Acidic Property and Oxidation Activity of MoO_3-V_2O_5-P_2O_5 Ternary Oxides

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The relationship between the acid-base properties and the oxidation activity of a series of ternary oxide catalysts, MoO_3–V_2O_5–P_2O_5, with different V/Mo composition and a constant phosphorus content, $P/(Mo+V)=0.1$, was investigated. The acidity was determined by means of the NH_3 adsorption and by studying the catalytic activity for acid-catalyzed reactions, such as dehydration of isopropyl alcohol and isomerization of 1-butene, in the presence of an excess of air. A new acidic site is generated by the combination of two binary oxides, *i.e.*, MoO_3–P_2O_5 and V_2O_5–P_2O_5, and a broad maximum in the acidity occurs at $V/(Mo+V)=0.4$—0.9. The basic property is so small that no satisfactory data can be obtained from the adsorption of acidic molecules such as CO_2, SO_2, and acetic acid. The catalysts, regardless of composition, are inactive for reactions which are accelerated by basic sites, such as oxidative dehydrogenation of isopropyl alcohol to acetone, oxidative decomposition of formic acid to CO_2, and oxidation of methanol to CO_2. The oxidation activities for butadiene and methanol can be tied to the acidity of the catalysts.

A variety of multi-component oxides containing more than three kinds of metal oxides have been proposed as being effective as practical catalysts. Why can a good performance be obtained only by the combination of several oxides? What is the role of each component in the catalytic action of a multi-component oxide? Moreover, what are the functions universally required for an oxidation catalyst?

We have studied selective oxidations on the basis of the idea that an acid-base-type interaction between the catalyst surface and the organic substance to be oxidized plays the determining role in mild oxidations, and as a result, the combination of metal oxides contributes to an enhancement or modification of the acid-base properties.[1)]

MoO_3, V_2O_5, and P_2O_5 are all typical acidic oxides. Therefore, composite oxides consisting of these oxides, naturally, are characterized by their acidic property. Actually, they have been proposed as catalysts suited only for "acid-formation" reactions, such as syntheses of maleic anhydride, phthalic anhydride, acrylic acid, and methacrylic acid.[2–4)]

As for the three binary systems made up by two of the three oxides, *i.e.*, MoO_3–V_2O_5, MoO_3–P_2O_5, and V_2O_5–P_2O_5, the relationship between the acid-base properties and the catalytic behavior in mild oxidations has been studied earlier.[5–7)]

In this work, we were interested in seeing how the replacement of molybdenum in the MoO_3–P_2O_5 ($P/Mo=0.1$) catalyst by vanadium induces a change in the catalytic behavior and, then, in confirming whether or not the change in the catalytic activity can be interpreted by the change of the acid-base properties.

Experimental

The catalysts used in this study were a series of ternary oxides, MoO_3–V_2O_5–P_2O_5, with nine different V/Mo compositions and a constant phosphorus content, $P/(Mo+V)=0.1$ (atomic ratio). The method of the preparation was the same as that employed in the previous studies.[5–7)] That is, the required quantities of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, NH_4VO_3, and 85 wt % H_3PO_4 were dissolved in hot water by using oxalic acid, if necessary, and to this was added 10—20 mesh pumice. Then, the mixture was evaporated with stirring. The catalyst were calcined in a stream of oxygen at 500 °C for 4—5 h.

The techniques of acidity measurement and the reaction procedures were the same as those employed earlier.[8)]

Results

Surface Properties. In Table 1 are shown the specific surface areas. They are of the order of 1 m^2/g over the entire range of composition and the effect of composition is found to be small.

TABLE 1. SURFACE AREAS OF THE MoO_3–V_2O_5–P_2O_5 CATALYSTS

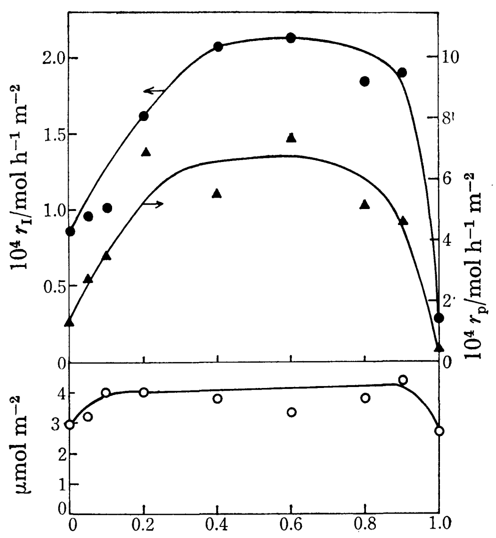
Composition[a)] V/(Mo+V)	Surface area (m^2/g)	Composition[a)] V/(Mo+V)	Surface area (m^2/g)
0	1.2	0.60	1.0
0.05	1.1	0.80	0.9
0.10	1.2	0.90	0.9
0.20	1.0	1.0	1.5
0.40	1.1		

a) $P/(Mo+V)=0.10$: atomic ratio.

The acidity (number of acidic sites) was measured directly by the irreversible adsorption of NH_3 at 200 °C using the static method.[8)] The results are shown in Fig. 1.

It seems difficult to determine in this way the acidity with satisfactory accuracy. Therefore, another attempt was made to determine the acidity indirectly, that is, the catalytic activity for certain acid-catalyzed reactions was investigated. The dehydration of isopropyl alcohol (IPA) to propylene and the isomerization of 1-butene to 2-butenes, in the presence of an excess of air, were chosen as the model reactions, as in the previous studies.[4–8)]

The reactions were carried out at the IPA and 1-butene concentrations of 1.33 and 1.0 mol% in air, respectively, and the total flow rate of 1.0 l/min, by changing the amounts of the catalysts in the range of 1



Atomic ratio V/(Mo+V)

Fig. 1. Acidity of MoO_3–V_2O_5–P_2O_5 as a function of the V/(Mo+V) ratio. P/(Mo+V)=0.1.
○: Irreversible adsorption of NH_3 at 200 °C, ▲: dehydration activity for IPA at 145 °C, r_p, ●: isomerization activity for 1-butene at 172 °C, r_I.

to 20 g. The MoO_3–V_2O_5–P_2O_5 catalysts exhibit a very high activity for the two reactions and, therefore, the reactions can occur, to a considerable extent, at a fairly low temperature. Propylene is the sole product in the reaction of IPA. The initial rate of IPA dehydration at 145 °C, r_p, and the rate of butene isomerization at 172 °C, r_I (mol/h·m^2 of catalyst), are plotted together with the amounts of adsorbed NH_3 in Fig. 1.

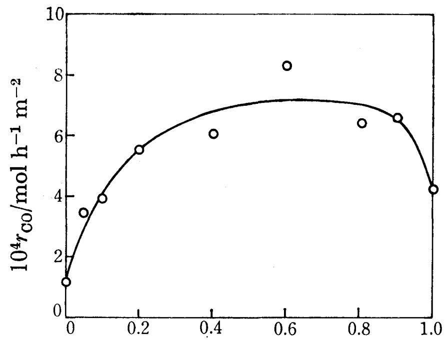
As for the basicity, we tried to measure it by the adsorption of SO_2 as well as CO_2, using the static method, and by the adsorption of acetic acid using the pulse method.[8] However, the amounts were so small that the effect of catalyst composition could not be obtained.

Decomposition of Formic Acid. It has been reported that the catalytic activity for decomposition of formic acid to CO and that for the oxidative decomposition to CO_2 can be tied to the acidic and basic properties, respectively, of the metal oxide catalysts.[9] Because of the simplicity of the reaction system, the catalytic activity for these reactions was tested.

The reaction was carried out at the concentration of 1.8 mol% HCOOH in air and the total flow rate of 1.0 l/min. The catalysts weighed 2 to 20 g. Details of the reaction procedures were described earlier.[9] The products were CO and H_2O, and the amount of CO_2 was negligibly small regardless of the catalyst composition. The initial rate of CO formation at 259 °C, r_{CO} (mol/h·m^2 of catalyst), are plotted in Fig. 2.

Oxidation of Butadiene. Since the MoO_3–V_2O_5–P_2O_5 catalysts are fairly acidic and rarely basic, satisfactory results can be expected merely for the activity in the oxidation of basic reactants and for the selectivity in the "base to acid" type reactions.[1] Therefore, the oxidation of butadiene was chosen as a model reaction.

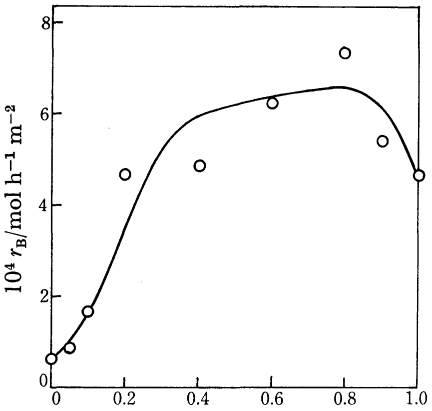
The reaction was carried out in an excess of air (C_4H_6=1.0 mol%) at 360—450 °C and at a constant



Atomic ratio V/(Mo+V)

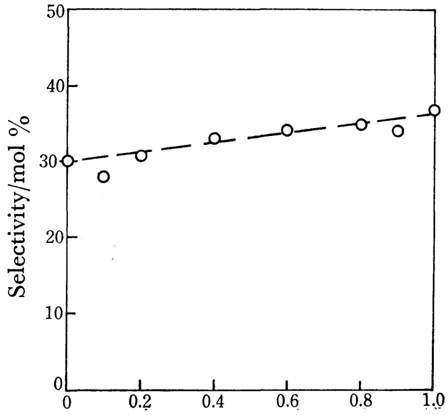
Fig. 2. Catalytic activity for the decomposition of formic acid to CO at different V/Mo compositions. r_{CO}: Rate of CO formation at 259 °C and 1.8 mol % HCOOH in air.

total flow rate (1.0 l/min). The amounts of the catalysts were varied in the range of 1 to 20 g to achieve a proper conversion. The rate of butadiene consumption at 365 °C, r_B (mol/h·m^2 of catalyst), was adopted as a measure of the activity, for convenience in the experimental procedures. The results are shown in Fig. 3.



Atomic ratio V/(Mo+V)

Fig. 3. Oxidation activity for butadiene as a function of the V/(Mo+V) ratio. r_B: Consumption of butadiene at 365 °C and 1.0 mol % C_4H_6 in air.



Atomic ratio V/(Mo+V)

Fig. 4. Selectivity of butadiene to maleic anhydride at a total conversion of 40—50 %. T=360—450 °C, C_4H_6=1.0 mol % in air.

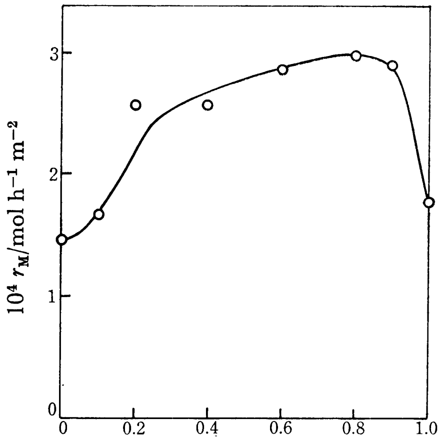


Fig. 5. Oxidation activity for methanol as a function of the V/(Mo+V) ratio. r_M: Rate of formaldehyde formation at 250 °C and 2.6 mol % CH_3OH in air.

The main products were maleic anhydride, CO, and CO_2. The selectivity of butadiene to maleic anhydride at a fixed conversion, 40—50%, was measured with each catalyst; it is shown in Fig. 4.

Oxidation of Methanol. The oxidation of methanol was tested, because the catalytic activity for this reaction was found to be correlated with the acid-base properties of the catalysts.[10]

The reaction was carried out at 2.6 mol% CH_3OH in air. Formaldehyde was almost the sole product and the amounts of CO_2 and CO were very small, even when the conversion was about 50%. The rate of formaldehyde formation at 250 °C, r_M (mol/h·m^2 of catalyst), is shown in Fig. 5.

Discussion

The activities for the two acid-catalyzed reactions vary in the same fashion with the variation of V/Mo composition. However, the shape of the NH_3-curve in Fig. 1 is not the same as that of the activity-curves. With regard to these results, one may be led to consider that the catalytic activities reflect the true acidity better than the amounts of NH_3, because the surface areas of the catalysts are so small that it is difficult to measure, with satisfactory accuracy, the amounts of adsorbed NH_3. In the following, it is sure that a new acidic site is generated by the combination of the MoO_3–P_2O_5 (P/Mo=0.1) and the V_2O_5–P_2O_5 (P/V=0.1) or by the replacement of molybdenum in the MoO_3–P_2O_5 by vanadium. The acidity attains a broad maximum at V/(Mo+V)=0.4—0.9. This feature of the acid-generation is different from that observed in the case of MoO_3–V_2O_5 binary system, where a sharp maximum in acidity occurs at V/(Mo+V)=0.85—0.90[5].

The possession of a very high activity for the two acid-catalyzed reactions proves that the MoO_3–V_2O_5–P_2O_5 catalysts are eminent in acidic property, as can easily be expected from the natures of MoO_3–P_2O_5 and V_2O_5–P_2O_5. On the other hand, the absence of the catalytic activity for the reactions which are promoted by basic sites, for example, the oxidative dehydrogenation of IPA to acetone,[1] the oxidative decomposition of formic acid to CO_2,[9] and the oxidation of methanol to CO_2,[10] indicates that the catalysts regardless of the V/Mo composition are very poor in basic property. The basic property of MoO_3 and V_2O_5 may be extinguished completely by P_2O_5.[7]

The presence of a parallelism between the activity for decomposition of formic acid to CO (Fig. 2) and the acidity (the activities for IPA dehydration and butene isomerization) supports the earlier view that catalytic activity for the CO formation is tied to the acidic property of the catalyst.[9]

The catalytic activity for the oxidation of butadiene (Fig. 3) also varies in the same fashion as do the activities shown in Fig. 1, except for the V/(Mo+V)=1 catalyst. This finding suggests that the oxidation of butadiene is decided mainly by the activation of butadiene by the acidic sites, as has been pointed out earlier.[1]

The selectivity to maleic anhydride is relatively high over the entire range of composition. This can easily be understood from the fact that the catalysts, regardless of composition, are fairly acidic and rarely basic, because one of requirements for an effective catalyst suited for "acid-formation" reactions is the possession of a sufficient acidic property.[1]

The catalysts, regardless of the composition, exhibit a very good selectivity in the oxidation of methanol to formaldehyde, which is consistent with the earlier proposal that formaldehyde is the sole product as long as the catalyst is acidic enough.[10] The presence of a parallelism between the catalytic activity for the formaldehyde formation (Fig. 5) and the acidities shown in Fig. 1 also supports the view that the activity for formaldehyde formation is decided mainly by the activation of methanol on acidic sites.[10]

It is concluded that the MoO_3–V_2O_5–P_2O_5 catalysts are eminent in acidic property but poor in basic property, regardless of the V/Mo composition, that a new acidic site is generated by the combination of the MoO_3–P_2O_5 and the V_2O_5–P_2O_5, and that the acidity attains a broad maximum at V/(Mo+V)=0.4—0.9. The catalytic behavior in the oxidation of butadiene and methanol can be explained relatively well in terms of the acid-base properties of the catalysts.

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