A Study of the Catalytic Partial Oxidation of Hydrocarbons. XI. The Catalytic Activity of the MoO_3-P_2O_5 and the MoO_3-Bi_2O_3-P_2O_5 in the Selective Oxidation of Butene, Butadiene, and Furan

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In the present work, the vapor-phase partial oxidation of *cis*-2-butene, butadiene, furan, and maleic anhydride was carried out over MoO_3–P_2O_5 (1 : 0.2 atomic ratio) and MoO_3–Bi_2O_3–P_2O_5 (1 : 1 : 0.2) with a contact time of 1.6 sec, at a concentration of 0.6—1.0%, and in air, in order to elucidate the difference between the two catalysts in their catalytic specificity for the oxidation of these reactants to maleic anhydride. Over the MoO_3–P_2O_5 catalyst, the selectivities of butene, butadiene, and furan to maleic anhydride were 13, 50, and 78% respectively. Over the MoO_3–Bi_2O_3–P_2O_5 catalyst, the formation of maleic anhydride from the reactants was very small, that of CO_2 was important, and the rate of maleic anhydride destruction was fairly high. It is considered that the MoO_3–Bi_2O_3–P_2O_5 catalyst has almost the same catalytic specificity as the MoO_3–P_2O_5 in the $C_4H_8 \rightarrow C_4H_2O_3$ step, but that its activity for maleic anhydride destruction is so high that maleic anhydride cannot be accumulated.

In a previous paper,[1,2] the selective oxidation of crotonaldehyde and butadiene over various vanadium- and molybdenum-type catalysts has been investigated from the viewpoint of furan production. Among the catalysts tested, the MoO_3–P_2O_5 catalyst system (P/Mo= 0.1—0.3 atomic ratio) showed the best selectivity to furan in the oxidation of the both reactants; in addition, this system showed a fairly stable activity even at 500°C.

Regarding the ternary catalyst system of MoO_3–Bi_2O_3–P_2O_5, this is well-known as a catalyst which has an excellent selectivity for such an allylic oxidation of olefins as 1-butene to butadiene and propylene to acrolein. Therefore, a good deal of work has been devoted to the investigation of the two reactions mentioned above and that of the physicochemical properties of the catalyst system. However, no literature gives definitive data on the important difference in the catalytic specificity between MoO_3–P_2O_5 and MoO_3–Bi_2O_3–P_2O_5, and past studies over molybdenum-type catalysts were limited to investigations under low oxygen concentrations.

In the present work, we compared the results over MoO_3–P_2O_5 and MoO_3–Bi_2O_3–P_2O_5 catalysts on the relative rate and selectivity in the oxidation of butene, butadiene, furan, and maleic anhydride in excess oxygen, and attempted to clarify the difference between the two catalysts in the catalytic features for each reaction step in the step-by-step oxidation of butene to maleic anhydride, and to elucidate how far the mechanism and the selectivity of the partial catalytic oxidation of these reactants depend on the presence of Bi_2O_3 in the MoO_3–P_2O_5 system.

Experimental

The vapor-phase air oxidation of *cis*-2-butene, butadiene, furan, and maleic anhydride was performed over MoO_3–P_2O_5 (Mo: P=1:0.2 atomic ratio) and MoO_3–Bi_2O_3–P_2O_5 (Mo: Bi:P=1:1:0.2) oxide catalysts in an ordinary flow-type reaction system, as has been shown in previous papers.[3,4]

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 catalyst volume was 40 m*l* (contact time=1.6 sec). The reaction temperature was varied from 200 to 600°C. The experimental and analytical procedures were the same as those employed in pervious works.[1–6]

The catalysts used in the experiments were prepared as follows: the required quantities of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_3PO_4 were dissolved in hot water, and in the case of the MoO_3–Bi_2O_3–P_2O_5 catalyst, an acidified $Bi(NO_3)_3$ solution was mixed with the former solution; pumice of a mesh size of 10 to 20 was added to the above mixture, and then the solution was evaporated with constant stirring and finally dried in an oven at 130°C. The amount of pumice was 500 m*l*/g atom of molybdenum. The catalyst was calcined under flowing air at 550°C for 5 hr.

The color of the MoO_3–P_2O_5 after sintering or use in the experiment was black, while that of the MoO_3–Bi_2O_3–P_2O_5 was light-yellow. This indicates that the state of molybdenum in the former catalyst is more reduced than that in the latter. The surface areas, measured with nitrogen by the BET method at −195°C, were about 3 m^2/g for both the catalysts.

Results and Discussion

Oxidation of cis-*2-Butene.* The oxidation of *cis*-2-butene was carried out over the MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–P_2O_5 catalysts in order to clarify the difference in the catalytic features between the two catalysts. The relationship of overall conversion (excluding isomerization) *vz.* the temperature is shown in Fig. 1. The MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–P_2O_5 have almost the same catalytic activity for the overall oxidation of butene.

The oxidation of butene is always accompanied by its isomerization. Oxygen is necessary in the isomerization as well as in the oxidation.[6] The sum of the conversion of *cis*-2-butene to such isomers as *trans*-2-

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[1] M. Ai and M. Ishihara, *Kogyo Kagaku Zasshi*, **73**, 2152 (1970).

[2] M. Ai, *ibid.*, **74**, 183 (1971).

[3] M. Ai, K. Harada, and S. Suzuki, *ibid.*, **73**, 524 (1970).

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

[5] M. Ai, This Bulletin, **43**, 3490 (1970).

[6] M. Ai, *ibid.*, **44**, 761 (1971).

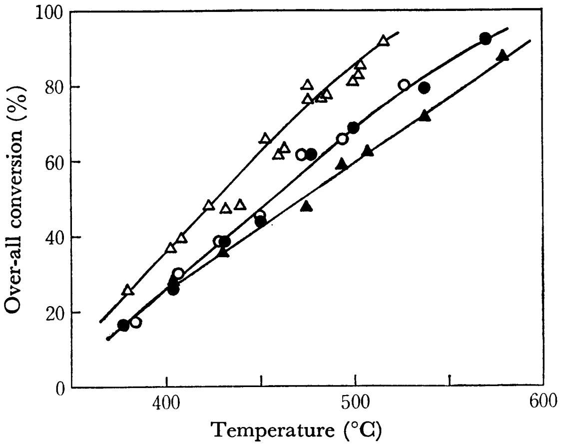

Fig. 1. Over-all conversion of butene and butadiene as a function of temperature.
contact time: 1.6 sec, C_4H_8 or C_4H_6: air=0.65: 100,
MoO_3–P_2O_5: C_4H_8, ○ C_4H_6, △
MoO_3–Bi_2O_3–P_2O_5: C_4H_8, ● C_4H_6, ▲

butene and 1-butene is plotted as a function of the reaction temperature in Fig. 2. It rises to a maximum due to the further oxidation of the isomers. The MoO_3–P_2O_5 has a higher isomerization activity than the MoO_3–Bi_2O_3–P_2O_5. This is in agreement with the data of Echigoya *et al.*[7,8] obtained by the use of MoO_3 and MoO_3–Bi_2O_3 in the oxidative dehydrogenation.

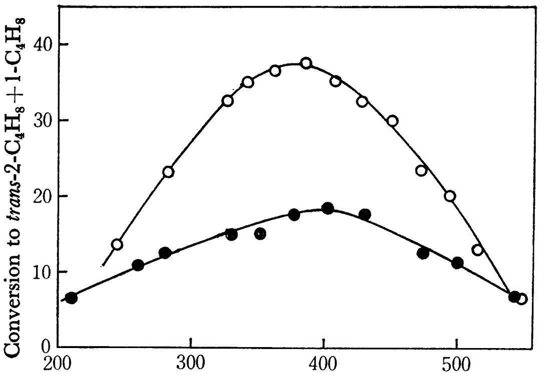

Fig. 2. Formation of isomers of *cis*-2-butene as a function of temperature.
MoO_3–P_2O_5: ○ MoO_3–Bi_2O_3–P_2O_5: ●

The formation of butadiene, which may be considered to be a primary intermediate in the step-by-step oxidation of butene to maleic anhydride, is shown as a function of the over-all conversion of butene (excluding isomerization) in Fig. 3. The slopes of these plots correspond to the differential selectivity at each conversion. Over the MoO_3–Bi_2O_3–P_2O_5 catalyst, the amount of butadiene passed through a maximum at a butene conversion of about 70% and was three times higher than that over the MoO_3–P_2O_3. It can thus be assumed that butadiene is less reactive than butene on the MoO_3–Bi_2O_3–P_2O_5, and that the catalyst is less active than MoO_3–P_2O_5 for butadiene oxidation, probably because butadiene is adsorbed weakly on the MoO_3–Bi_2O_3–P_2O_5 catalyst.[5,9,10]

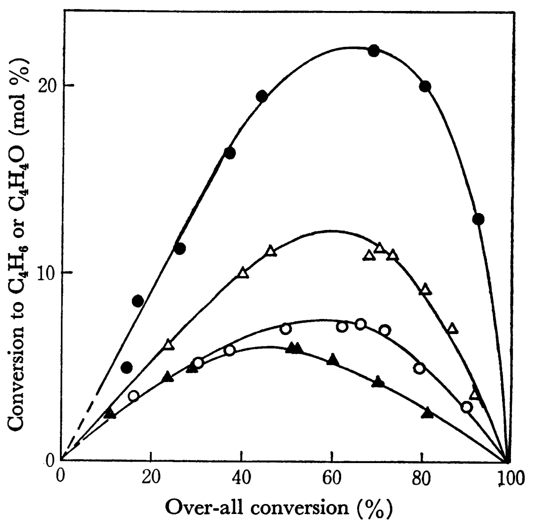

Fig. 3. Formation of intermediates (butadiene and furan) as a function of over-all conversion.
MoO_3–P_2O_5: C_4H_6, ○ C_4H_4O, △
MoO_3–Bi_2O_3–P_2O_5: C_4H_6, ● C_4H_4O, ▲

The formation of maleic anhydride over the MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–P_2O_5 catalysts is shown as a function of over-all conversion of butene in Figs. 4 and 5 respectively. Over the MoO_3–P_2O_5 catalyst, the maximum selectivity to maleic anhydride is 13% at the butene conversion of about 80%, and the amount of maleic anhydride does not exceed 10%. It is found

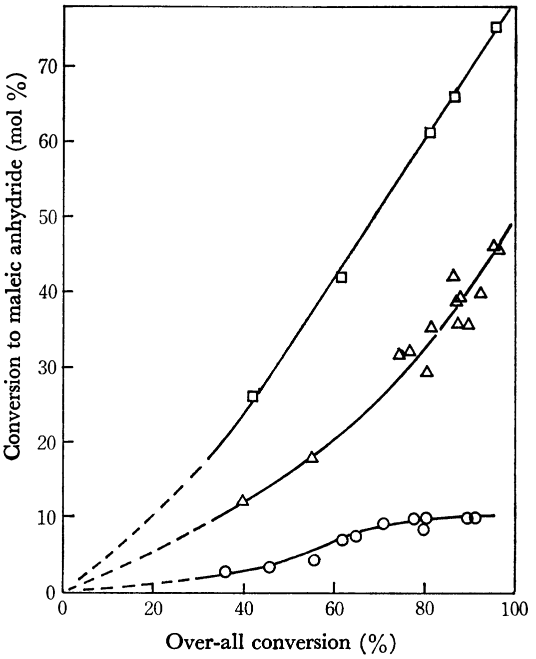

Fig. 4. Formation of maleic anhydride over MoO_3–P_2O_5
Reactant: C_4H_8, ○ C_4H_6, △ C_4H_4O, □

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[7] E. Echigoya, T. Watanabe, and R. Nakamura, *Kogyo Kagaku Zasshi*, **72**, 1092 (1969).

[8] Ph. A. Batist, B. C. Lippens, and G. C. Schuit, *J. Catal.*, **5**, 55 (1966).

[9] J. H. de Boer and R. J. A. M. van der Borg, Actes du Deuxieme Congress Internationale de Catalyse, Edition Thechnip, Paris, (1961), p. 919.

[10] P. Zwietering and F. Hartog, *J. Catal.*, **2**, 79 (1963).

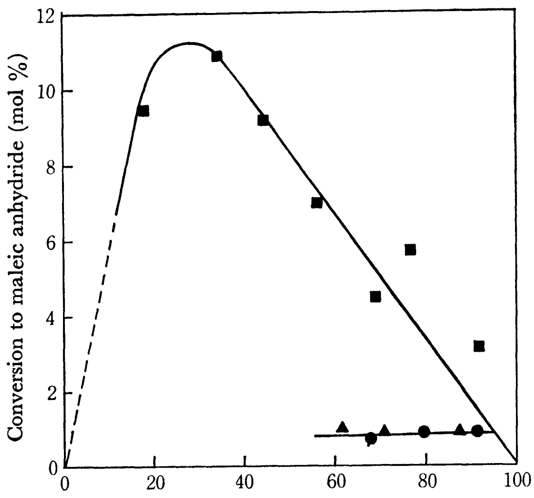

Fig. 5. Formation of maleic anhydride over MoO_3–Bi_2O_3–P_2O_5.
Reactant: C_4H_8, ● C_4H_6, ▲ C_4H_4O, ■

that the result is much inferior to that obtained by the use of vanadium-containing catalysts.[4–6] On the other hand, the MoO_3–Bi_2O_3–P_2O_5 shows a much lower maleic anhydride formation; it is less than 1% even at a butene conversion of 80—90%.

Figure 6 shows the formation of carbon dioxide (CO_2) and carbon monoxide (CO). Over the MoO_3–P_2O_5 catalyst, the formation of CO is superior to that of CO_2, while over the MoO_3–Bi_2O_3–P_2O_5, that of CO is inferior to that of CO_2, and the MoO_3–Bi_2O_3–P_2O_5 gives more CO_2 and less CO than the MoO_3–P_2O_5. The results indicate that, on the MoO_3–Bi_2O_3–P_2O_5 catalyst, a relatively good butadiene formation is obtained even in the presence of a large excess of oxygen, but the further oxidation of butadiene may proceed to complete oxidation. It may be concluded that neither the MoO_3–P_2O_5 nor the MoO_3–Bi_2O_3–P_2O_5 catalyst is adequate for the selective oxidation of butene to maleic anhydride.

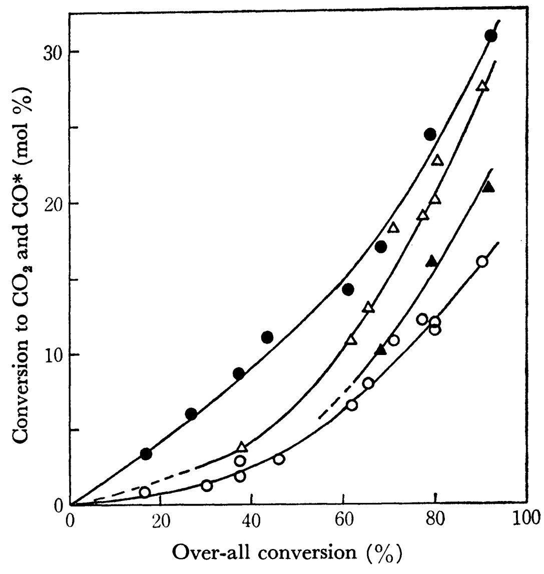

Fig. 6. Conversion of butene to CO_2 and CO as a function of over-all conversion.
MoO_3–P_2O_5: CO_2, ○ CO, △
MoO_3–Bi_2O_3–P_2O_5: CO_2, ● CO, ▲
* 1/4 of the real amount of the formation.

Oxidation of Butadiene. Butadiene conversion-temperature data for both the catalysts are shown in Fig. 1. The MoO_3–P_2O_5 has a considerably higher activity for butadiene oxidation than the MoO_3–Bi_2O_3–P_2O_5. Figure 1 indicates also that, on the MoO_3–Bi_2O_3–P_2O_5 catalyst, butadiene is less reactive than butene, while, on the MoO_3–P_2O_5, butadiene is more reactive than butene. These results agree with the data of butadiene formation from butene (Fig. 3).

The formation of furan, a primary intermediate of butadiene oxidation, is shown in Fig. 3. Contrary to the case of butadiene formation from butene, the amount of furan produced over the MoO_3–Bi_2O_3–P_2O_5 was only half that obtained over the MoO_3–P_2O_5 catalyst.

Over the MoO_3–P_2O_5 catalyst, the selectivity to maleic anhydride increases slightly with an increase in the butadiene conversion, reaching 50% at a butadiene conversion of about 100% (Fig. 4). It is found that the catalyst shows almost the same selectivity of butadiene to maleic anhydride as does the MoO_3–V_2O_5 catalyst (Mo/V=1—4), although its oxidation rate is far lower than that of the latter.[6,11] On the other hand, over the MoO_3–Bi_2O_3–P_2O_5 catalyst, only a small amount of maleic anhydride was obtained (less than 1%) (Fig. 5), much as in the case of butene oxidation.

As is shown in Fig. 7, the formation of CO_2 and CO is not so great in the case of the MoO_3–P_2O_5 catalyst,

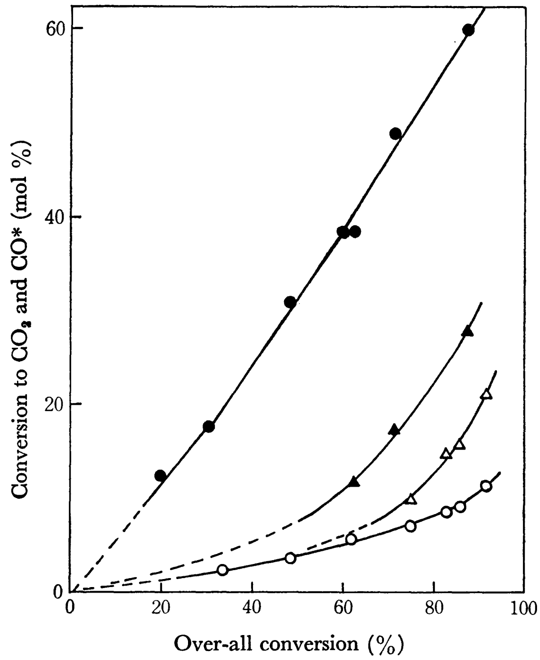

Fig. 7. Conversion of butadiene to CO_2 and CO as a function of over-all conversion.
MoO_3–P_2O_5: CO_2, ○ CO, △
MoO_3–Bi_2O_3–P_2O_5: CO_2, ● CO, ▲
* 1/4 of the real amount of the formation.

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[11] M. Ai, *Kogyo Kagaku Zasshi*, **73**, 950 (1970).

but in the case of the MoO_3–Bi_2O_3–P_2O_5 catalyst, both of them, especially CO_2, are produced to a significant extent. From these results, it may be concluded that the MoO_3–P_2O_5 catalyst shows relatively good results in the selective oxidation of butadiene to furan and maleic anhydride, but that the MoO_3–Bi_2O_3–P_2O_5 catalyst is not adequate to these formations, especially maleic anhydride formation.

Oxidation of Furan. Furan is considered as an intermediate in the consecutive oxidation of butene or butadiene to maleic anhydride.[2,3,5,10] Thus, the oxidation of furan was tested over the MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–P_2O_5 catalysts in order to ascertain the catalytic action of the catalysts on this reaction step. The relationship between the furan conversion and the temperature is shown in Fig. 8. The MoO_3–P_2O_5 catalyst has a higher activity than the MoO_3–Bi_2O_3–P_2O_5 for furan oxidation, much as in butadiene oxidation. We cannot explain why the two catalysts show different results in the formation of furan from butadiene (Fig. 3). It can be estimated, though, that this difference probably results from the character of the adsorption on the catalyst surface.

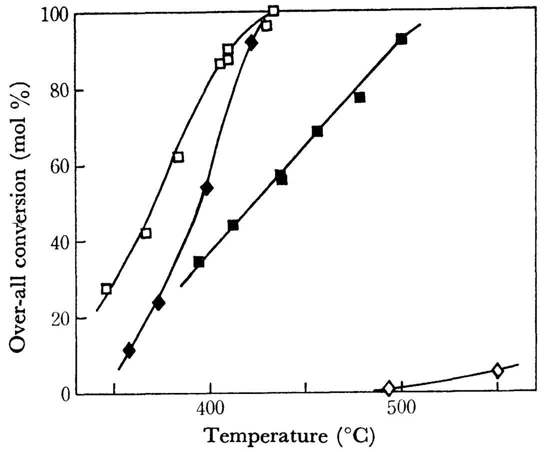

Fig. 8. Over-all conversion of furan and maleic anhydride as a function of temperature.
contact time; 1.6 sec,
C_4H_4O: air = 1: 100, $C_4H_2O_3$: air = 0.6: 100,
MoO_3–P_2O_5: C_4H_4O, □ $C_4H_2O_3$, ◇
MoO_3–Bi_2O_3–P_2O_5: C_4H_4O, ■ $C_4H_2O_3$, ◆

The conversion of furan to maleic anhydride is shown in Figs. 4 and 5. Over the MoO_3–P_2O_5 catalyst, the selectivity to maleic anhydride is quite good, reaching about 78% at a furan conversion of 80—90%. These results are superior to those obtained from V_2O_5, V_2O_5–P_2O_5, and V_2O_5–MoO_3 catalysts.[3,5,6,11] The MoO_3–Bi_2O_3–P_2O_5 catalyst gives a considerably smaller formation of maleic anhydride than does the MoO_3–P_2O_5 catalyst, and the amount of maleic anhydride passed through a maximum at a furan conversion at about 30%. These results reveal that, under the reaction conditions used here, the degradation of maleic anhydride occurs on the catalyst—that is, maleic anhydride is an intermediate in the oxidation of furan to CO_2 and CO, and that the rate of maleic anhydride decomposition is about 6 times faster than that of its formation.[9,10]

For lack of a suitable method of analysis, the amount of the polymer was obtained as the remainder in the mass-balance of the other products (Fig. 9). The formation of the polymer is higher on the MoO_3–Bi_2O_3–P_2O_5 catalyst than on the MoO_3–P_2O_5 catalyst. It is considered that the greater part of the reaction in this step preceeds on a side pathway on the MoO_3–Bi_2O_3–P_2O_5 catalyst rather than on the MoO_3–P_2O_5. The formation of CO_2 and CO is very low over the MoO_3–P_2O_5, while over the MoO_3–Bi_2O_3–P_2O_5 considerably great amount of them are formed and CO_2 is a major product (Fig. 10).

Oxidation of Maleic Anhydride. The oxidation of maleic anhydride was examined in order to ascertain the activity of the MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–

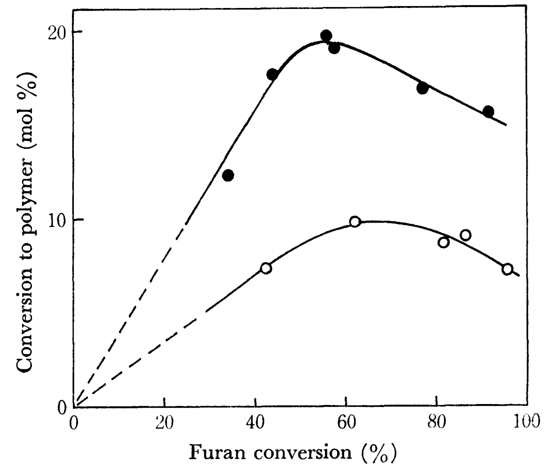

Fig. 9. Polymer formation *versus* furan conversion.
MoO_3–P_2O_5, ○ MoO_3–Bi_2O_3–P_2O_5, ●

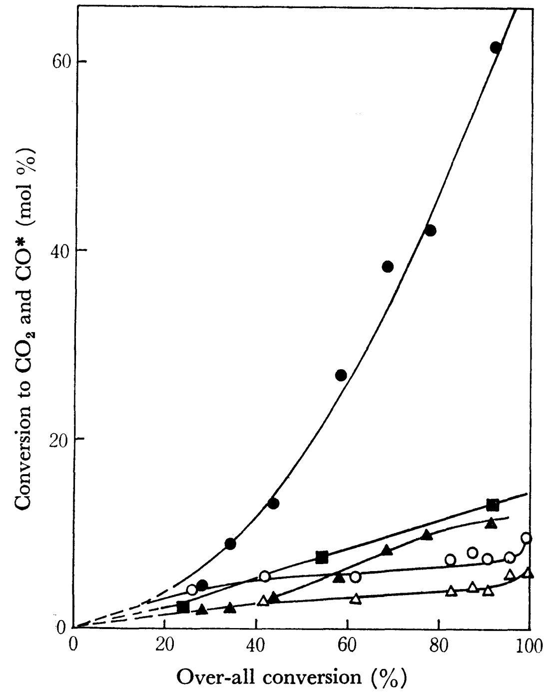

Fig. 10. Conversion of furan and maleic anhydride to CO_2 and CO as a function of over-all conversion.
C_4H_4O oxidation: MoO_3–P_2O_5; CO_2, ○ CO, △
MoO_3–Bi_2O_3–P_2O_5; CO_2, ● CO, ▲
$C_4H_2O_3$ oxidation: MoO_3–Bi_2O_3–P_2O_5; CO, ■
* 1/4 of the real amount of the formation.

P_2O_5 catalysts in the oxidation. Over the MoO_3–P_2O_5 catalyst, maleic anhydride was scarcely oxidized, even at 550°C. This indicates that the MoO_3–P_2O_5 catalyst was almost inactive for maleic anhydride degradation. On the other hand, the MoO_3–Bi_2O_3–P_2O_5 was considerably active in the reaction (Fig. 8). It is also found that, on the catalyst, maleic anhydride is more liable to be oxidized than are butene, butadiene, and furan. Besides CO_2 and CO, no other products were detected. In the degradation of maleic anhydride, the formation of CO was not important; the major product was CO_2 (85%) (Fig. 10).

A Discussion of the Effect of Bi_2O_3 Addition to MoO_3–P_2O_5 on the Reaction Mechanism. The selectivities of the reactants to maleic anhydride over the MoO_3–P_2O_5 catalyst may be summarized as follows: C_4H_8, 13; C_4H_6, 50; and C_4H_4O, 78%. An assumption has been made that the main reaction in the oxidation of butene to maleic anhydride proceeds as follows, in the same manner as over V_2O_5–P_2O_5: $C_4H_8 \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow C_4H_2O_3$.[3,5] The selectivites towards the main reaction pathway in each consecutive step have been calculated from the data of selectivity to maleic anhydride in a manner similar to that used in earlier works:[5,6] $C_4H_8 \rightarrow C_4H_6$; 26, $C_4H_6 \rightarrow C_4H_4O$; 64, and $C_4H_4O \rightarrow C_4H_2O_3$; 78%. It has been concluded that this catalyst has an excellent selectivity for the furan-to-maleic anhydride step and a relatively good one for the butadiene-to-furan step, but a low selectivity for the butene-to-butadiene step, much like the V_2O_5-alone catalyst.[4,6]

On the other hand, over the MoO_3–Bi_2O_3–P_2O_5 catalyst, it is hard to get any information about the reaction scheme, from the data on maleic anhydride. Therefore, we will attempt to discuss the reaction on the basis of the data on CO_2 and CO. As regards CO_2 and CO, over such catalyst as V_2O_5, V_2O_5–P_2O_5, V_2O_5–MoO_3, and MoO_3–P_2O_5, whose activity for maleic anhydride oxidation, is very low, the amount of CO_2 formed in the oxidation of butene, butadiene, and furan was always less than that of CO,[1–6,10] but in the case of maleic anhydride oxidation, the main product was CO_2—that is, maleic anhydride undergoes destructive oxidation to CO_2. Margolis and others[12] indicate that, over the MoO_3–Bi_2O_3–P_2O_5 catalyst, the oxidation of CO to CO_2 is difficult and that the main sources of CO_2 formation are acids, while those of CO formation are aldehydes, and that this catalyst has a high activity for acid destruction.

In the first approximation, an assumption is made that, over the MoO_3–Bi_2O_3–P_2O_5 catalyst, the amount of CO_2 formed in each step from C_4H_8 to $C_4H_2O_3$ is the same as that of CO. From the data of the selectivities to CO_2 and CO for each reactant (Table 1), the portion of each reactant destined to maleic anhydride and decomposed immediately to CO_2 and CO is roughly calculated; for example, in the case of butene, the selectivities to CO_2 and CO are 37 and 27% respectively. As those in the oxidation of maleic anhydride are 85 and 15%, the balance of CO_2 and CO can be expressed by the equation:

$$37 = 0.85x + A$$

$$27 = 0.15x + A$$

where x is the portion of butene destined to maleic anhydride ($0.85x$ and $0.15x$ indicate the CO_2 and CO originated from the decomposition of maleic anhydride) and where A is the CO_2 and CO formed in the steps before $C_4H_2O_3$. After the elimination of A, x is 14%. If the amount of CO_2 formed in the steps before $C_4H_2O_3$ is less than that of CO, the value of x becomes a little higher. The results are shown in Table 1.

TABLE 1. MAXIMUM SELECTIVITY TO CO_2 AND CO AND VALUE OF x

Reactant	C_4H_8	C_4H_6	C_4H_4O	$C_4H_2O_3$
Selectivity to CO_2	37	68	70	85
Selectivity to CO	27	37	13	15
x	14	44	82	(100)

These results indicate that the approximate selectivity of each reactant to maleic anhydride is: C_4H_8, 14; C_4H_6, 44; and C_4H_4O, 82%. This means that the MoO_3–Bi_2O_3–P_2O_5 catalyst has about the same selectivity to maleic anhydride as the MoO_3–P_2O_5 catalyst. It is considered that the MoO_3–BiO_3–P_2O_5 catalyst has nearly the same catalytic specificity as the MoO_3–P_2O_5 catalyst in the oxidation step from C_4H_8 to $C_4H_2O_3$, but its activity for maleic anhydride oxidation is so very high that maleic anhydride cannot be accumulated. The difference in the catalytic features between the MoO_3–P_2O_5 and the MoO_3–Bi_2O_3–P_2O_5 catalysts may be mainly attributed to that in the activity of maleic anhydride destruction. Thus, we can conclude that no satisfactory maleic anhydride yield can be expected by the use of the MoO_3–Bi_2O_3–P_2O_5 catalyst.

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