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A Study of the Partial Catalytic Oxidation of Hydrocarbons. V. The Effect of Phosphorus Addition to the Vanadium Catalyst on the Oxidation of Butene, Butadiene, and Furan

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In the present investigation, the vapor-phase partial oxidation of *cis*-2-butene, butadiene, and furan was carried out over V_2O_5 and V_2O_5-P_2O_5, (1 : 1.6 atomic ratio), with various contact times, at 350°C, and at the concentration of 0.6—1.6% in air, in order to elucidate the effect of phosphorus addition to V_2O_5, on the selectivity and mechanism of butene oxidation. Oxidation activity decreased remarkably with an increase in the phosphorus content. In the presence of phosphorus (P/V=1.6), selectivity for the $C_4H_8 \rightarrow C_4H_6$ step and $C_4H_6 \rightarrow C_4H_4O$ step were considerably increased, from 46 to 88 and from 72 to 93 mol% respectively, while selectivity for the $C_4H_4O \rightarrow$maleic anhydride (MA) step fell from 60 to 50 mol%, due to the increase in polymer formation. From the results, it was concluded that V_2O_5 and V_2O_5-P_2O_5 catalysts show similar oxidation activity with regard to butene, butadiene, and furan, and that the quantities of the intermediate products are fairly much affected by the activity of the catalyst as well as by the difference in reactivity between the starting material and the intermediate over the catalyst.

Previous papers have studied the mechanism of the partial catalytic oxidation of butene, butadiene, crotonaldehyde, furan, (C_4H_4O), *etc.* over V_2O_5, V_2O_5-P_2O_5 and V_2O_5-MoO_3 catalysts,[1-4] and it has been proposed that, on V_2O_5-P_2O_5 (1 : 1.6 atomic ratio), the main reaction pathway for the catalytic oxidation of butene to maleic anhydride (MA) proceeds through the following successive steps:

$$C_4H_8 \rightarrow C_4H_{8\,\text{ads.}} \rightarrow C_4H_{6\,\text{ads.}} \rightarrow C_4H_4O_{\,\text{ads.}} \rightarrow \text{MA}$$

Moreover, side reactions destined to complete combustion proceed parallel to the main pathway in each consecutive step, and the selectivity and the rate of maleic anhydride formation are determined by the steps after furan.[1]

By the addition of phosphorus to the V_2O_5 catalyst, the selectivity for maleic anhydride formation from butene was considerably increased; this may attributed to the increase in selectivity for the $C_4H_8 \rightarrow C_4H_4O$ steps, not for the $C_4H_4O \rightarrow$MA steps.[2]

In the present work, we attempted to ascertain how the phosphorus addition to the V_2O_5 catalyst affects each reaction step in the step-by-step oxidation of butene to maleic anhydride formation, and to elucidate this effect on the mechanism and the selectivity of the partial catalytic oxidation of butene, butadiene, and furan.

Experimental

The vapor-phase air oxidation of butene, butadiene, and furan was carried out over vanadium and vanadium-phosphorus (V : P=1 : 1.6 atomic ratio) oxide catalysts in an ordinary flow-type reaction system at atmospheric pressure as has been shown in previous papers.[1,2] The reactor was a steel tube (1.8 cm id) whose surface was coated with aluminium; it was immersed in a molten lead bath.

The volume concentrations of the reactants were 0.6—1.0% in air, the flow rate (at 25°C) was kept at 1.5 *l*/min, and the contact time, which was defined as the ratio of the catalyst volume (m*l*) to the flow rate, was varied from 0.006 to 1.8 sec. The reaction temperature was always kept at 350°C. The exit gases leaving the reactor passed first through a series of three hot, and then four cold, packed water scrubbers in order to recover the solid and volatile acids and carbonyl compounds. At the end of 2 hr, the contents of the scrubbers were collected and a sample was titrated with 0.1 N NaOH, using a pH meter. The yields of maleic and other acids were calculated from the titration curves. The reactant gas, the exit gas, and a sample of the water-scrubber contents were analyzed by means of gas chromatography.

The following method was employed to prepare the catalysts. V_2O_5 catalyst: NH_4VO_3 was disolved in hot water by using oxalic acid, and then pumice, with a mesh size of from 10 to 20, was added; the solution was then evaporated with constant stirring, and finally dried in an oven at 130°C. The amount of pumice was 400 m*l*/g atom of vanadium. V_2O_5-P_2O_5 catalyst:

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[1] M. Ai, K. Harada and S. Suzuki, *Kogyo Kagaku Zasshi*, **73**, 524 (1970).

[2] M. Ai, T. Niikuni and S. Suzuki, *ibid.*, **73**, 165 (1970).

[3] M. Ai, *ibid.*, **73**, 946 (1970).

[4] M. Ai, *ibid.*, **73**, 950 (1970).

NH_4VO_3 and H_3PO_4 were dissolved in water (P/V= 1.6 atomic ratio), and the solution was heated with constant stirring. After it had evaporated nearly to dryness, the paste-like substance remaining was molded into pellets 3×3 mm in size, and finally these were dried at 130°C. The activation of the catalysts was performed under flowing air, at 500°C, for 5 hr.

In an earlier paper dealing with the oxidation of butene[2)], we used a series of unsupported V_2O_5-P_2O_5 catalysts and learned that P_2O_5-poor catalysts show a failure in mechanical strength. Therefore, in this work, we used pumice for the V_2O_5 catalyst in order to increase its mechanical strength. It was confirmed that this supported V_2O_5 catalyst showed the same catalytic performance as the unsupported V_2O_5 catalyst prepared by the simple evaporation of the NH_4V_3O-$C_2H_2O_4$ solution.[2)] It can be considered, therefore, that the external surface of the pumice is coated with a thick layer of V_2O_5 that there is no practical difference in surface structure between supported and unsupported V_2O_5 catalysts.

Results and Discussion

Effects of Phosphorus Addition on the Oxidation Activity. The rates of the oxidation of butene, butadiene, and furan over V_2O_5 or V_2O_5-P_2O_5 catalysts can be considered to be of the first order[*1] for the reactant concentration under the reaction conditions used here. The rate constants at 350°C (k sec^{-1}) over both V_2O_5 and V_2O_5-P_2O_5 were calculated for each reactant from the conversion-contact time data, they are shown as functions of the phosphorus content in Fig. 1. The oxidation activity of the catalyst decreased markedly upon the addition of phosphorus to V_2O_5, even when the quantity added was very small. The reactivities of all these reactants on these catalysts were of about the same magnitude. For example, the activity of V_2O_5-P_2O_5 (1 : 1.6 atomic ratio) catalyst was about one-thirtieth that of the V_2O_5 catalyst alone. However, the extent of the deactivation by phosphorus addition was about the same for the butene, butadiene, and furan oxidations. The results are listed in Table 1.

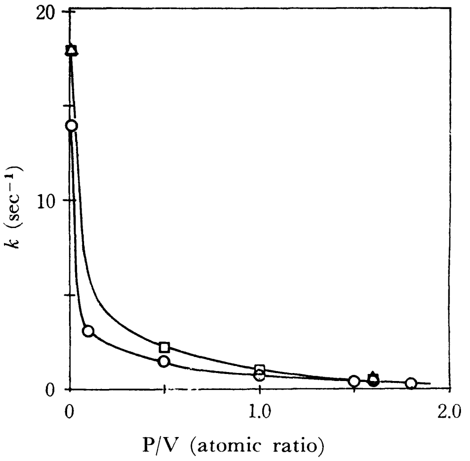

Fig. 1. Oxidation rate constant at 350°C (k sec^{-1}) as a function of P_2O_5/V_2O_5 ratio.
○: butene △: butadiene □: furan

TABLE 1. OXIDATION RATE CONSTANT AT 350°C: k (sec^{-1})

Reactant	C_4H_8	C_4H_6	C_4H_4O
$k^{I}(V_2O_5)$	14	18	18
$k^{II}(V_2O_5$-$P_2O_5)$	0.4	0.6	0.6
k^{II}/k^{I}	1/35	1/35	1/30

Effects of Phosphorus Addition on the Maleic Anhydride Formation. The formation of maleic anhydride from butene, butadiene, and furan over V_2O_5 and V_2O_5-P_2O_5 catalysts at 350°C is shown is a function of the reactant conversion in Figs. 2 and 3. Selectivities to maleic anhydride are given as a slope of the curves.

The V_2O_5 catalyst has a high oxidation activity in comparison with V_2O_5-P_2O_5, but it showed only a poor selectivity to maleic anhydride: less than 20%. When butene conversion was more than 70%, the formation of maleic anhydride decreased; therefore, it did not exceed 15 mol%. In the case of butadiene oxidation, however, the selectivity to maleic anhydride was 43%, fairly good in comparison with that from butene. From

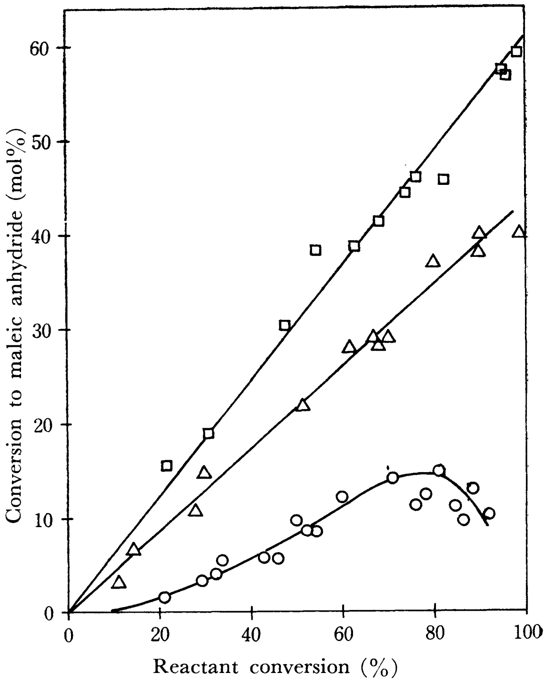

Fig. 2. Effect of reactants on maleic an hydride formation over V_2O_5 catalyst.
○: butene △: butadiene □: furan

[*1] log (C_0/C) is proportional to the contact time (W/F).

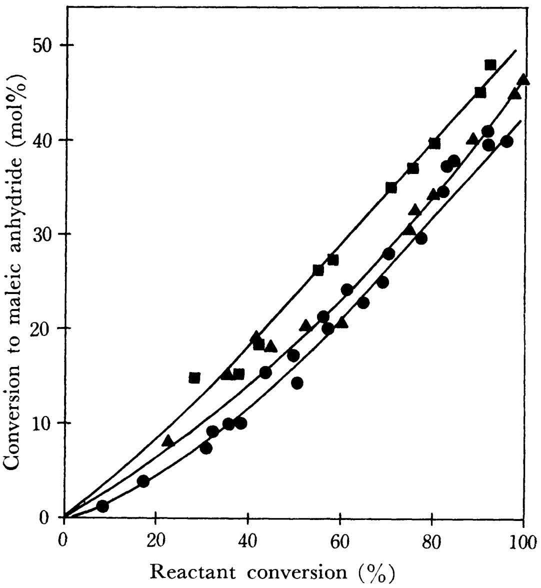

Fig. 3. Effect of reactants on maleic anhydride formation over V_2O_5-P_2O_5 (1 : 1.6).
●: butene ▲: butadiene ■: furan

furan oxidation, the selectivity to maleic anhydride became higher, as was expected, and reached 60 mol%. The decrease in selectivity to maleic anhydride at high conversion may be caused by the destruction of the maleic anhydride formed (Fig. 6); this tendency was more remarkable in the case of butene oxidation than in the cases of butadiene and furan. This phenomenon is probably to be attributed at least in part, to the fact that the reactivity of butene is lower than that of butadiene or furan, *i.e.*, the oxidation of butene requires severer condition, but for a more definite explanation, more studies will be required.

On the other hand, the V_2O_5-P_2O_5 (1 : 1.6) catalyst, whose activity was fairly low, showed a good selectivity, for butene to maleic anhydride (42%), while, in the selectivity to maleic anhydride, no marked difference was observed among the butene, butadiene, and furan oxidations, although it increased slightly in this order, as had been expected. The results are summairzed in Table 2.

Table 2. Selectivity to maleic anhydride (%)

Catalyst	Reactant		
	C_4H_8	C_4H_6	C_4H_4O
V_2O_5	20	43	60
V_2O_5-P_2O_5 (1 : 1.6)	42	46	50

Effect of Phosphorus Addition on the Reaction Pathway. From a perusal of the data in Table 2, the selectivities towards the main reaction pathway in each consecutive step, such as $C_4H_8 \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow MA$, were calculated; for example, the selectivity in the $C_4H_6 \rightarrow C_4H_4O$ step over the V_2O_5 catalyst was found to be that, from 100 mol of C_4H_6, 43 mol of MA are formed. As the selectivity in the $C_4H_4O \rightarrow MA$ step is 60%, the portion destined to become by-products in the $C_3H_4O \rightarrow$ MA step is $40/60 \cdot 43 = 29\%$. The sum ($43 + 29 = 72$) corresponds to the selectivity in the $C_4H_6 \rightarrow C_4H_4O$ step. In the same manner, the selectivity in $C_4H_8 \rightarrow C_4H_6$ step can also be obtained. The results are shown in Table 3.

Table 3. Selectivities of the steps (%)

Steps	$C_4H_8 \rightarrow C_4H_6$	$C_4H_6 \rightarrow C_4H_4O$	$C_4H_4O \rightarrow MA$
V_2O_5	46	72	60
V_2O_5-P_2O_5	88	93	50

On the other hand, the portions of the main and the side reactions in each consecutive step, based on 100 mol of reacted butene, can be calculated from the value of the selectivity in each step (Table 3). From the results obtained, the probable scheme of butene oxidation over V_2O_5 and V_2O_5-P_2O_5 catalysts may be proposed to be as follows (the notations in brackets mean selectivity):

V_2O_5 catalyst

$$\begin{tikzcd}
100\ C_4H_8 \arrow[r, "46", "(54/46)"'] \arrow[d] & C_4H_6 \arrow[r, "33", "(28/72)"'] \arrow[d] & {} \\
54 & 13 &
\end{tikzcd}$$

$$\begin{tikzcd}
C_4H_4O \arrow[r, "20", "(40/60)"'] \arrow[d] & MA \\
13 & \text{by-products} \arrow[l]
\end{tikzcd}$$

V_2O_5-P_2O_5 catalyst ($P/V = 1.6$)

$$\begin{tikzcd}
100\ C_4H_8 \arrow[r, "88", "(12/88)"'] \arrow[d] & C_4H_6 \arrow[r, "83", "(7/93)"'] \arrow[d] & {} \\
12 & 5 &
\end{tikzcd}$$

$$\begin{tikzcd}
C_4H_4O \arrow[r, "42", "(50/50)"'] \arrow[d] & MA \\
41 \arrow[r] & \text{by-products}
\end{tikzcd}$$

The results reveal that:

(1) With the V_2O_5 catalyst, the selectivity to maleic anhydride from butene oxidation is mainly determined by the low selectivity of the $C_4H_8 \rightarrow C_4H_4O$ step (33%), especially in the $C_4H_8 \rightarrow C_4H_6$ step (46%).

(2) In the case of butene oxidation, selectivity to the side pathway destined to form by-products was twice that in the butadiene oxidation.

(3) The presence of phosphorus in V_2O_5 increases the selectivities of both the $C_4H_8 \rightarrow C_4H_6$ and $C_4H_6 \rightarrow C_5H_4O$ steps: from 46 to 88% and from 72 to 93% respectively, while in the $C_4H_4O \rightarrow$ MA step, on the other selectivity to maleic anhydride falls from 60 to 50%.

(4) The incorporation of phosphorus with

V_2O_5 has little effect on the selectivity of butadiene to maleic anhydride. It may be considered that, even over the V_2O_5 catalyst, the selectivity to the side pathway in the $C_4H_6 \rightarrow C_4H_4O$ step is not very important (28%), that the favorable effect of phosphorus addition is not very efficient in this step, and that it is cancelled by its unfavorable effect in the $C_4H_4O \rightarrow$ MA step.

Side Reaction in the $C_4H_4O \rightarrow$ MA Step. On both V_2O_5 and V_2O_5-P_2O_5 catalysts, the major products from furan oxidation were maleic anhydride, CO_2, CO, the polymer, and a small amount of acetic acid (3—5% for the maleic anhydride formed). Since the reactivity of acetaldehyde, ketones, *etc.* were not great in these reaction conditions, they had to be found in the product gases, if they existed at all. Thus, it can be considered that furan was oxidized directly to maleic anhydride, CO, CO_2, and the polymer, without proceeding *via* some stable intermediate products. The selectivities in this process may be listed as follows:

Catalyst	V_2O_5	V_2O_5-P_2O_5
↗ MA	60%	50%
Furan → CO + CO_2	30%	30%
↘ polymer	10%	20%

The amount of the polymer was obtained as the remainder in the mass-balance of the products (Fig. 4).

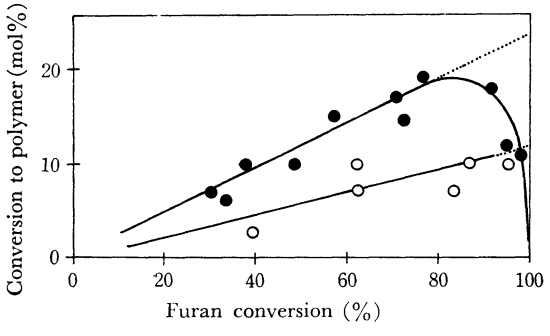

Fig. 4. Polymer formation *verses* furan conversion.
○: V_2O_5 ●: V_2O_5-P_2O_5 (1 : 1.6)

With the addition of phosphorus in V_2O_5, the formation of the polymer doubled at the expense of a decrease in the maleic anhydride formation. It may be considered that polymer formation is promoted by phosphorus, which probably produces some acid species in the catalyst.

Side Reaction in $C_4H_8 \rightarrow C_4H_4O$ Steps. Many sorts of products from butene, butadiene, and furan oxidation on the V_2O_5-P_2O_5 catalyst have been already reported in the previous paper[1], while on the V_2O_5 catalyst, the major by-products were CO and CO_2, with the others being almost negligible except for small quantities of acetone and acrolein (2—3%). From butene oxidation on V_2O_5, very much acetaldehyde (AcH) and acetic acid (AcOH) were formed (Fig. 5). We have represented here the value of the conversion AcH+AcOH, assuming that two moles of AcOH+AcH are formed from one mole of butene, although it is not clear if two moles are formed or only one mole.

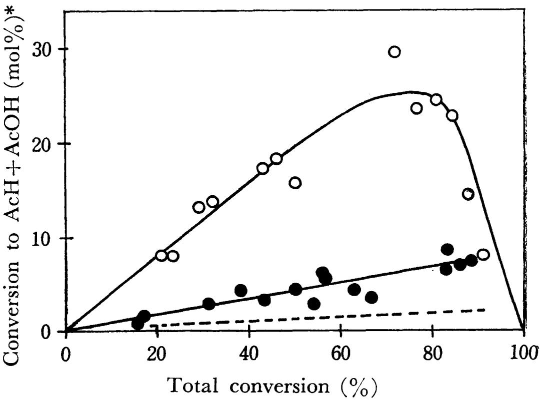

Fig. 5. Conversion to AcH+AcOH* *versus* total conversion.
* basing on the assumption that 2 mol of AcH+AcOH are formed from 1 mol of C_4 compound.
solid line: butene oxidation (○: V_2O_5, ●: V_2O_5-P_2O_5)
dashed line: butadiene oxidation on V_2O_5 or V_2O_5-P_2O_5

The results reveal that:

(1) On both V_2O_5 and V_2O_5-P_2O_5 catalysts, about one half of the side reaction in the $C_4H_8 \rightarrow C_4H_6$ step leads to AcOH+AcH formation, and the other half, to complete combustion: CO, CO_2, *etc.*

(2) Selectivity to the side reaction of butene is twice as much as that of butadiene, a difference which may be attributed to the tendency to scission of a double-bond of butene. Therefore, it may be concluded that the selectivities to complete combustion are of about the same magnitude between butene and butadiene.

CO and CO_2 formation are shown as functions of the maleic anhydride formed in Figs. 6 and 7. The selectivity ratio of CO or CO_2 formation to maleic anhydride is described as a slope of the curve. Over the V_2O_5-P_2O_5 catalyst, the CO_2 formation was independent of the sort of reactants; this indicates that the sources of the CO_2 formation are the $C_4H_4O \rightarrow$ MA steps. Moreover, the selectivity ratio of CO_2 to maleic anhydride decreased with an increase in the reactant conversion. In the $C_4H_8 \rightarrow C_4H_4O$ steps, only CO was formed as a complete combustion product, and the ratio increased with the reactant conversion. On the other hand, on the V_2O_5 catalyst, CO_2 is formed also in the $C_4H_8 \rightarrow C_4H_4O$

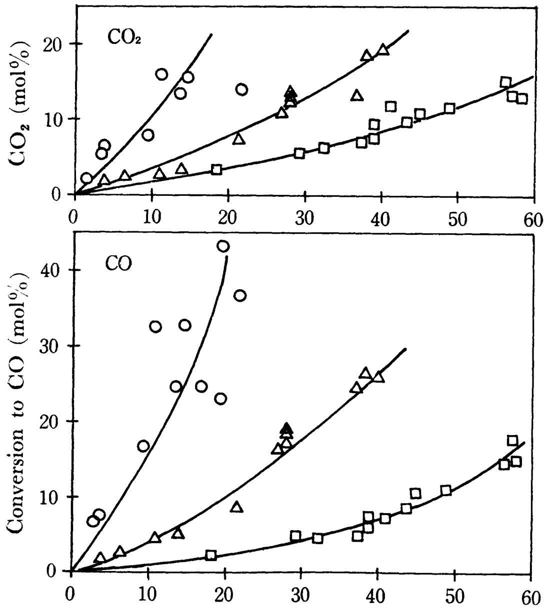

Fig. 6. Conversion* to CO and CO_2 as a function of maleic anhydride formation on V_2O_5.
* 1/4 of the real amount of the formation
○: butene △: butadiene ☐: furan

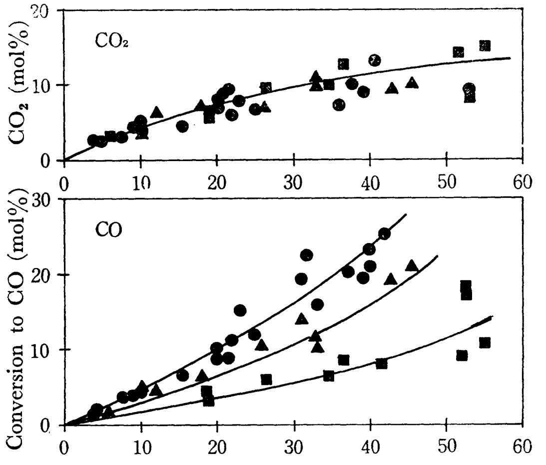

Fig. 7. Conversion* to CO and CO_2 as a function of conversion to maleic anhydride on V_2O_5–P_2O_5.
* 1/4 of the real amount of the formation
●: butene ▲: butadiene ■: furan

steps, but CO is still predominant.

Amounts of Intermediate Products. The amounts of the intermediates formed in the oxidation of butene and butadiene to maleic anhydride are plotted as a function of the reactant conversion (Figs. 8 and 9). In all the cases investigated, they passed through a maximum at a reactant conversion of about 50%.

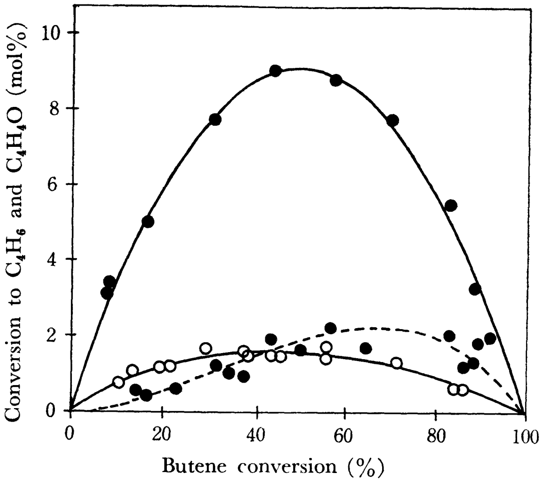

Fig. 8. Conversion to C_4H_6 and C_4H_4O *versus* butene conversion.
solid line: formed butadiene
dashed line: formed furan
○: V_2O_5 ●: V_2O_5-P_2O_5 (1 : 1.6)

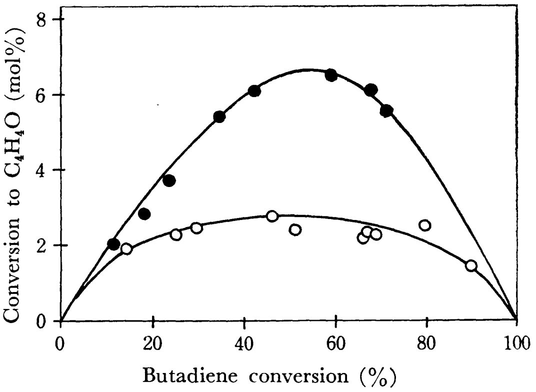

Fig. 9. Conversion to C_4H_4O *versus* butadiene coversion.
○: V_2O_5 ●: V_2O_5-P_2O_5 (1 : 1.6)

The consecutive reaction on the catalyst surface can be explained by the following reaction scheme[5]:

$$\begin{tikzcd} A \arrow[d, shift left, "K_A"] & B \arrow[d, shift right, "K_d"'] & \\ A_a \arrow[u, shift left] \arrow[r, "K_1"] & B_a \arrow[u, shift right, "K_a"'] \arrow[r, "K_2"] & MA \end{tikzcd}$$

where A is the starting material; B, the intermediate, and MA, the fully-oxygenated compound (maleic anhydride), and where the subscript "a" means "adsorbed."

A steady-state treatment based on the assumption that A_a is in equilibrium with A results, after the elimination of the time and integration[5], in:

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[5] J. H. de Boer and R. J. A. M. van der Borg, Actes du Deuxieme Congres Internationale de Catalyse, Editions Thechiq, Paris, (1961), p. 919., and P. Zwietering and F. Hartog, *J. Catal.*, **2**, 79 (1963).

$$B = \frac{S}{r-1}(A-A^r)$$

where:

$$r = \frac{K_a K_2}{K_1 K_A (K_2+K_d)}, \quad S = \frac{K_d}{K_2+K_d}$$

A and B are the mole fractions of the starting material and the intermediate in the reaction product. K_a is adsorption equilibrium constant; K_1 and K_2, the reaction rate constants, and K_a and K_d, the adsorption and desorption rate constants.

The values of r and S for butene and butadiene oxidation over both V_2O_5 and V_2O_5-P_2O_5 were calculated from the maximum amount of the primary intermediate products (butadiene from butene and furan from butadine) and the reactant conversion at this point. They are shown in Table 4.

TABLE 4. r AND S VALUES

Steps	$C_4H_8 \to C_4H_6 \to$		$C_4H_6 \to C_4H_4O \to$	
Catalyst	V_2O_5	V_2O_5-P_2O_5	V_2O_5	V_2O_5-P_2O_5
r	2	2	2	2
S	0.14	0.41	0.13	0.31
k*	18	0.6	18	0.6

* for intermediate oxidation at 350°C

The results reveal that the value of r, which represents the reactivity ratio of feed to the primary intermediate, remains almost unchanged with the variation in reactants and catalyst composition, and that V_2O_5 and V_2O_5-P_2O_5 catalysts show similar oxidation activities for butene, butadiene and furan. It can be concluded that a satisfactory yield of oxygenated intermediates can not be expected from these vanasium-type catalysts.

On the other hand, the value of S, which represents the portion of the intermediate that leaves the surface, increases with a decrease in the oxidation activity of the catalyst; this means that the higher the catalyst activity becomes, that is, the stronger the intermediate adsorption becomes, the larger the portion of the adsorbed intermediate species which goes directly into the next step, without desorbing to the gas phase.

The amount of the intermediate products was considerably affected by the activity of the catalyst as well as by the difference in reactivity between the starting material and the intermediate over the catalyst. Therefore, a mild catalyst is indispensable in order to obtain good yields of intermediate products.