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Oxidation Activity and Acidity of V_2O_5–P_2O_5 Catalyst

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The oxidations of 1-butene, butadiene, and hydrogen in a large excess of air were carried out over various V–P oxide catalysts with different P_2O_5 contents. 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 surface area and the acidity per unit of surface area sharply decrease with an increase in the P_2O_5 content up to about 20 mol% P_2O_5, while with a further increase in the P_2O_5 they remain almost unchanged. The activity per unit of surface area for the oxidation of butene and butadiene, as well as that for the isomerization of butene, changes in the same direction as the acidity per unit of surface area. The equilibrium constant for the adsorption of olefin changes analogously. The activity per unit of surface area for the oxidation of hydrogen is not affected by the P_2O_5 content. The effects of the P_2O_5 introduced into V_2O_5 on the activity and selectivity are discussed from the viewpoint of the acidic nature of the catalysts.

The oxidation of olefins to carboxylic acids, usually performed at very high conversions using small amounts of olefins in excess air, belongs to the category of the selective oxidations, different from the oxidation to epoxide and those to dienes and aldehydes. The basic requirements for the acid-formation reaction have not yet been satisfactorily defined, since only a few fundamental studies have been made of it, in contrast to the numerous studies of the two above-cited types of oxidations.[1,2] The catalysts used for the acid-formation reactions are generally mixed metal oxides based, in most cases, on V_2O_5, but sometimes on MoO_3, WO_3, SeO_2, As_2O_5, *etc.* It should be noted that all of those substances are typical acidic oxides.

In the oxidation of butadiene to maleic anhydride, most V_2O_5-based catalysts give a relatively high selectivity of 50—60 mol%, while when butene is used as the starting material, the high selectivity of 40—50 mol% is limited to the V_2O_5-based catalysts containing large amounts of P_2O_5. We found in earlier studies[3–5] that the inclusion of P_2O_5 in V_2O_5 increases the selectivity in the first step in the series of consecutive steps from butene to maleic anhydride…that is, in the step of allylic oxidation; $C_4H_8 \rightarrow C_4H_6$.

The present paper is an attempt to make an improvement in the study of the P_2O_5 effect by introducing the idea that the acidic nature of the catalyst governs to a considerable extent the activity and selectivity of the mild oxidations.[6–10]

Experimental

The vapor-phase oxidation of 1-butene, 1,3-butadiene, and hydrogen, the dehydration of *iso*-propyl alcohol (IPA), and the dehydrogenation of ethanol were carried out over a series of vanadium-phosphorus (V_2O_5–P_2O_5) catalysts, while varying the P_2O_5 content from 0 to 67 mol%, in an ordinary continuous-flow-type reaction system, The concentrations of butene, butadiene, hydrogen, IPA, and ethanol were, unless otherwise indicated, about 0.67, 0.67, 3.0, 1.65, and 2.2 mol% in air respectively. The total flow rate (at 25 °C) was kept constant at 1.5 l/min, and the amount of the catalyst used was 2—20 g. The reactor and the experimental and analytical procedures were the same as those employed in previous works.[3–10]

The catalysts used in these experiments were prepared as follows; the required quantities of NH_4VO_3 and H_3PO_4 were dissolved in hot water, together with oxalic acid, if necessary, after which 10—20 mesh pumice was mixed with the solution; then the mixture was evaporated with vigorous stirring. The amount of pumice was 500 ml (about 150 g)/g atom of vanadium and phosphorus. The catalyst was subsequently calcined, under flowing air, at 500 °C for about 4 hr.

Results

Surface Area. The surface area of the catalysts was measured by the BET method using nitrogen at −195 °C (Table 1). It falls markedly with an increase in the P_2O_5 content up to 20 mol% P_2O_5.

Acidity of the Catalyst. Since it is difficult to measure directly the acidity of the V_2O_5–P_2O_5 catalysts, we used the activity for the dehydration of IPA as a measure of the acidity, much as in previous works.[7,8]

A gaseous mixture of IPA and air was passed over 2—10 g of the catalyst at temperatures of 160—220 °C.

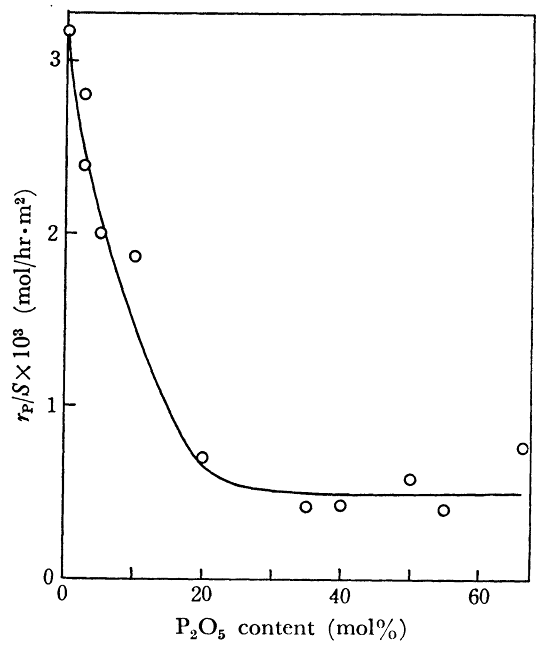

Fig. 1. Rate of IPA dehydration per unit surface area (r_P/S) as a function of the P_2O_5 content. Temp=185°C, IPA=1.65mol% in air.

Table 1. Properties and activities of V_2O_5–P_2O_5 catalysts

Catalyst compd P/V	Surface area (m^2/g)	Rate of IPA dehydration $r_p \times 10^3$	Dehydrogenation of ethanol: Rate $r_a \times 10^3$	Dehydrogenation of ethanol: $\frac{CH_3CHO}{CH_2{=}CH_2}$	Isomerization of 1-butene: Rate $I \times 10^2$	Isomerization of 1-butene: $\frac{cis\text{-}C_4H_8}{trans\text{-}C_4H_8}$	Oxidation activities for Butene $r_B \times 10^4$	Oxidation activities for Butadiene $r_B' \times 10^4$
0/100	3.5	11.2	19.2	19	3.94	1.1	25	37
2.5/97.5	3.14	7.5	14.1	12	2.62	1.2	10.7	10
2.5/97.5	3.0	8.4						16
5/95	2.6	5.4						
10/90	1.4	2.7	3.3	12	1.01	1.2	5.4	3.5
20/80	0.71	0.5			0.45	1.25	1.0	
35/65	0.69	0.3			0.40	1.3	0.58	1.2
40/60	0.66	0.32			0.2	1.2	0.5	1.5
50/50	0.75	0.30	0.4	1.3	0.3	1.1	2.7	1.5
55/45	1.05	0.4					2.5	0.8
67/33	1.0	0.9			0.45		3.1	0.5

As has been reported in the previous papers,[7–10] propylene was the main product and the rate was almost independent of the IPA concentration at about 185 °C. The initial rate of the dehydration at 185 °C, r_p (mol/hr·g-cat), was chosen as a measure of the acidity (Table 1). The activity per unit of surface area, r_p/S (mol/hr·m^2), is plotted as a function of the P_2O_5 content in Fig. 1. r_p/S falls sharply with the P_2O_5 content in the $P_2O_5 < 20$ mol% region and remains almost unchanged with a further increase in the P_2O_5.

Basicity of the Catalyst. As the basicity of the simple V_2O_5 catalyst is very small (the amount of the adsorption of acetic acid vapor at 150 °C, as measured by means of a chromatographic method,[11] was 1—2 μmol/g-cat, while that of CO_2 at 20 °C, as measured by a conventional static apparatus, was $1—2 \times 10^{-2}$ ml/g-cat (0.5—1 μmol/g-cat)), it seems hard to get reliable data on the basicity of the V_2O_5–P_2O_5 catalysts by these methods.

It has been reported[12–16] that the dehydrogenation of alcohol is related to the basic properties of the catalyst, although the reaction mechanism has not yet been established firmly. Since, on the V_2O_5–P_2O_5 catalysts, the activity for the dehydrogenation of IPA is very small compared with that for its dehydration, the reaction of ethanol was carried out in a manner similar to that of IPA. The initial rate of the dehydration of ethanol to acetaldehyde at 260 °C, r_a (mol/hr·g-cat), and the ratio of acetaldehyde/ethylene are listed in Table 1. These results suggest that the basic properties of the catalyst also decrease upon the addition of P_2O_5.

Isomerization of Butene. The oxidation of butene over V_2O_5-type catalysts is always accompanied by its isomerization, which is generally said to be attributable to acidic or basic sites of the catalyst. As a measure of the isomerization activity, we adopted for convenience the ratio of $(cis\text{-}2\text{-}C_4H_8 + trans\text{-}2\text{-}C_4H_8)/(1\text{-}C_4H_8 + cis\text{-}2\text{-}C_4H_8 + trans\text{-}2\text{-}C_4H_8)$; I under these conditions: temperature of 260 °C, 1-butene of 0.67 mol% in air, a catalyst of 5∼20 g. The results are also listed in Table 1. Figure 2 shows the relation between the isomerization activity per unit of area (I/S) and the acidity per unit of area (r_p/S). The $cis\text{-}2\text{-}C_4H_8/trans\text{-}2\text{-}C_4H_8$ ratio is about 1.2 for every catalyst. These results indicate that the isomerization of olefin is catalyzed by acidic sites of the catalyst.[17]

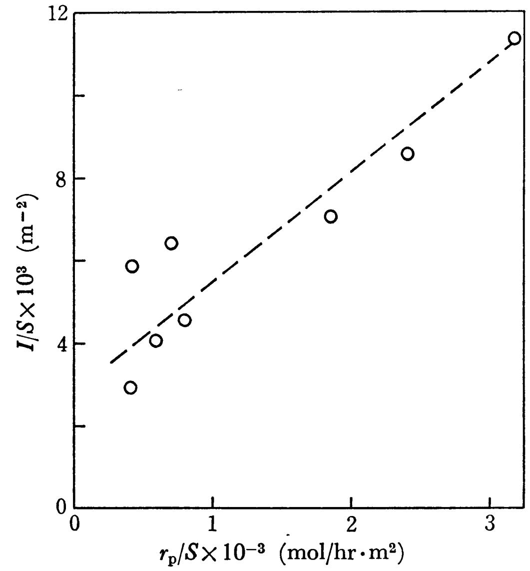

Fig. 2. Relation between I/S and r_P/S.
Isomerization; 260°C, 0.67mol% $1\text{-}C_4H_8$ in air,

$$I = \frac{(cis\text{-}2\text{-}C_4H_8 + trans\text{-}2\text{-}C_4H_8)}{(1\text{-}C_4H_8 + cis\text{-}2\text{-}C_4H_8 + trans\text{-}2\text{-}C_4H_8)}$$

The variation in these activities has been effected by changing the P_2O_5 content.

Oxidation Activity for Olefins. The effects of the P_2O_5 content on the activity for the oxidation of such olefins as 1-butene and butadiene were examined. The reaction was carried out at 330 °C. The initial rates of the overall consumption of butene and butadiene, r_B and r_B' (mol/hr·g-cat), were also obtained; they are listed in Table 1. The activities for butene and butadiene vary in a similar way and fall sharply with the P_2O_5 content when the P_2O_5 catalyst is less than 20 mol%.

Figure 3 shows the relation between the oxidation activities for olefins per unit of surface area, r_B/S and r_B'/S, and the acidity per unit of surface area. It is found that the oxidation activity for olefins increases with an increase in the acidity of the catalyst.

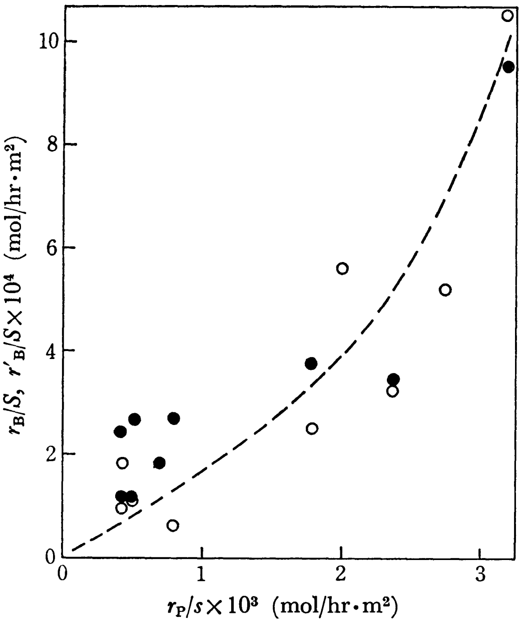

Fig. 3. Oxidation activities for olefins *versus* dehydrantio activity for IPA. The variation in these activities has been effected by changing the P_2O_5 content. ● = butene oxidation (r_B/S), ○ = butadiene oxidation (r'_B/S), at 330°C.

Oxidation Activity for Hydrogen. It has been established that hydrogen and parafinic hydrocarbons act upon metal-oxide catalysts as electron donors to some extent. However, this tendency might be so weak that the oxidation activity for these compounds is really governed by the availability of surface oxygen rather than by the activation of the reactant.[18] This leads us to consider that the oxidation activity for hydrogen reflects the availability of oxygen in some measure at least.

Since hydrogen was quite stable compared with olefins and IPA over the V_2O_5–P_2O_5 catalysts, a high temperature of more than 400 °C was required to achieve appreciable conversion. The initial rates of hydrogen consumption at 435 °C, r_H (mol/hr·g-cat) and r_H/S (mol/hr·m^2), are plotted as a function of the P_2O_5 content in Fig. 4. It is found that the activity decreases with the P_2O_5 content, but the activity per unit of surface area remains almost unchanged within the range of experimental error.

Adsorption of Olefin. Information on the affinity of olefin for the catalysts may be obtained if the oxidation rates conform to the following Langmuir-Hinshelwood type equation:

$$r = k \cdot N_a \cdot N_0 \cdot \left(\frac{KP}{1+KP}\right) \cdot \left(\frac{K_0{}^n P_0{}^n}{1+K_0{}^n P_0{}^n}\right)$$

where r is initial rate of oxidation, k is the rate constant, N_a and N_0 are the numbers of sites available for olefin and oxygen, K and K_0 are the equilibrium constants for the adsorption of olefin and oxygen, and P and P_0 are the partial pressures of olefins and oxygen respectively. When oxygen is in a large excess with respect to olefin and P_0 remains constant, $N_0 \cdot K_0{}^n \cdot P_0{}^n/(1+K_0{}^n P_0{}^n)$ is a constant value for any one catalyst. Therefore, the above equation can be simplified as:

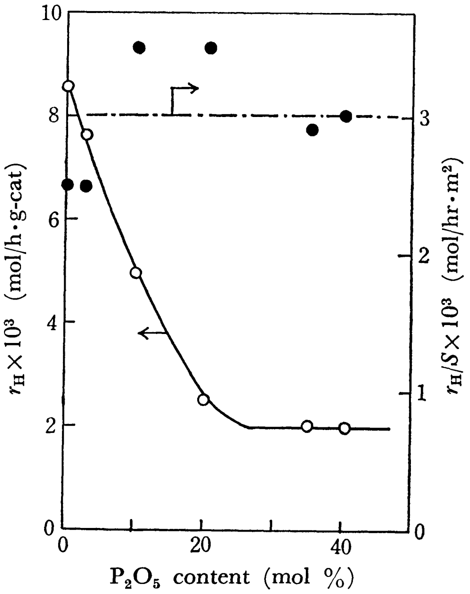

Fig. 4. Oxidation rate of hydrogen (r_H) and the specific rate r_H/S) as a function of the P_2O_5 content. Temp = 430°C, hydrogen = 3 mol% in air, ○ = r_H, ● = r_H/S.

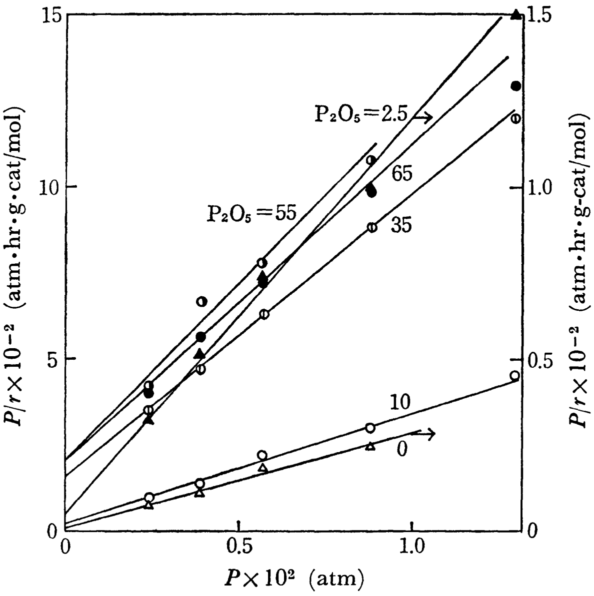

Fig. 5. Test of equation; $r = k' \cdot \frac{KP}{1+KP}$: a plot of P/r *versus* P.

$$r = k' \cdot \frac{KP}{1+KP},$$

where $k' = k \cdot N_a \cdot$(availability of surface oxygen).

To test this equation, another series of butadiene oxidations was carried out at 330 °C by changing the initial concentration from 0.24 to 1.9 mol% in air (partial pressure = 0.24×10^{-2}—1.9×10^{-2} atm). The value of r was obtained at each P for every catalyst. Figure 5 shows a plot of P/r against P.

Good linear relations were obtained between P/r and P for every catalyst; this indicates the validity of the above equation. The values of k' and K were

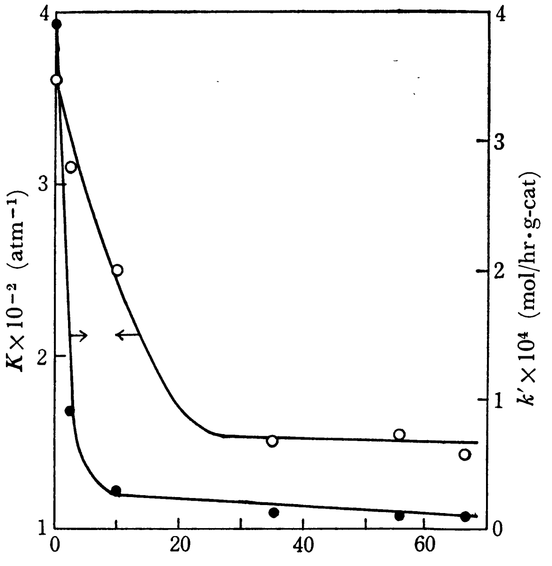

Fig. 6. The values of K and k' *versus* the P_2O_5 content. ○ = K, ● = k'.

calculated from the slopes and from the intersections with the ordinate. They are plotted as a function of the P_2O_5 content in Fig. 6. K decreases with the P_2O_5 value up to about 20 mol% P_2O_5, much like the acidity, r_p/S (Fig. 6).

The temperature-dependency of k' and K was also examined (Table 2). The activation energies of the oxidation (E) were in the neighborhood of 20 kcal/mol, and the effect of the P_2O_5 content on the value of E was not clear. The values of K were almost independent of the temperature. It was also found that the amount of butadiene adsorbed on the simple V_2O_5 measured directly by a static apparatus was about 0.1 ml STP/g-cat, almost independent of the temperature in the region of 20—200 °C, and that no adsorption of butadiene was detected by a usual gas-chromatographic technique.[19] These results also suggest that the bond of olefin on the V_2O_5-type catalyst is so loose that the heat of the adsorption cannot be obtained.

Table 2. Values of k' and K

Catalyst P/V	Temp (°C)	$k' \times 10^4$ (mol/hr·g)	E (kcal/mol)	$K \times 10^{-2}$ (atm^{-1})
0/100	283	1.17	20	4.1
	294	1.63		3.9
	305	2.3		4.2
10/90	294	0.30	18	2.3
	305	0.43		2.3
50/50	317	0.18	25	1.2
	330	0.29		1.0

Discussion

The introduction of P_2O_5 to V_2O_5 causes a decrease in both (1) the surface area and (2) the acid-base properties. The action is remarkable only in the low P_2O_5 range. Probably, the active species of V_2O_5 are gradually modified into other kinds of species with the inclusion of P_2O_5 up to about 20 mol%, while a further increase in the P_2O_5 content causes no substantial change in the nature of the active species.

The decrease in the surface area may be, in part, associated with the fact that a sort of fusion appears at the beginning of the calcination, especially for the catalysts containing relatively high P_2O_5 values.

It should be noted that P_2O_5 is a unique additive which decreases the acidity as well as the basicity of the V_2O_5 catalyst (the additions of all the other oxides, such as Al_2O_3, WO_3, MoO_3, SO_3, and TiO_2, which increase the acidity of the V_2O_5 catalyst decrease the basicity).[20]

By taking into account the fact that the affinity of the catalyst for such basic compounds as olefins reflects the acid strength, the results shown in Fig. 6 suggest that the acid strength of the catalyst also decreases with an increase in the P_2O_5 content and changes in the same direction with the acidity, as has often been observed.[21]

The results shown in Fig. 4 suggest that the availability of surface oxygen (r_H/S) is almost uninfluenced by the P_2O_5 addition. However, this does not accord with the fact that the basicity of the catalyst, which is supposed to be related to the activation of an electron-acceptor-type reactant (oxygen),[20,22] decreases with the P_2O_5 addition. Even if the availability of oxygen decreases with the P_2O_5 addition, it may be considered, from the results of Fig. 3, that the activity for the oxidation of olefins on the acidic-metal oxides is predominantly dependent on the activation of olefins; this phenomenon may be attributed to the acidic sites of the catalyst, as has already been observed by us in the cases of MoO_3–Bi_2O_3–P_2O_5,[6] MoO_3–P_2O_5–X_nO_m,[9] MoO_3–P_2O_5,[10] and V_2O_5–MoO_3.[23] Recently a similar conception has been proposed by Haber *et al.*[24]

Concerning the selectivity to maleic anhydride,[5] the acidic property may be a requirement for satisfactory catalysts for such a type of partial oxidation as basic reactant→acidic product, because the acidic catalysts are active in relation to the basic reactant and inactive in relation to the acidic product. This conception holds well for the oxidation of butadiene.[6,8,20,22] However, in the case of butene oxidation. another factor must also affect the selectivity. When butene is oxidized over V_2O_5-based catalysts not containing P_2O_5, the C–C fission, probably at the double bond,[25] takes place in preference to the allylic C–H fission and the main products are oxygen-containing compounds with a lower number of carbon atoms, such as acetic acid, which are easily oxidized to CO_2 or CO, while in the case of butadiene, the C–C fission is not the main reaction.[20] It is, therefore, conceivable that the selectivity of butene to maleic anhydride is greatly controlled by the C–C fission of butene.[3–5]

The decrease in the activity for the C–C fission of butene due to the P_2O_5 addition is probably attributable either to the acidic or basic properties of the catalyst. The addition of such metal oxides as Al_2O_3, TiO_2, MoO_3, and WO_3 decreases the basicity of the V_2O_5 catalyst. However, it promotes the oxidation of butene to acetic acid.[20] Therefore, it should be considered that the activity for the C–C fission is related to the acidic property—strictly speaking, the acid strength. That is to say, the catalyst must be acidic in order to get acidic products, but the acidic nature is necessary in an appropriate strength for the maximum selectivity from butene; too high a acid-strength destroys the C–C bond of butene and decreases the selectivity.

We would like to consider that the addition of P_2O_5 to V_2O_5-based catalysts plays a role in lowering the acid strength to a proper extent and, consequently, in suppressing the C–C fission of butene and increasing the selectivity in the step of allylic oxidation: $C_4H_8 \rightarrow C_4H_6$.

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