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A Study of the Catalytic Partial Oxidation of Hydrocarbons. VI. The Effect of Molybdenum Addition to the Vanadium Oxide Catalyst on the Oxidation of Butene to Maleic Anhydride

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In the present work, the vapor-phase partial oxidation of *cis*-2-butene was carried out using V_2O_5-MoO_3 catalysts with different compositions, at 350°C, and at a butene content of 0.65% in air, in order to elucidate the effect of the addition of MoO_3 to the V_2O_5 catalyst on the selectivity and the mechanism for maleic anhydride formation. Two types of catalytic specificities were found, depending upon the Mo content: in the range of less than 20 atom% Mo, the specificity was similar to that of V_2O_5 alone, while in the range of more than 50 atom% Mo, a different specificity was observed, one which gave 1.2 times the yield of maleic anhydride than did V_2O_5 alone or the Mo-poor catalysts. The increase in the selectivity of butene to maleic anhydride which occurred when a large amount of MoO_3 was doped is considered to be caused by the increase in the selectivity of the $C_4H_4O \rightarrow MA$ step, not in that of the $C_4H_8 \rightarrow C_4H_6$ or $C_4H_6 \rightarrow C_4H_4O$ step. The selectivity of the side pathway in the $C_4H_8 \rightarrow C_4H_6$ step was so great that no satisfactory maleic anhydride yield from butene can be expected by the use of the V_2O_5-MoO_3 catalyst.

In previous papers, the mechanism of the catalytic oxidation of butene to maleic anhydride (MA) over V_2O_5 and V_2O_5—P_2O_5 catalysts, and the effect of the addition of P_2O_5 to a V_2O_5 catalysts, have been investigated.[1-3]

Regarding the binary system of V_2O_5–MoO_3, the effect of the catalyst composition on the selectivity and the mechanism of butadiene and furan (C_4H_4O) oxidation have also been reported in a former paper.[4] The results showed that the selectivity of butadiene to maleic anhydride is increased about 20% by the addition of a large amount of MoO_3 to the V_2O_5 catalyst; this increase is considered to be attributable to the increase in selectivity for the $C_4H_4O \rightarrow MA$ step, not to that for the $C_4H_6 \rightarrow C_4H_4O$ step. Nevertheless, the effect of the catalyst composition on butene oxidation is still obscure.

In the present work, we attempted to ascertain how the addition of MoO_3 to the V_2O_5 catalyst affects each reaction step in the step-by-step oxidation of butene to maleic anhydride and to elucidate this effect on the mechanism and the selectivity of the partial catalytic oxidation of butene.

Experimental

The vapor-phase air oxidation of *cis*-2-butene with a large amount of oxygen was carried out over various vanadium-molybdenum oxide catalysts with different compositions, in an ordinary flow-type reaction and at atmospheric pressure, as has been shown in the previous papers.[1-4]

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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, This Bulletin, **43**, 3490 (1970).
[4] M. Ai, *Kogyo Kagaku Zasshi.*, **73**, 950 (1970).

The volume concentration of butene was about 0.65% in air, and the flow rate was kept at 1.5 *l*/min. The contact time was varied between 0.002 and 1.6 sec. This was done by changing the amount of the catalysts. The reaction temperature was always kept at 350°C. The experimental and analytic procedures were also the same as those employed in the previous works.[1-4]

The catalysts employed in the experiments were prepared as follows: the required quantities of NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$ were dissolved in hot water by using oxalic acid, after which, pumice, of a mesh size of 10 to 20, was added to the above solution; then the solution was 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 and molybdenum. The catalyst was calcined under flowing air, at 500°C, for 5 hr.

Results and Discussion

Effect on the Oxidation Activity. Figure 1 shows the total butene conversion (excepting isomerization) at 350°C as a function of the contact time for various compositions of V_2O_5–MoO_3 catalysts. As the plot of log (C_t/C_0), where C_0 and C_t are the concentrations of butene in the charge and the effluent gas respectively, against the contact time gave a straight line, the rate of butene oxidation can be considered to be nearly of the first order for the butene concentration. The rate constants, calculated at 350°C over various V_2O_5–MoO_3 catalysts, were compared with those of butadiene or furan oxidation reported in a previous paper[4] (Fig. 2).

The oxidation of butene, butadiene, and furan were of the same order of magnitude at the same catalyst composition; they formed the sequence; $C_4O_8 < C_4H_6 < C_4H_4O$. The oxidation activity for each reactant increased gradually with the addition of MoO_3 in the range of less than 20 atom%, and then it decreased little by little with an increase in the Mo content in the region over 20 atom% Mo. It thus seems that, in MoO_3-rich compositions, MoO_3 acts only as a diluent. This result was very similar to that of benzene oxidation reported by Ioffe.[5]

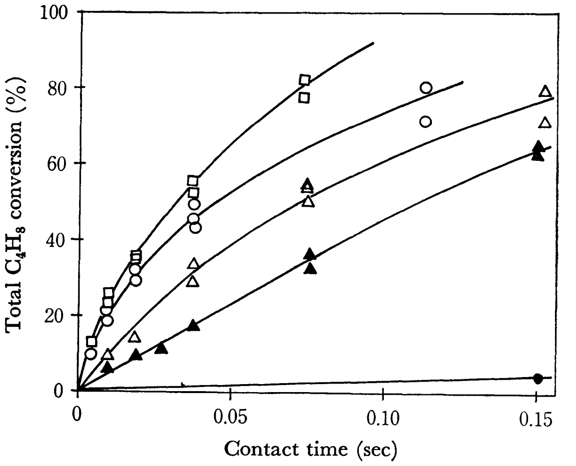

Fig. 1. Total conversion of butene as a function of contact time.
at 350°C, C_4H_8 : air = 0.65 : 100, catalyst composition (atomic ratio)
○: Mo/V = 0, □: 1/4, △: 1, ▲: 4/1, ●: Mo only

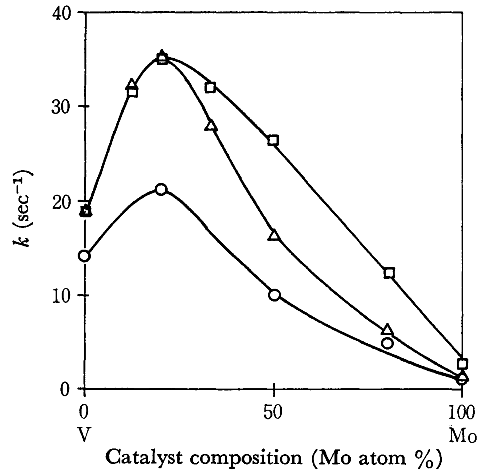

Fig. 2. The relationship of the oxidation activity *versus* the catalyst composition.
at 350°C, reactant : air = 0.6—1.0 : 100
○: C_4H_8, △: C_4H_6, □: C_4H_4O

Isomerization of Butene. The oxidation of butene was always accompanied by its isomerization. The conversion of *cis*-2-butene to such isomers as *trans*-2-butene and 1-butene is shown as a function of the total *cis*-2-butene conversion in Fig. 3. The results revealed that the formation of the isomers decreased with an increase in the oxidation activity of the catalyst. To clarify the cause of this, the conversion of *cis*-2-butene to *trans*-2-butene and 1-butene was plotted *versus* the contact time at 350°C for each catalyst (Fig. 4). The results suggest that the isomerization activity was independent of the compositions of V_2O_5 and MoO_3, and that only the oxidation activity was affected by the catalyst composition. In the case of a continuous experiment like this, it was observed that, in the absence of oxygen in the charge, neither the isomerization of

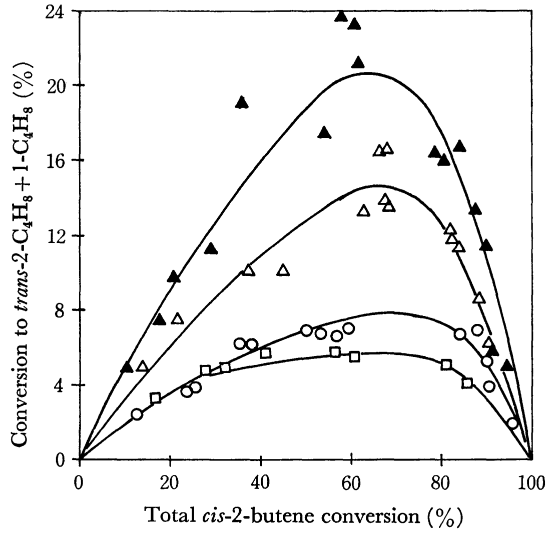

Fig. 3. Formation of isomers of *cis*-2-butene as a function of total *cis*-2-butene conversion.
at 350°C, C_4H_8 : air = 0.65 : 100
○: Mo/V = 0, □: 1/4, △: 1, ▲: 4/1

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[5] I. I. Ioffe, *Kinetics and Catalysis (USSR) (Eng. Transl.)*, **3**, 165 (1962); **7**, 670 (1966).

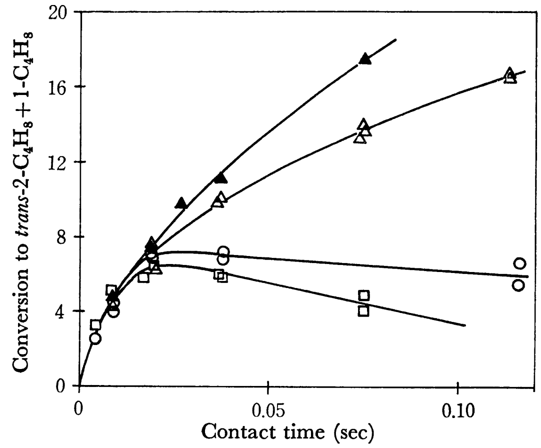

Fig. 4. The relationship of the conversion of *cis*-2-butene to *trans*-2-butene and 1-butene *versus* contact time for each catalyst.
at 350°C, butene: air=0.65:100
○: Mo/V=0, □: 1/4, △: 1, ▲: 4/1

butene nor oxidation occurred over these catalysts; therefore it was considered that the presence of oxygen was necessary even to the isomerization of butene.

Effect on the Maleic Anhydride Formation. The formation of maleic anhydride from butene over V_2O_5–MoO_3 catalysts with different compositions and at 350°C is shown as a function of the total butene conversion in Fig. 5. Selectivity to maleic anhydride was defined thus: conversion to maleic anhydride/total butene conversion. The slopes of these plots, therefore, correspond to the differential selectivity at each butene conversion. These plots of the performance gave two lines, depending upon the Mo content in the catalyst, *i. e.*, Mo-poor (Mo<20 atom%) and Mo-rich (Mo>50 atom%) catalysts. Over the catalysts containing less than 20% Mo, the selectivity to maleic anhydride was less than 20% and did not vary with the Mo content. When the butene conversion was more than 70%, the formation of maleic anhydride decreased, probably because of the destruction of maleic anhydride; therefore, the formation did not exceed 15%. On the other hand, in the case of the Mo-rich catalysts, selectivity to maleic anhydride was also constant with an increase in the Mo content, and the selectivity at butene conversion of 70% reached 24%. The maximum formation of maleic anhydride reached 20 mol%.

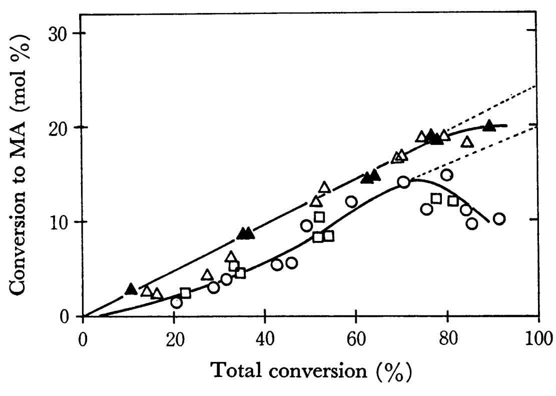

Fig. 5. Effect of catalyst composition on maleic anhydride formation.
at 350°C, C_4H_8: air=0.65:100
○: Mo/V=0, □: 1/4, △: 1, ▲: 4/1

Effect on Intermediate Formation. The formation of butadiene and furan, which may be considered as a primary and a secondary intermediate respectively, in the step-by-step oxidation of butene to maleic anhydride, is shown in Fig. 6. The results reveal that the higher the oxidation activity of the catalyst became, the lower the intermediate formation became, while the maximum conversion to the intermediate always occurred at about 40% butene conversion. However, the amount of intermediate products over the V_2O_5–MoO_3 catalyst was far lower than that obtained over the V_2O_5–P_2O_5 catalyst.[1,3)]

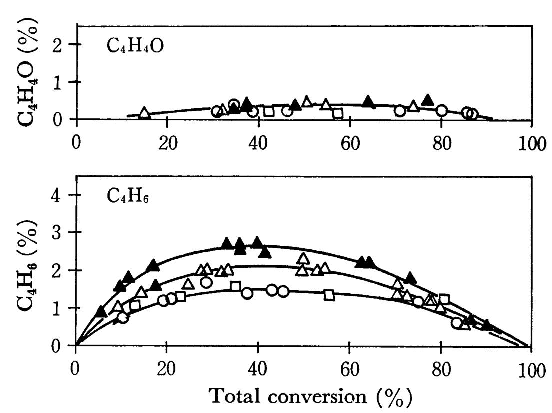

Fig. 6. Effect of catalyst composition on intermediates (butadiene and furan) formation. (Notation as in Fig. 5)

Effect on Side Reactions. A number of by-products have been found in the oxidation of butene over the V_2O_5–P_2O_5 catalyst,[1)] while over the V_2O_5 and V_2O_5–MoO_3 catalysts, the major by-products were CO, CO_2, acetaldehyde (AcH), and acetic acid (AcOH); the other products were almost negligible. The conversion to AcH+AcOH (based on the assumption that two moles of AcOH or AcH are formed from one mole of butene, *i. e.*, 1/2 of the real amount of AcH+AcOH) is shown as a function of the total butene conversion in Fig. 7. The results show that the selectivity of butene to AcH and AcOH is almost independent of the catalyst

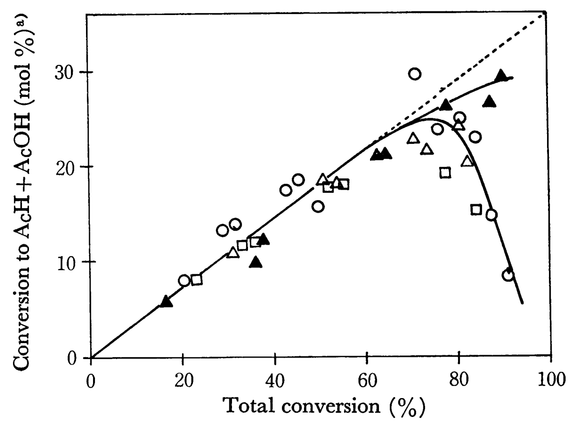

Fig. 7. Conversion to AcH+AcOH$^{a)}$ as a function of total butene conversion for various composition of V-Mo catalyst.
a) Basing on the assumption that 2 mol of AcH+AcOH are formed from 1 mol of C_4 compound. (Notation as in Fig. 5)

composition and is about 36% at a butene conversion of less than 70%. The formation of AcH and AcOH decreased, the amount being greatest at a conversion of about 80%, probably because of the destruction of AcH and AcOH.

The conversions to CO and CO_2 are shown as a function of the butene conversion in Figs. 8 and 9. The results reveal that the formation of CO and CO_2 increases rapidly at conversions of above 80%, probably because of the destruction of AcH, AcOH, and maleic anhydride. The CO_2 formation is independent of the catalyst composition, while the CO formation gives one of two lines, depending upon the Mo content, similarly catalyst containing more than 50% Mo showed a low selectivity to CO formation, *i. e.*, the formation was about a half of that obtained by means of the Mo-poor catalyst.

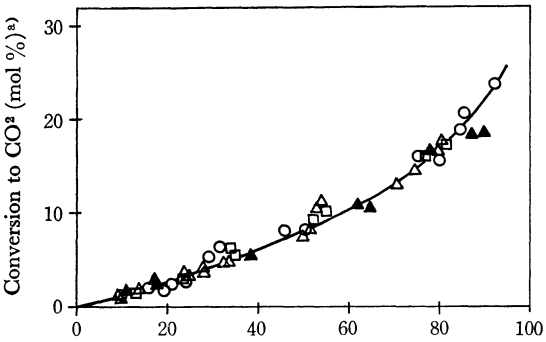

Fig. 8. Conversion$^{a)}$ to CO^2 as a function of total butene conversion for various composition of V-Mo catalysts.
a) 1/4 of the real amount of the formation.
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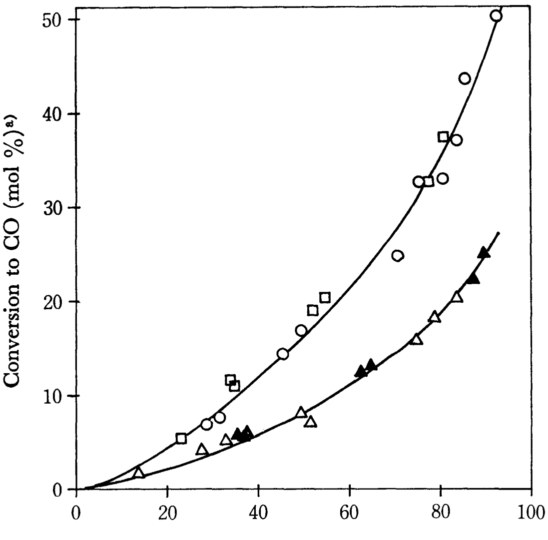


Fig. 9. Conversion$^{a)}$ to CO as a function of total butene conversion for various composition of V-Mo catalysts.
a) 1/4 of the real amount of the formation.
(Notation as in Fig. 5)

Discussion of the Effect of the MoO_3 Addition. In combination with the data in the previous report,[4] the selectivity to maleic anhydride is summarized in Table 1.

Table 1. Selectibity to maleic anhydride (%)

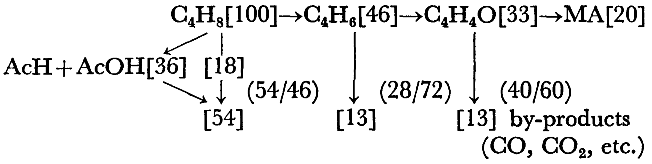
Catalyst	Reactant		
	C_4H_8	C_4H_6	C_4H_4O
V_2O_5, V_2O_5-MoO_3(Mo<20 %)	20	43	60
V_2O_5-MoO_3 (Mo >50 %)	24	53	73

Table 2. Selectibities of the steps (%)

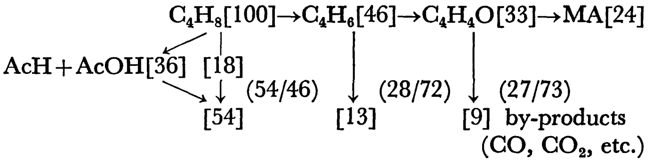
Catalyst	Step		
	$C_4H_8 \downarrow C_4H_6$	$C_4H_6 \downarrow C_4H_4O$	$C_4H_4O \downarrow$ MA
V_2O_2, V_2O_5-MoO_3 (Mo >20 %)	46	72	60
V_2O_5-MoO_3 (Mo >50 %)	46	72	73

Since the amount of the intermediate (butadiene or furan) formed in the oxidation of butene and butadiene[4] to maleic anhydride over the V_2O_5–MoO_3 catalyst was quite small, it is difficult to know exactly how the main reaction pathway for the oxidation of butene proceeds. An assumption has been made that the main reaction proceeds, in the same manner as over the V_2O_5–P_2O_5 catalyst,[1,3] as follows: $C_4H_8 \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow$ MA. The selectivities towards the main reaction pathway in each consecutive step have been calculated and reported in an earlier paper;[3] they are shown in Table 2. From the above results and the results of butadiene oxidation,[4] the probable scheme of the butene oxidation over Mo-poor (Mo<20 atom%) and Mo-rich (Mo>50 atom%) catalysts may be proposed to be as follows:

V_2O_5, V_2O_5–MoO_3 (Mo<20 atom%)



V_2O_5–MoO_3 (Mo>50 atom%)



From the results it was found that the addition of less than 20 atom% Mo to V did not affect the catalytic specificity and the Mo-poor catalyst gave the same specificity as V_2O_5 alone, although the doping modified the oxidation activity. On the other hand, the addition of more than 50 atom% Mo to V gave another catalytic specificity, one which was milder and which brought a higher selectivity to maleic anhydride. These two kinds of catalytic specificities may be caused by two different catalytic species. Similar results were observed in toluene oxidation over the V_2O_5–MoO_3 catalyst system.[6] In the range of less than 30 atom% Mo, maleic anhydride was formed mainly, while in the

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[6] M. Ai, *Kogyo Kagaku Zasshi*, **73**, 946 (1970).

addition of more 40 atom% Mo to V benzaldehyde was the major product.

Many past studies devoted to the physico-chemical properties of the binary system of the V_2O_5–MoO_3 catalyst[5,7–10] have indicated that, in the range of less than 14 atom% Mo, MoO_3 forms a solid solution of the substituted type with V_2O_5, and the active species was considered to be V_2O_5, modified by MoO_3, while the addition of more 33 atom% Mo to V formed a mixture of a new compound (probably $Mo_6V_9O_{40}$) and MoO_3.

Therefore, it may be suggested that, in the Mo-poor catalyst, V_2O_5 acts as an active species, while in the Mo-rich catalyst, the new compound ($Mo_6V_9O_{40}$) acts as the active species and MoO_3 acts only as a diluent. A perusal of the results indicates that the 20% increase (from 20 to 24%) of the selectivity of butene to maleic anhydride which occurred when a large amount of MoO_3 in V_2O_5 was doped may be attributed to the 20% increase (from 60 to 73%) in the selectivity in the $C_4H_4O \rightarrow MA$ step, not in the $C_4H_8 \rightarrow C_4H_6$ or $C_4H_6 \rightarrow C_4H_4O$ step. That is the addition of MoO_3 did not affect the selectivity in the $C_4H_8 \rightarrow C_4H_4O$ step. It may be concluded that, for butene oxidation, satisfactory results cannot be expected by the use of the binary system of V_2O_5–MoO_3.

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7) S. Yoshida, *Shokubai,* **10**, 90 (1968).

8) R. Munch and E. D. Pierron, *J. Catal.*, **3**, 406 (1964).

9) K. Tarama, S. Teranishi, and T. Yasui, *Kogyo Kagaku Zasshi*, **60**, 1222 (1955).

10) A. Magneli and B. Oughton, *Acta Chem. Scand.*, **5**, 585 (1951).