_2O_5	$POCl_3$	$POCl_3$	THF[a]	*14*
F	V_2O_5	98% H_3PO_4	$C_6H_5CH_2OH$	Isobutanol	*15*

[a] Tetrahydrofuran.

In this work, the effects of the method of preparation and the P/V composition on the acid–base properties and the catalytic action for the oxidation of *n*-butane and 1-butene were studied, and an attempt was made to ascertain how the oxidation activity and selectivity can be related to the acid–base properties.

EXPERIMENTAL

Catalysts

Catalysts were prepared by six methods described in earlier works. The methods are summarized in Table 1. The P/V means the atomic ratio bassing on the amounts of reactants used. The precursors were dried at 130°C for 6 h and then heated at 300°C for 6 h. Thereafter, they were broken up and sieved to 10–20 mesh size. The calcination was performed at 450°C in a stream of air (ca. 1.5 vol/vol/min) for 6 h.

Oxidation of n-Butane and 1-Butene

The reactions were carried out in an ordinary flow-type reaction system. The initial concentration of hydrocarbon was 2.2 mol% in air, total flow rate (at 20°C) was 280 ml/min (ca. 0.7 mol/h), and the amount of catalyst used was in the range of 0.3–30 g. Usually, the data were taken at least 8 h after the start of the experiment. The reactor and the procedures were the same as those used in a previous work (*16*).

Acidity Measurements

NH_3 adsorption. The acidity was measured by means of the adsorption of NH_3 from the gas phase, using the static method. The technique of the measurements has been described in earlier papers (*17–19*).

Catalytic activity for acid-catalyzed reaction. As measures of acidity of catalyst, the catalytic activities for two acid-catalyzed reactions such as dehydration of ethanol to ethylene and isomerization of 1-butene to 2-butenes were measured (*4, 18, 19*). The reactions were carried out in a flow reaction system. The initial concentrations of ethanol and 1-butene were 1.6 and 1.2 mol% in air, respectively. The total flow rate was kept constant at 400 ml/min (ca. 1.0 mol/h) and the amount of catalyst used was 1.0 to 20 g.

Basicity Measurements

SO_2 adsorption. The amount of SO_2 adsorbed was measured, using the static method (*17–19*).

Catalytic activity for base-catalyzed reaction. As a model of base-catalyzed reaction, oxidative dehydrogenation of ethanol to acetaldehyde was used and the catalytic activity for this reaction was measured as an index of the basic property (*4, 18, 19*). The reaction conditions were the same as those used in the dehydration of ethanol.

TABLE 2

Structure of the V_2O_5–P_2O_5 Catalysts

Catalyst	P/V atomic ratio				
	0.8–0.9	1.0	1.1–1.2	1.6	2.0
A	β-$VOPO_4$ α-$VOPO_4$	α-$VOPO_4$ β-$VOPO_4$	α-$VOPO_4$	Amorph[a]	Amorph[a]
B	β-$VOPO_4$	β-$VOPO_4$ α-$VOPO_4$	Amorph[a]	Amorph[a]	Amorph[a]
C	Unknown[b] α-$VOPO_4$	$(VO)_2P_2O_7$ Unknown[b]	$(VO)_2P_2O_7$	$(VO)_2P_2O_7$	$VO(PO_3)_2$
D	—	—	$(VO)_2P_2O_7$	Amorph[a]	—
E	β-$VOPO_4$	$(VO)_2P_2O_7$ β-$VOPO_4$	$(VO)_2P_2O_7$	Amorph[a]	$VO(PO_3)_2$
F	—	—	$(VO)_2P_2O_7$	$(VO)_2P_2O_7$	Amorph[a]

[a] Amorph = amorphous.

[b] Unknown = unknown phase.

Note. References used for the identification; α-$VOPO_4$ (*8*), β-$VOPO_4$ (*8, 20*). $(VO)_2P_2O_7$ (*6, 8*), $VO(PO_3)_2$ (*8, 21*).

Apparatus

X-Ray powder analysis was carried out with a Rigaku Denki diffractometer using Cu*Kα* radiation.

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

RESULTS

Structure

The structures of the catalysts used in the oxidation of *n*-butane were determined by means of their X-ray diffraction patterns (Table 2). The structures are related to the content of phosphorus to a certain extent. The results may be summarized as follows:

(i) The main structure is β-$VOPO_4$ at P/V = 0.8–0.9.

(ii) $(VO)_2P_2O_7$ or α-$VOPO_4$ is observed at P/V values from 1.1 to 1.2.

(iii0 Both β-$VOPO_4$ and $(VO)_2P_2O_7$ or α-$VOPO_4$ are observed in the range intermediate between the above two ranges, P/V = 1.

(iv) The crystallinity decreases with the content of phosphorus at P/V > 1.

(v) At P/V = 1.6, $(VO)_2P_2O_7$ is the sole phase observed.

(vi) At P/V = 2.0, the presence of $VO(PO_3)_2$ is observed in some cases.

Surface Area

The effects of the composition and the method of preparation on the specific surface area were studied (Fig. 1). The V–P (E) and V–P (F) catalysts possess a high surface area, as has been stated in the patents (*14, 15*).

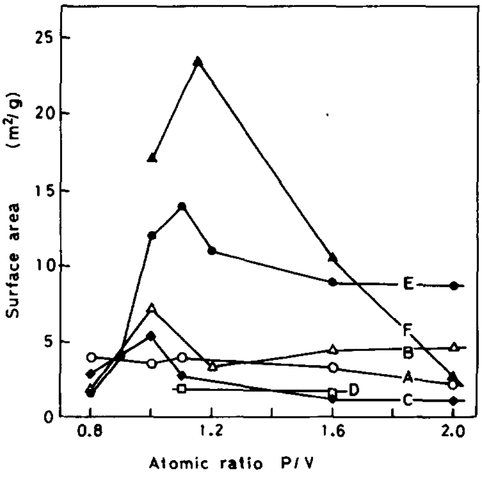

FIG. 1. Surface area of the V_2O_5–P_2O_5 catalysts.

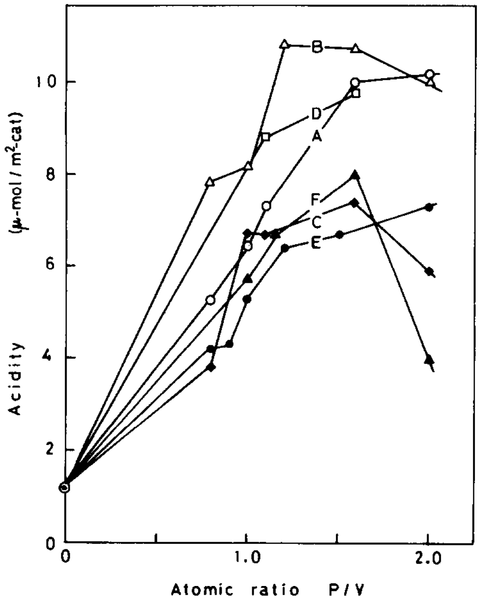

FIG. 2. Acidity of the V_2O_5–P_2O_5 catalysts.

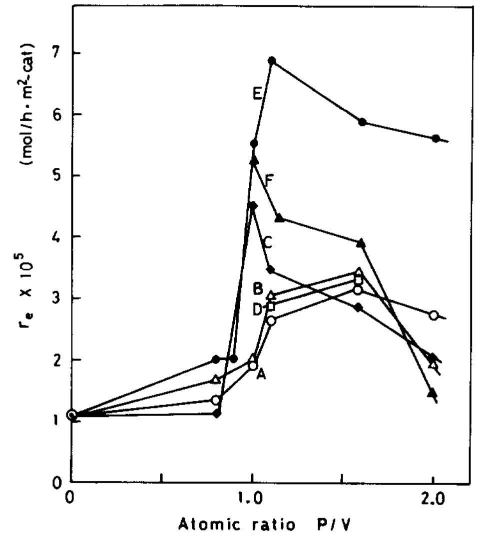

FIG. 3. Catalytic activity for dehydration of ethanol.

Acidic Property

The acidity (number of acidic sites) per unit of the surface areas of the catalysts, as determined by the amount of NH_3 irreversibly adsorbed at a pressure of about 300 mm Hg and 200°C, is plotted as a function of the phosphorus content in Fig. 2. The acidity increases steadily with an increase in the phosphorus content up to about P/V = 1.6.

As other measures of the acidic property, the catalytic activity for two acid-catalyzed reactions were obtained. Figure 3 shows the rate of the dehydration of ethanol to ethylene at 220°C, r_e (mol/h · m² of catalyst). In the cases of the V–P (C), V–P (E), and V–P (F) catalysts, the activity sharply increases at P/V = 1.0 and then decreases with a further increase in the phosphorus content. On the other hand, in the cases of the V–P (A), V–P (B), and V–P (D) catalysts, the activity increases less sharply in the wide P/V range from 1.1 to 1.6.

Figure 4 shows the rate of the isomerization of 1-butene to 2-butenes at 160°C, r_i (mol/h · m² of catalyst). In the cases of the V–P (C), V–P (E), and V–P (F) catalysts, the activity sharply increases at P/V = 1.0, much as in the case of the dehydration of ethanol (Fig. 3). However, in the cases of the V–P (A), V–P (B), and V–P (D) catalysts, the activity decreases a little with the phosphorus content in the P/V range from 0.8 to 2.0.

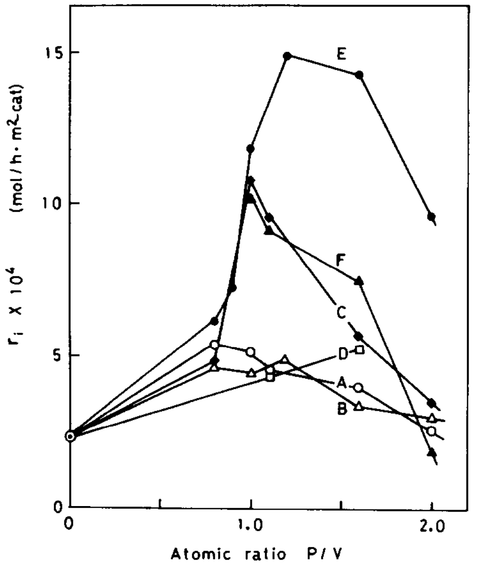

FIG. 4. Catalytic activity for isomerization of butene.

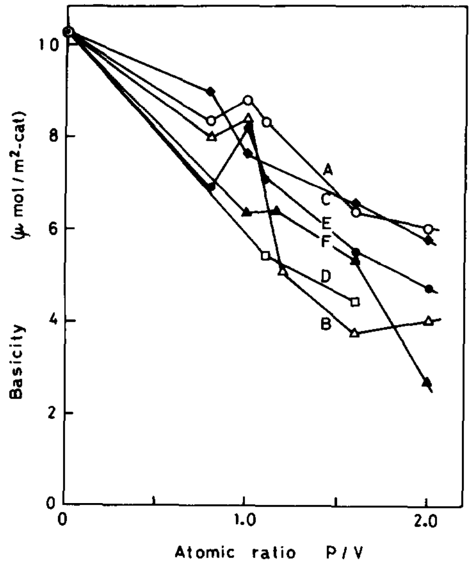

FIG. 5. Basicity of the V_2O_5–P_2O_5 catalysts.

Basic Property

Since the amount of SO_2 irreversibly adsorbed on the V_2O_5–P_2O_5 catalysts is too small to be measured, the amount of SO_2 reversibly adsorbed at 20°C was used as an index of the basicity. The basicity per unit of the surface area is plotted in Fig. 5. As can be predicted, the basicity decreases with an increase in the phosphorus content.

As another index of the basic property, the catalytic activity for oxidative dehydrogenation of ethanol was measured. Figure 6 shows the rate at 200°C, r_a (mol/h · m^2 of catalyst). With an increase in the phosphorus content, the activity decreases much more sharply than the basicity obtained by the SO_2 adsorption (Fig. 5).

Oxidation Activity

The oxidation activity was studied for both *n*-butane and 1-butene. The consumption of a reactant with a fixed amount (20.0 m^2) of the catalyst at 480°C (*n*-butane) and at 370°C (1-butene) is plotted as a function of the phosphorus content in Figs. 7 and 8.

The oxidation activity for *n*-butane and that for 1-butene decrease in a manner analogous with the increase in the phosphorus content. The difference in the specific oxidation activity depending on the difference in the method of catalyst preparation is relatively small.

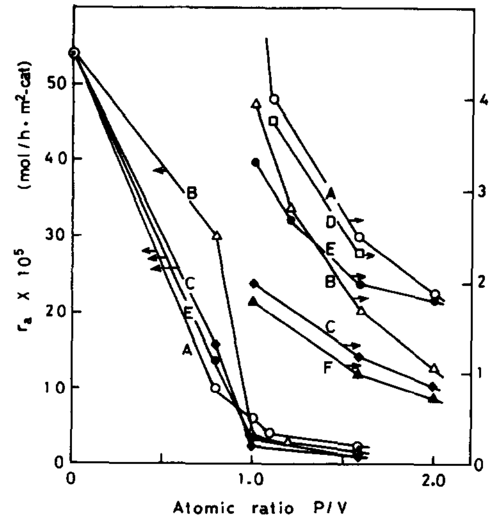

FIG. 6. Catalytic activity for oxidative dehydrogenation of ethanol.

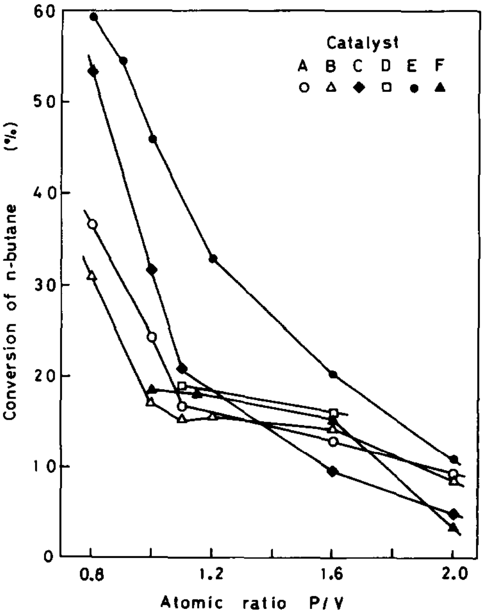

FIG. 7. Catalytic activity for oxidation of *n*-butane.

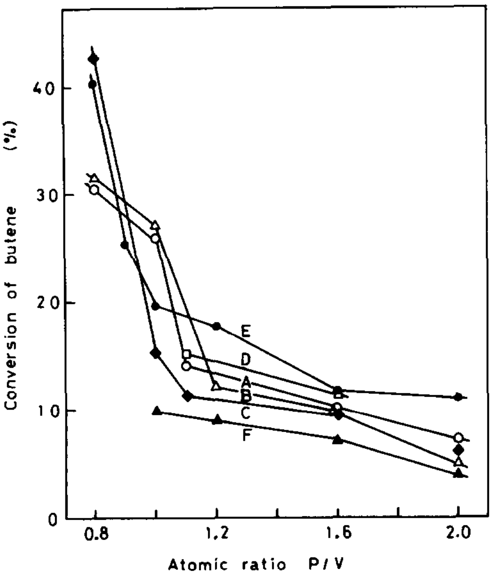

FIG. 8. Catalytic activity for oxidation of butene.

Oxidation Selectivity

The main products in the oxidation of *n*-butane were maleic anhydride and carbon oxides, and the amounts of the other products were negligibly small. The selectivity to maleic anhydride at a fixed level (50%) of *n*-butane conversion was compared in Fig. 9.

In the cases of the V–P (C), V–P (E), and V–P (F) catalysts, the selectivity sharply increases at P/V = 1.0, attains a maximum at P/V = 1.0 to 1.2, and then decreases with a further increase in the phosphorus content. On the other hand, in the cases of the V–P (A), V–P (B), and V–P (D) catalysts, the increase in the selectivity at P/V = 1.0 is slight, but the selectivity steadily increases up to P/V = 2.0.

Next, the selectivity in the oxidation of 1-butene was studied. In this case, the amounts of the intermediate products, such as butadiene and furan, are so great that the estimation of the selectivity to maleic anhydride at a conversion of 50% is difficult. Therefore, the selectivity was compared at a high level of 1-butene conversion, 99 to 100%, where almost all of the intermediate products are consumed. As for the stability of maleic anhydride, it has been known that maleic anhydride is stable enough under the conditions used for the oxidation of butene (*22*) (Fig. 10).

The selectivity steadily increases with the phosphorus content up to P/V = 1.6, and there no clear difference in the selectivity depending on the difference in the method of catalyst preparation is observed.

DISCUSSION

As may be seen in Table 2, the structure is related to the phosphorus content, to a certain extent, but the effect of the method of catalyst preparation on the structure is still obscure.

Since phosphorus oxide is an acidic oxide, it can easily be predicted that the acidity will increase and the basicity will decrease with an increase in the phosphorus content. However, there exists a large discrepancy in the fashion of variation between the values obtained by means of the adsorption method (Figs. 2 and 5) and those obtained by means of the catalytic activity (Figs. 3, 4, and 6). This discrepancy may be caused by the variation in the acid- or base-strength, which cannot be measured by the

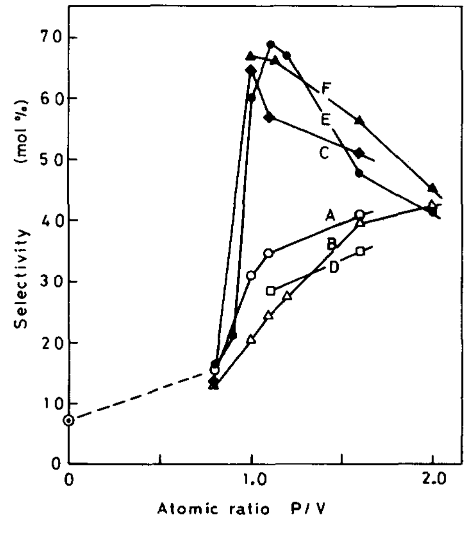

FIG. 9. Selectivity to maleic anhydride at a *n*-butane conversion of 50%.

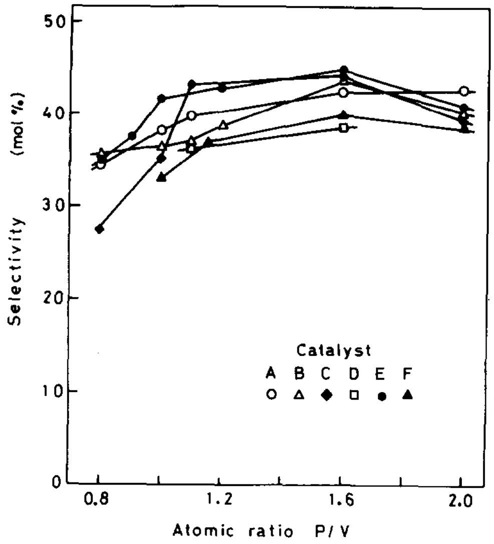

FIG. 10. Selectivity to maleic anhydride at a butene conversion of 99 to 100%.

adsorption method. Certainly, the acidity and basicity obtained by the adsorption method include a number of sites whose acid- or base-strength is too low to play a role in catalyzing the reactions. On the other hand, the values obtained by the catalytic activity can reflect the variation in the acid- or base-strength as well as in the number of sites.

In line with this thought, it can be said that, in the cases of the V–P (C), V–P (E), and V–P (F) catalysts, a marked generation of strong-acid sites occurs at P/V = 1.0 and that the acid strength decreases gradually with a further increase in the phosphorus content. On the other hand, in the cases of the V–P (A), V–P (B), and V–P (D) catalysts, there is little or no generation of strong-acid sites.

As for the basic property, the values obtained by the catalytic activity (Fig. 6) decrease much more sharply than those obtained by the SO_2 adsorption (Fig. 5). This may be caused by the decrease in the base strength with an increase in the phosphorus content.

The oxidation activity for both *n*-butane (Fig. 7) and 1-butene (Fig. 8) decrease greatly with the phosphorus content, much as does the activity for the oxidative dehydrogenation of ethanol (Fig. 6), but unlike the acidic property (Figs. 2, 3, and 4). This indicates that the oxidation activity is governed by the basic property, which is related to the oxidizing function of the catalyst (*13*) and that the oxidation activity is independent of the acidic property, unlike the cases of many other V_2O_5-based mixed oxides, such as V_2O_5–MoO_3 (*23*), V_2O_5–TiO_2 (*24*), V_2O_5–SnO_2 (*17*), V_2O_5–Fe_2O_3 (*19*), and V_2O_5–Co_3O_4 (25).

Possibly, the basic sites, especially the sites of stronger bases, are preferentially extinguished by addition of a large amount of phosphorus, and, as a result, the V_2O_5–P_2O_5 catalysts are deficient in basic property to catalyze the oxidation reactions. Therefore, the rate of oxidation is controlled by the action of the basic or oxidation sites rather than by the activation of hydrocarbon on acidic sites (*13*). This may be the main difference between the V_2O_5–P_2O_5 catalysts and the other V_2O_5-based oxides.

It should also be noted that the effect of the method of catalyst preparation on the specific oxidation activity (activity per unit of surface area) is relatively small. In addition, it seems difficult to connect the oxidation activity with the presence of a special phase.

As may be seen in Fig. 10, the selectivity in the oxidation of 1-butene to maleic anhydride is scarcely affected by the difference in the method of catalyst preparation, and it steadily increases with the phosphorus content up to P/V = 1.6. These results are consistent with those obtained in earlier studies (*8, 22*). It has been proposed that the addition of phosphorus plays a role in extinguishing the basic sites which promote the oxidative dehydrogenation of 2-butanol and, accordingly, conducts the reaction into a side pathway as follows (*16, 26*):

$$C_4H_8 \rightleftarrows C_2H_5CH(OH)CH_3 \rightarrow C_2H_5COCH_3 \rightarrow 2\ CH_3COOH$$

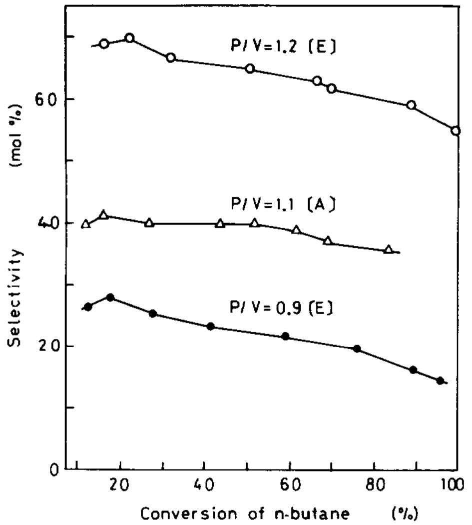

FIG. 11. Selectivity to maleic anhydride as a function of the conversion of *n*-butane.

However, in the case of the oxidation of *n*-butane, the situation is not the same; that is, the selectivity depends greatly on the method of catalyst preparation and the composition (Fig. 9).

Since the conditions required for the oxidation of *n*-butane are much more severe than those for the oxidation of 1-butene, the effect of the consecutive degradation of the maleic anhydride thus produced on the selectivity was examined for the P/V = 1.2 (E), P/V = 0.9 (E), and P/V = 1.1 (A) catalysts (Fig. 11). As may be seen in Fig. 11, the variation in the selectivity with the increase in the conversion is small, indicating that consecutive degradation is not a factor deciding the selectivity.

It was thus postulated that the large variation in the selectivity in the oxidation of *n*-butane is caused by the reaction of butane, i.e., the first in a series of consecutive steps;

$$C_4H_{10} \rightarrow C_4H_8 \rightarrow C_4H_6 \rightarrow \text{furan} \rightarrow \text{maleic anhydride}$$

The selectivity (Fig. 9) varies in the same manner as the catalytic activity for the two acid-catalyzed reactions does (Figs. 3 and 4). This leads us to consider that the high selectivity in the oxidation of *n*-butane is related to the generation of strong-acid sites. Indeed, it has been proposed that the activation of a reactant molecule, which is attributed to an acid–base–type interaction between catalyst and reactant, is one of the necessary conditions for a selective oxidation (*13*). Possibly, the presence of strong-acid sites is required to activate *n*-butane, because paraffinic hydrocarbons are deficient in their affinity with the catalyst. This view is supported by the fact that 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$)-based catalysts, which possess strong-acid sites, also exhibit a high selectivity in the oxidation of *n*-butane to maleic anhydride (*27*).

It should be noted that the activity and the selectivity are not always controlled by the same factor. In the case of the oxidation of *n*-butane with V_2O_5–P_2O_5 catalysts, for example, the activity is controlled by the basic or oxidizing function, while the selectivity is controlled by the acidic property. This may be the reason why lower-phosphorus catalysts are used for the oxidation of *n*-butane.

On the other hand, in the case of the oxidation of butene, the selectivity is more important than the activity, for olefins are much more reactive than paraffins. Therefore, the higher-phosphorus catalysts, which possess the highest selectivity (Fig. 10), are chosen.

The generation of strong-acid sites appears to be connected with the presence of the $(VO)_2P_2O_7$ phase, as has been stated by Schneider (*14*), but further quantitative analyses of the phases will be needed to prove this argument.

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