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The Effect of the Difference in the Oxidation State of the Second Component Added to MoO_3 on the Generation of the Acidic Property

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The effect of the difference in the oxidation state of the second component added to MoO_3 on the generation of acidic sites was studied with regard to Sn^{2+}—Sn^{4+}, Fe^{2+}—Fe^{3+}, Cr^{3+}—Cr^{6+}, and Cu^{+}—Cu^{2+}. It was found that a markedly lager amount of acidic sites is generated by the combination of Sn^{2+}, Fe^{2+}, or Cr^{3+} with MoO_3 than by that of Sn^{4+}, Fe^{3+}, or Cr^{6+} respectively. As a general feature of metal-oxide combination, it is proposed that the addition of a metal ion in a lower oxidation state to MoO_3 brings about a markedly more significant acidity generation than that of a metal ion in a higher oxidation state. An explanation to account for the results was attempted in relation to the reducing function of the second component.

It is widely known that a combination of different metal oxides sometimes induces a significant acidity-generation and that this character of metal oxides has actually been applied to the preparation of a catalyst. For understanding the acidity-generation, an explanation has been proposed by Tanabe *et al.* based on the acidity-basicity data for many binary-oxides.[1,2]

However, it still seems difficult to understand the acidity-generation in the case of transition-metal oxides in which the oxidation state is variable. It is, therefore, important to find some general rules effective for predicting the acidity-generation of mixed oxides containing transition-metal oxides, such as MoO_3, V_2O_5, WO_3, and U_3O_8.

It was found in studying Sn–Mo oxides[3] that the acidity-generation is markedly affected by the oxidation state of tin in the starting material as well as by the method of catalyst preparation. This finding led us to a prediction that the acidity-generation is related to the oxidation state of the second component added to a transition-metal oxide.

In the present study, MoO_3 was chosen as the first component, and the effect of the oxidation state of the second component was studied with regard to Sn^{2+}—Sn^{4+}, Fe^{2+}—Fe^{3+}, Cr^{3+}—Cr^{6+}, and Cu^{+}—Cu^{2+}.

Experimental

Catalysts. The catalysts used in this study were nine kinds of MoO_3–X_nO_m with different X/Mo ratios, where X refers to four different metals. They were prepared as follows.

Mo–Sn Oxides: The required quantity of either $SnCl_2$ or $SnCl_4$ was dissolved in water. To this solution, a dilute aqueous ammonia solution was added to precipitate the corresponding hydroxide. After filtering and washing, the paste-like hydroxide was added to an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and 10 to 20 mesh pumice was mixed with the solution; then the mixture was evaporated with stirring. The amount of pumice was about 500 ml per g atom of metal. The catalyst was calcined under flowing oxygen at 500 °C for 4 to 5 h. The catalysts were denoted as MoO_3–Sn^{2+} and MoO_3–Sn^{4+} respectively.

Mo–Fe Oxides: As the starting materials we used iron(II) oxalate dihydrate, $FeC_2O_4\cdot 2H_2O$, for Fe^{2+} and ammonium tris(oxalato) ferrate(III) trihydrate, $(NH_4)_3Fe(C_2O_4)_3\cdot 3H_2O$, for Fe^{3+}. Aqueous solutions of each compound were mixed with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Pumice was then added to the solution or slurry thus obtained. The further procedures were the same as those used in the case of Mo–Sn oxides. The catalysts were denoted as MoO_3–Fe^{2+} and MoO_3–Fe^{3+} respectively.

Mo–Cr Oxides: $Cr(NO_3)_3\cdot 9H_2O$ and CrO_3 were used as the starting materials. The further procedures were the same as above. The catalysts were denoted as MoO_3–Cr^{3+} and MoO_3–Cr^{6+}.

Mo–Cu Oxides: As the starting materials we used CuCN and CuCl for Cu^{+} and $Cu(CH_3CO_2)_2\cdot H_2O$ for Cu^{2+}. The catalysts were denoted as MoO_3–CuCN, MoO_3–CuCl, and MoO_3–Cu^{2+} respectively.

Catalytic-activity Measurements. The vapor-phase dehydration of 2-propanol and the oxidation of propylene and methanol were carried out in an ordinary continuous-flow system. The reactor and the experimental procedures were the same as those employed in previous works.[4–7]

Results

Mo–Sn Oxides. The effect of the difference in the oxidation state of tin on the specific surface area was checked by the BET method using nitrogen at −196 °C. As may be seen in Fig. 1, the surface area

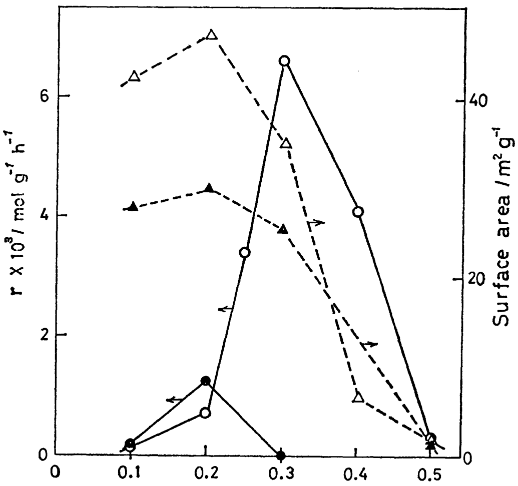

Fig. 1. Surface area and catalytic activity for dehydration of 2-propanol.

r=Rate at 160 °C and 1.7 vol% 2-propanol in air. ○,△: MoO_3–Sn^{2+}, ●,▲: MoO_3–Sn^{4+}.

of both the MoO_3–Sn^{2+} and MoO_3–Sn^{4+} systems are of the same order of magnitude and vary in the same way with an increase in the Mo content; that is, they pass through a maximum at Mo/(Mo+Sn) atomic ratio=0.2 and then sharply decline with the Mo-content at Mo/(Mo+Sn)>0.4.

As a measure of the acidity of a catalyst, the catalytic activity for the dehydration of 2-propanol was chosen for convenience as in the previous studies.[4–6] The initial rate of dehydration was measured at low conversion levels. The rate at 160 °C is plotted as a function of the catalyst composition in Fig. 1. As has been reported earlier,[5] a dramatically high acidity is obtained in the case of the MoO_3–Sn^{2+} catalyst at the Mo/(Mo+Sn) atomic ratio of 0.3, while the generation of acidic sites is much less remarkable in the case of the MoO_3–Sn^{4+} catalysts.

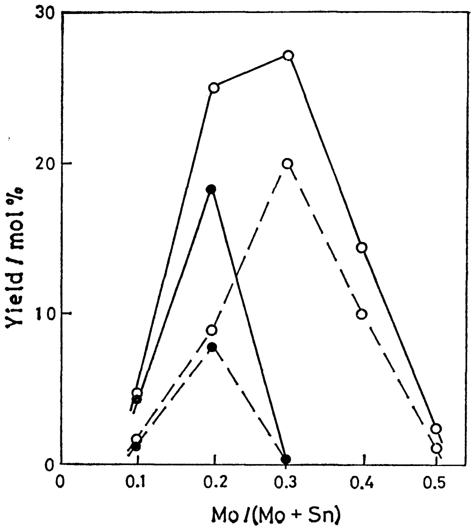

Fig. 2. Yield of acetone in the oxidation of propylene. Feed rates=propylene-20/oxygen-15/nitrogen-24/water vapor-104 ml/min (at 25 °C), catalyst used=20 g, full line=at 240 °C, broken line=at 190 °C, ○: MoO_3–Sn^{2+}, ●: MoO_3–Sn^{4+}.

As another example of an acid-catalyzed reaction, the oxyhydration of propylene to acetone was chosen.[8] The yields of acetone obtained from the MoO_3–Sn^{2+} and MoO_3–Sn^{4+} catalysts are plotted in Fig. 2. The results are well consistent with those shown in Fig. 1, suggesting the validity of these results.

Mo–Fe Oxides. The specific surface areas of the MoO_3–Fe^{2+} and MoO_3–Fe^{3+} systems are compared in Fig. 3. The surface area of the MoO_3–Fe^{3+} system is a little greater than that of the MoO_3–Fe^{2+} system, though the surface areas of both the systems pass through a broad maximum at Mo/(Mo+Fe) atomic ratio=0.2 with an increase in the Mo-content.

As an index of the acidity of the catalyst, the initial rate of 2-propanol dehydration at 200 °C is plotted as a function of the catalyst composition in Fig. 3. The acidity of the MoO_3–Fe^{2+} catalyst is much higher than that of the MoO_3–Fe^{3+} catalysts.

As another example of an acid-catalyzed reaction, the oxidation of methanol to formaldehyde was chosen.[7] The rates of formaldehyde formation at 260 °C obtained from the two series of catalysts are plotted in Fig. 4. The activity for methanol oxidation varies in the same way as that for 2-propanol dehydration, also suggesting the validity of the results.

Mo–Cr Oxides. Figure 5 shows the surface areas of the MoO_3–Cr^{3+} and MoO_3–Cr^{6+} systems. They are of the same order of magnitute, except for the Mo/(Mo+Cr^{3+})=0.9 catalyst.

The initial rate of 2-propanol dehydration at 200 °C is plotted in Fig. 6. The acidity of the MoO_3–Cr^{3+} catalysts is much higher than that of the MoO_3–Cr^{6+} catalysts, though the acidity of the two systems vary in the same way with an increase in the Mo-content. It is interesting to note that the maximum

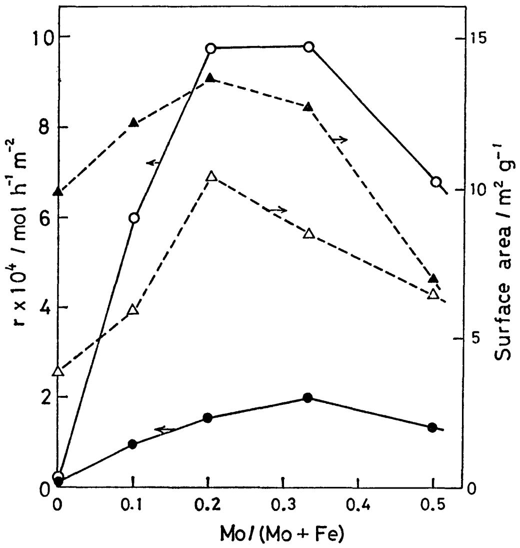

Fig. 3. Surface area and catalytic activity for dehydration of 2-propanol.
r=Rate at 200 °C and 1.7 vol% 2-propanol in air, ○,△: MoO_3–Fe^{2+}, ●,▲: MoO_3–Fe^{3+}.

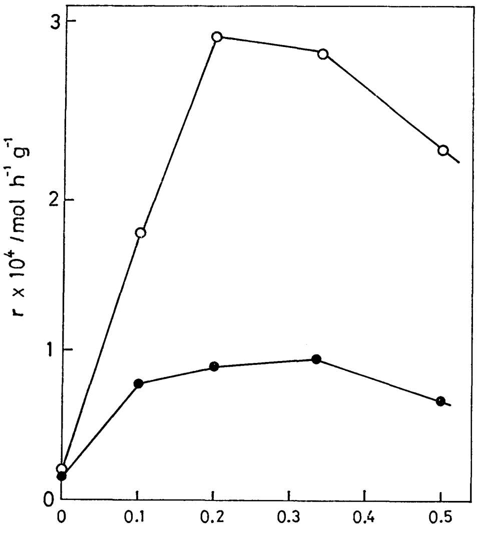

Fig. 4. Catalytic activity for oxidation of methanol to formaldehyde.
r=Rate at 260 °C and 6.3 vol% methanol in air, ○: MoO_3–Fe^{2+}, ●: MoO_3–Fe^{3+}.

Table 1. Dehydration of 2-propanol over Mo-Cu oxide catalysts[a)]

Catalyst (mole ratio) MoO_3-CuCN	Conversion %	Catalyst (mole ratio) MoO_3-CuCl	Conversion %	Catalyst (mole ratio) MoO_3-Cu^{2+}	Conversion %
100— 0	3.0	100— 0	3.0	100— 0	3.0
90—10	3.0	90—10	3.0	90—10	5.0
80—20	3.0	80—20	2.7	80—20	5.0
67—33	2.0	67—33	2.5	67—33	8.0
50—50	2.0	50—50	2.3	50—50	8.0
		33—67	1.0	33—67	2.0

a) Temperature = 200 °C, catalyst used = 10 g, 2-propanol = 1.7 vol% in air, total flow = 1.0 l/min.

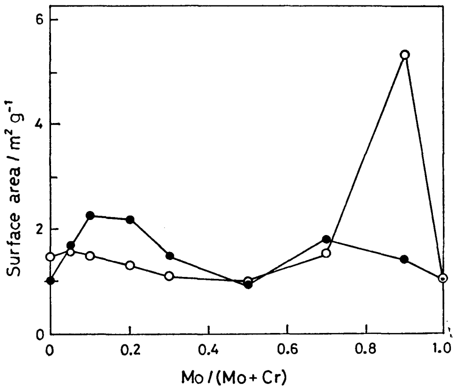

Fig. 5. Surface area of the MoO_3-Cr^{3+} and MoO_3-Cr^{6+} catalysts.
○: MoO_3-Cr^{3+}, ●: MoO_3-Cr^{6+}.

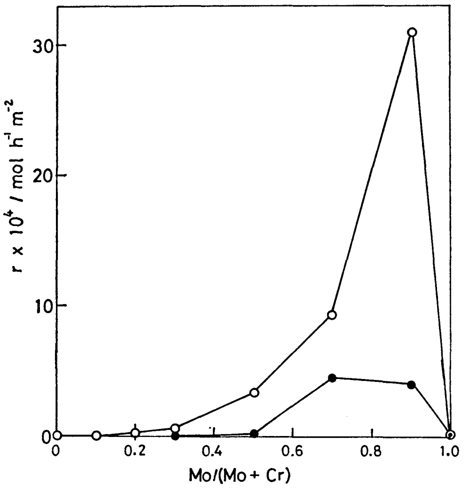

Fig. 6. Catalytic activity for dehydration of 2-propanol. r = Rate at 200 °C and 1.7 vol% 2-propanol in air.
○: MoO_3-Cr^{3+}, ●: MoO_3-Cr^{6+}.

acidity occurs in Mo-rich regions, unlike the cases of the Mo–Sn and Mo–Fe oxides.

Mo–Cu Oxides. The rate of 2-propanol dehydration was measured at 200 °C for three series of Mo–Cu catalysts, *i.e.*, the MoO_3–CuCN, MoO_3–CuCl, and MoO_3–Cu^{2+} systems. As may be seen in Table 1, the catalytic activity is very low, regardless of the kind and amount of copper compounds. It is concluded that new acidic sites are not generated by the combination of copper with molybdenum. It is, therefore, impossible to ascertain the effect of the difference in the oxidation state of copper.

Discussion

From the experimental findings, it can be deduced as a general feature of metal-oxide combination that the addition of a metal ion in a lower oxidation state to molybdenum oxide brings about a markedly more significant acidity-generation than that of a metal ion in a higher oxidation state, though the surface area is changed only a little with the difference in the oxidation state.

As a possible explanation for this feature of metal-oxide combination, we would like to consider as follows. The combination of a metal ion in a lower oxidation state, which can act as a reductant and so has a special affinity for an oxidant such as the molybdenum ion, induces a reduction of the molybdenum ion, resulting in the generation of an anion vacancy on the molybdenum ion. Possibly, a kind of valence control may take place as a result of the combination, though the situation is much more complex than in the case when oxides of nontransition metals are mixed. On the other hand, it may be hard for the anion vacancy to form with the combination of the metal ion in a higher oxidation state with molybdenum, because the additive metal ion is lacking in the reducing function.

It has already been reported that the reduction of Mo–Al oxide by hydrogen brings about a marked increase in the acidity and that this acidity generation is explained by the formation of an anion vacancy on the molybdenum ion.[9–11)]

This view is also supported by the finding that the combination of other metal ions having no reducing function, such as Al^{3+}, Si^{4+}, and Zn^{2+}, brings about a much lower acidity-generation than that of Sn^{2+}, Fe^{2+}, or Cr^{3+}.[12)]

Actually, the colors of the MoO_3–Sn^{2+} and MoO_3–Fe^{2+} catalysts are darker than the corresponding MoO_3–Sn^{4+} and MoO_3–Fe^{3+} catalysts, even after calcination in an oxygen atmosphere, suggesting the presence of the molybdenum ion in lower oxidation states. It is interesting to note that the reduced molybdenum cannot be reoxidized by the heat treatment in gaseous oxygen.

There may naturally exist other factors deciding the acidity-generation in a combination of transition-metal oxides. For example, the composition showing a maximum acidity is different depending on the second components, and the acidity-generation is not observed in the case of the combination of Cu^+ and Cu^{2+} with MoO_3. This study will be followed by a second part in which other factors deciding the acidity-generation will be studied, based on data for various kinds of mixed oxides.

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