Activity for the Oxidation of Methanol of a Molybdena Monolayer Supported on Tin Oxide

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A molybdenum oxide monolayer was prepared on SnO_2, and the relationship between its structure and its activity for methanol oxidation was studied. Surface molybdate is stabilized due to the interaction with the SnO_2 surface, thus forming a monolayer consisting of MoO_6 in <6 nm^{-2} of the Mo surface concentration and <*ca.* 75% of the coverage. So far as the supported molybdenum oxide forms a monolayer, the turnover frequency of methanol oxidation increases linearly with the Mo surface concentration; this is evidence for two neighboring Mo sites as an active site for the reaction. On further loading, however, MoO_3 forms a large isolated crystal in the macropore without formation of a multiple overlayer, and strong acid sites are created. Large crystals and acid sites thus formed are, however, not available for the reaction, since the turnover frequency is constant. Conclusions here drawn may be applicable to catalysts prepared by mixing oxides. © 1992 Academic Press, Inc.

INTRODUCTION

Methanol oxidation into formaldehyde has been industrialized by the use of an Fe_2O_3–MoO_3 mixed catalyst based upon the discovery of its high activity by Adkins and Peterson in 1931 (*1*). An active component of this catalyst is molybdenum oxide, and iron oxide and a spinel compound $Fe_2(MoO_4)_3$ are believed to enhance the activity of molybdenum oxide (*2*). However, SnO_2 also enhances the activity of MoO_3, as reported by the authors (*3*). The SnO_2–MoO_3 mixed catalyst possessed a higher activity than Fe_2O_3–MoO_3 when the activities were tested in our experimental conditions. Our previous investigation revealed that no compound consisting of tin and molybdenum oxides was detected, and partially reduced Mo^{5+} sites in the boundary were suspected as an active site. The high activity of SnO_2–MoO_3 for methanol oxidation was investigated from the viewpoints of the surface composition (*4*) and the solid acidity (*5*). Because these catalysts were prepared by mixing metal oxides, however,

it was hard to understand the active sites and their relevance to the catalytic reaction.

One of the methods to overcome this difficulty may be a study with a molybdena monolayer on tin oxide, because only molybdenum oxide directly interacting with the SnO_2 basal plane is exposed on the surface. The simple structure of the molybdena monolayer will allow us to understand the relationship between structure and catalytic activity. Ready formation of molybdena monolayers on Al_2O_3, ZrO_2, and TiO_2 has already been confirmed in previous investigations (*6–10*). The purpose of this investigation is, therefore, to prepare a molybdena monolayer on SnO_2 and additionally to identify the active sites available for methanol oxidation. Findings obtained on the supported catalysts will be compared with those of mixed oxide catalysts.

EXPERIMENTAL METHOD

Tin Oxide and Supported Catalysts

Tin oxide was prepared from a $SnCl_2$ solution. To the solution, NH_4OH was added to precipitate the hydroxide, which was then

washed until the chloride ion was removed. The hydroxide gel thus obtained was dried and calcined at 773 K for 2 h.

Supported catalysts were prepared by the impregnation method. Tin oxide was added to ammonium heptamolybdate solution, and the pH of the solution was adjusted to 10 by using NH_4OH, since it affected the equilibrium between molybdenum cations (11). After excess water was evaporated on a hot plate at ca. 383 K, the precipitate was dried at 393 K for 12 h, followed by calcination at 773 K in a stream of oxygen for 3 h, unless otherwise described.

SnO_2–MoO_3 mixed catalysts were prepared from a mixture of tin hydroxide gel and ammonium heptamolybdate solution. The catalysts used in the previous investigation (3) were utilized also in this study.

Characterization

The method and principle of benzaldehyde–ammonia titration (BAT) has been described elsewhere (12). The usual pulse technique was used, where helium carrier gas was passed through a liquid nitrogen trap to remove water and oxygen impurities and flowed into a reactor. The oxide sample was oxidized at 773 K before measurements, and benzdaldehyde was injected at 523 K until is eluted without reaction. Benzaldehyde was adsorbed as benzoate anion on the surface of SnO_2, but not on MoO_3. The selective adsorption made it possible to differentiate between surfaces exposed and covered by the metal oxide. Finally, ammonia was reacted at 773 K until benzonitrile was no longer produced. The density of benzoate adsorbed was calculated from the sum of benzonitrile formed.

The IR spectra of the supported catalysts were taken with a Jasco infrared spectrophotometer FT/IR3 with a diffuse reflectance attachment. The oxide sample was diluted by 3 wt% in KBr powder. UV–VIS reflectance spectra of the catalyst were taken with a Jasco UVIDEC-505 spectrophotometer. A MgO plate was used as a reference of the reflectance.

Temperature-programmed desorption (TPD) of ammonia was performed using an apparatus made of glass lines with vacuum pumps and a thermal conductivity detector. The catalyst was evacuated at 773 K to 10^{-4} Torr, oxidized at 773 K by oxygen, and then evacuated at 293 K. To the catalyst, an excess amount of ammonia was admitted. After saturated adsorption of ammonia, helium carrier gas was passed through the TPD cell, which was kept at 40 Torr. Temperature was increased linearly with time at a rate of 10 K min^{-1}, until ammonia was deleted completely.

Methanol Oxidation

Oxidation of methanol was carried out at 498 K by a continuous flow method. A reactant mixture of 3.4% CH_3OH/15.2% O_2/81.4% N_2 was fed into a Pyrex glass reactor by bubbling the gas through methanol chilled to 273 K. Product analysis was performed using on-line gas chromatography with thermal conductivity detectors in view of the extremely low sensitivity of the flame ionization detector to formaldehyde. Conditions for the gas chromatography are described elsewhere (10). The weight of the catalyst was chosen so that the conversion of methanol was usually less than 20%, in order to measure the activity in differential reaction conditions.

RESULTS

Spreading of Molybdenum Oxide

The method of benzaldehyde–ammonia titration was applied to catalysts in order to measure the spreading of molybdenum oxide on tin oxide. The surface area of exposed support was measured, and then the coverage, defined as percent of the surface covered by MoO_3 divided by the total BET surface area, was plotted against the surface concentration of molybdenum in Fig. 1. (The surface concentration of molybdenum is given in Table 1.) It increased with increase of the Mo surface concentration up to 6 Mo nm^{-2}, and became gradually a constant value, ca. 75%.
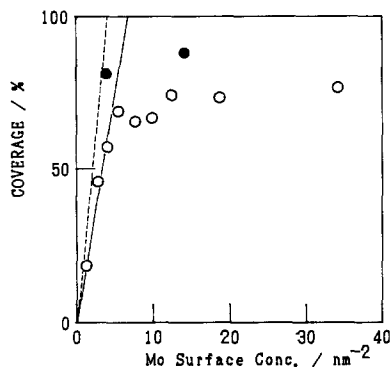
FIG. 1. Increase of coverage by molybdenum oxide with increase of the surface concentration of molybdenum on supported catalyst (O). Coverages of mixed catalysts also were plotted (●).

Dotted and solid lines show the monolayer relationship between coverage and surface concentrations, where isolated molybdenum oxide with tetrahedrally coordinated MoO_4 or molybdenum oxide monolayer with octahedrally coordinated MoO_6 spreads on supports, respectively. Calculations were made assuming 0.252 nm^2 and 0.147 nm^2 as the MoO_4 (13) and MoO_6 (14) cross-sectional areas, respectively. Because the experimentally observed coverage increased along these lines up to 6 Mo nm^{-2}, about 4 wt% loading, a MoO_3 monolayer with tetrahedral or octahedral configurations was found to be formed. On further loading of MoO_3, however, the coverage did not increase any more.

On the other hand, the total BET surface area divided by grams of SnO_2 did not decrease when the loading of molybdenum oxide was increased, indicating unblocking of the pores of SnO_2 (Fig. 2).

Spectra of Catalysts

Diffuse reflectance IR spectra of catalysts, in Fig. 3, show a continuous change of structure of MoO_3 supported on SnO_2. A small absorption at 950 cm^{-1} was found on the catalysts with more than 4 wt% of the loading. Strong absorptions at 995, 890, and 820 cm^{-1} were added to the 950 cm^{-1} band

on the catalysts with more than 10 wt% of the loading. The latter absorptions are ascribable to the freely isolated MoO_3, since these were observed also on MoO_3. The 995 and 890 cm^{-1} bands are identified as stretching vibrations of terminal Mo=O and bridged Mo–O–Mo, respectively, while the absorption at 950 cm^{-1} to the surface molybdate (9). Free MoO_3 was thereby found in the concentration where the coverage deviated largely from the monolayer relationship.

On the other hand, UV–VIS spectra of catalysts showed a subtle change of structure; only the spectra of 1 wt% MoO_3/SnO_2 showed different behavior (Fig. 4). From comparison with those reported previously (15), combination bands at 270 and 340 nm on the catalysts with more than 2 wt% of loading were identified as those of MoO_6 octahedral species. The spectrum on the 1 wt% loading seemed to be the molybdenum tetrahedral species, since the 340-nm band was missing. In other words, the molybdenum was loaded as the MoO_4 tetrahedral species only in extremely low concentration.

TPD

Temperature-programmed desorption of ammonia was studied to determine the acidic profiles, because the acid sites on SnO_2–MoO_3 were reported to be active for
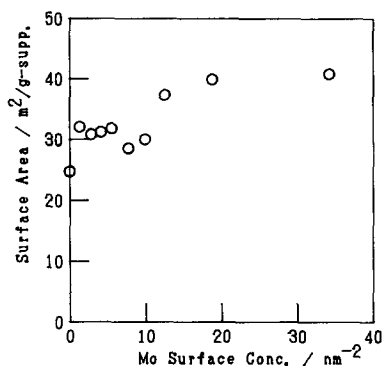

FIG. 2. Plot of surface area divided by g SnO_2 against the surface concentration of molybdenum.
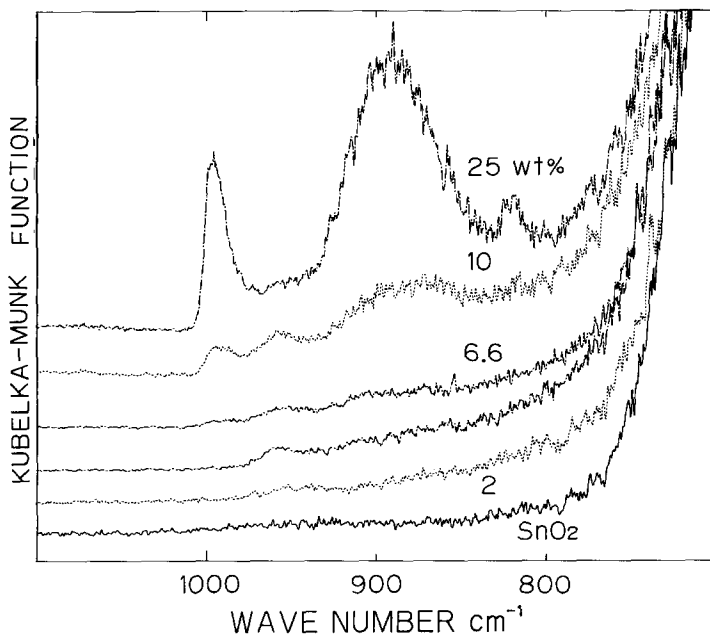
FIG. 3. IR spectra of SnO_2 and supported catalysts. Number in figure shows the MoO_3 loading in wt%. IR intensity is shown in the Kubelka–Munk function.

methanol oxidation (5). As shown in Fig. 5, TPD spectra were changed drastically by the loading of MoO_3. The spectrum on SnO_2 was characterized as composed of two desorption peaks at lower and higher temperatures, 400 and 700–800 K, respectively. The intensity of the latter high-temperature peak decreased gradually by the loading of MoO_3, and almost disappeared at 4 wt% loading. The behavior was consistent with that of molybdena monolayer spreading shown above, because the high-temperature desorption peak disappeared when the monolayer covered the surface of SnO_2 almost completely at the 4 wt% loading. On loadings of more than 5 wt% MoO_3, another high-temperature peak at ca. 600 K appeared, and the intensity increased with increase of MoO_3.

Another run of TPD experiments with a detector of mass spectroscopy revealed that nitrogen was desorbed from SnO_2 at ca. 700–800 K. The strong acidity was not found on tin oxide, but by mixing with MoO_3, as reported by Ai (16), on the basis of adsorp-

tion of pyridine and dehydration of isopropyl alcohol. The activity of isopropyl alcohol dehydration was confirmed also in the present study. The high-temperature peak appearing not only on SnO_2 but on the low loading MoO_3/SnO_2 was thereby not ascribable to acid sites, but to those of ammonia adsorbed on sites of SnO_2.

On the other hand, the desorption at about 600 K on the more than 5 wt% MoO_3/SnO_2 was assigned to ammonia adsorbed on acid sites. Because the low-temperature peak at 350 K was observed on any catalysts, it could be identified as physically or weakly adsorbed ammonia. It was thereby found that acid sites on the MoO_3/SnO_2 was created when the excess amount of MoO_3 to cover the surface of support as a monolayer was loaded.

Methanol Oxidation

Oxidation of methanol on these catalysts formed primarily formaldehyde with by-products methylformate, CO, CO_2, and dimethylether, shown in Table 1. The reaction
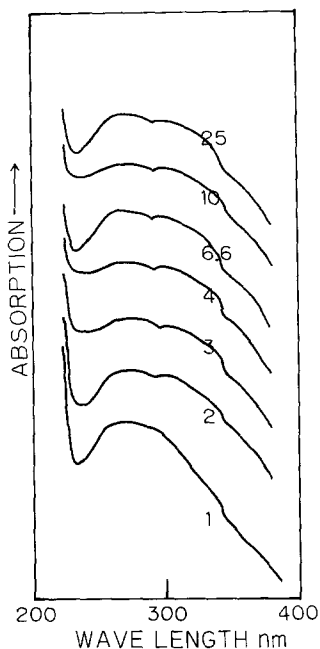
FIG. 4. UV–VIS spectra of supported catalysts. Number in figure shows the MoO_3 loading in wt%.

on SnO_2 yielded CO mainly, while the loading of MoO_3 on SnO_2 created activity for partial oxidation of methanol into formaldehyde and methylformate. Although methylformate was formed significantly on the less than 3 wt% MoO_3/SnO_2, those with more than 4 wt% loading produced formaldehyde almost exclusively.

The number of molybdenum atoms exposed on the surface was calculated by assuming that the surface area covered by an octahedrally coordinated molybdenum atom was 0.147 nm^2, as estimated from the structure of an octahedral site in MoO_3 (*14*). Because the formation of CO and CO_2 was small enough to neglect, only the rate of formation of formaldehyde and methylformate was used to calculate the turnover frequency (TOF). Because methylformate is believed to be consecutively produced via formaldehyde, and two oxidation steps are required for the formation of methylformate, the TOF of methanol oxidation is defined as

$$\frac{\text{molecules formed}}{\text{molybdenum atoms exposed}} \text{(formaldehyde} + 2 \times \text{methylformate)} \, sec^{-1}.$$

As shown in Fig. 6, the TOF of methanol oxidation increased with the surface concentration up to 6 Mo nm^{-2}, where it arrived at a constant value. In other words, the TOF increased with the Mo concentration, so far as molybdenum oxide was loaded as a monolayer. A strong relationship between the loading of molybdenum and the catalytic activity was thereby obtained. The maximum TOF obtained on the fully covered
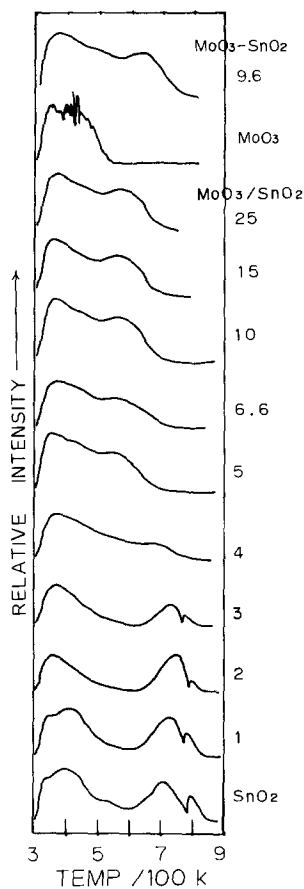

FIG. 5. Temperature-programmed desorption of ammonia on SnO_2, supported catalysts, MoO_3, and mixed catalysts. Number in figure shows the MoO_3 loading or content in wt%. The intensity of desorption is normalized by surface area of oxide; the peak area is proportional to the number of desorbed molecules per m^2.

TABLE 1

Catalytic Activity for Methanol Oxidation

Catalyst	Mo conc. (nm^{-2})	FA	DME	MF	DMM	CO_2	CO
		nmol/m^2					
SnO$_2$		0	0	0	0	0	3
MoO$_3$/SnO$_2$							
MoO$_3$ wt%							
1	1.3	3	0	13	0	1	10
2	2.8	76	0	66	0	6	50
3	4.1	318	0	90	0	0	0
4	5.5	609	4	56	0	0	0
5	7.7	739	23	29	0	0	0
6.6	9.9	601	11	36	0	1	0
10	12.5	735	27	51	0	0	0
15	18.8	769	14	49	0	10	0
25	34.2	719	29	50	0	0	0
SnO$_2$-MoO$_3$ mixed							
MoO$_3$, wt%							
9.6	3.9	237	14	39	10	0	69
19.3	14.2	258	26	15	57	0	0

Note. FA, formaldehyde; DME, dimethylether; MF, methylformate; DMM, dimethoxymethane.

MoO$_3$/SnO$_2$ (*ca.* 6 nm^{-2} of the Mo concentration) was larger than those previously obtained on molybdena on ZrO$_2$ (0.05 s^{-1}), TiO$_2$ (0.02 s^{-1}), and Al$_2$O$_3$ (0.005 s^{-1}) (*10*). The TOF on unsupported MoO$_3$ (0.002 sec^{-1}) was much smaller than those of MoO$_3$/SnO$_2$ catalysts. Even when the molybdenum oxide was loaded to over 25 wt%, the TOF did not decrease to the value on unsupported MoO$_3$. In other words, the activity of the surface molybdate was kept during the loading of large amount of MoO$_3$.

On the other hand, the TOF of the formation of methylformate is also calculated in Fig. 6. The TOF of methylformate possessed a maximum at a low concentration of Mo, *ca.* 4 nm^{-2}.

On Mixed Oxide Catalysts

Experiments as mentioned above were done with SnO$_2$–MoO$_3$ prepared by mixing of oxides in order to compare with the supported catalysts. Two kinds of mixed oxide catalyst, SnO$_2$–MoO$_3$ (MoO$_3$ conc., 9.6 wt% and 19.3 wt%), were used. The molybdenum surface concentrations were 3.9 and 14.2 nm^{-2}, respectively, all the Mo atoms being assumed to be exposed on the surface. The coverage by molybdenum oxide could be included in or could exceed the monolayer relationship, as shown in
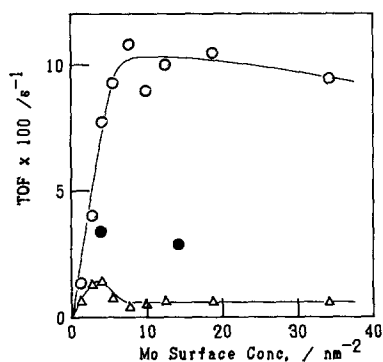

FIG. 6. Dependence of TOF for oxidation of methanol into formaldehyde and methylformate (○) and for oxidation into methylformate (△) upon the surface concentration of molybdenum. Oxidation of methanol into formaldehyde and methylformate on mixed oxide catalysts is also plotted (●).

Fig. 1. The TPD spectrum on the SnO_2–MoO_3 (9.6 wt%) clearly revealed desorption from acid sites at 650 K. The turnover frequency in Fig. 6 followed the relation found in the supported catalyst on the SnO_2–MoO_3 (9.6 wt%), but deviated largely on the SnO_2–MoO_3 (19.3 wt%). Reaction selectivity was analogous to those of supported catalysts except for the formation of dimethoxymethane (Table 1).

DISCUSSION

Structure of Surface Molybdate on Tin Oxide

As shown in measurements of spreading of molybdenum oxide and IR and UV–VIS spectra of catalysts, molybdenum oxide is stabilized as a monolayer in less than 4 wt% of the loading and less than 6 nm^{-2} of the surface concentration. Because the coverage increases linearly with the Mo concentration, the molybdate with a common structure spreads up to 6 Mo nm^{-2}. Because the relationship between coverage and molybdenum concentration increases along the lines estimated from the monolayer, it is certain that the molybdate forms a monolayer on the surface of tin oxide. Although it is difficult for BAT measurements to distinguish between tetrahedral and octahedral configurations of the molybdate, UV–VIS spectra showed the existence of MoO_6 species except at extremely low concentrations of molybdenum. Although the structure of the surface monolayer is unknown exactly, it seems to be a kind of polymeric species consisting of multiple atoms.

Formation of freely isolated MoO_3 was observed on further loading; however, the molybdena monolayer was kept exposed on the surface, because the 950 cm^{-1} band of the IR spectrum was still observed, and the turnover frequency for methanol oxidation did not decrease. In other words, molybdenum oxide did not accumulate on the molybdena monolayer, and the excess MoO_3 was isolated in fairly large pores of the tin oxide. Differences in structure and/or chemical properties between the molybdena mono-layer and MoO_3 may result in differences in behavior.

These characteristics for the molybdenum oxide, either spread or isolated on the surface of SnO_2, are analogous to those on Al_2O_3, ZrO_2, and TiO_2 which were previously reported (10). The obtained structure of MoO_3 may be affected by chemical properties of tin oxide, since these metal oxides possess different crystal morphologies. The tin oxide may stabilize the molybdenum oxide due to the strong interaction in the interface layer. The combination of SnO_2 and MoO_3 with different chemical properties may form the surface molybdate even in the mixed oxide catalyst.

Another striking finding in this study is the creation of strong acid sites at high loadings of MoO_3. The strong acidity of SnO_2–MoO_3 by which dehydration of alcohol or hydration of olefin is catalyzed has been envisaged (5, 9, 17, 18), but the origin of the acid sites is not known. Since no binary compound was observed in this system, and the strong acid site was found neither on SnO_2 nor on MoO_3, it has been suspected only that the acid site is generated in the boundary between tin and molybdenum oxides. However, the strong acid sites are not found on the molybdena monolayer, but under conditions of excess loading of MoO_3. One can suspect therefore that the acid sites are located near the isolated species of MoO_3. This is supported by the high intensity of the strong acid sites on mixed oxide catalysts where the low dispersion of MoO_3 is suspected.

Active Sites for Methanol Oxidation

Turnover frequency for the methanol oxidation increased with increased molybdenum concentration, so far as the molybdate was stabilized as a monolayer. Further loading of molybdenum did not enhance its activity, thus indicating that the surface molybdate at high concentration was an active surface layer for the oxidation. Difference in Mo configuration, MoO_4 or MoO_6, is a possible reason for the variation of TOF,

since it depends upon the concentration of molybdenum (6). However, this could be disregarded, because the configuration of the molybdenum atom was unaltered except at extremely low concentrations, as found from UV–VIS spectra. The linear relationship of TOF with number of molybdenum atoms, i.e.,

$$\text{rate/[Mo]} = k\,\text{[Mo]},$$

can be transformed into

$$\text{rate} = k\,\text{[Mo]}^2,$$

where k and [Mo] denote rate constant and number of surface molybdenum atoms exposed. In other words, the rate of oxidation is proportional to the square of the number of molybdenum atoms and thus a second-order reaction with respect to molybdenum atoms. It is thereby suggested that two molybdenum atoms play the role of active site simultaneously. Activity for methanol oxidation may be generated when two adjacent molybdenum atoms are loaded on the surface of tin oxide.

This conclusion is supported by previous investigations on the activity of MoO_3 for methanol oxidation. Tatibouet and Volta et al. first reported the structure-sensitivity of methanol oxidation on MoO_3 and proposed an active site consisting of two molybdenum atoms (19). Usually, it is believed that methanol is readily adsorbed on MoO_3 as a methoxy group, followed by abstraction of hydrogen as the rate-determining step (20–22). Two molybdenum sites are required for catalyzing the reaction, because one molybdenum site is required for the adsorption of methanol, and another for dehydrogenation. The proposal of twin active sites is thereby rationalized by the most plausible mechanism. Current investigations by Bennett and co-workers (23) and Busca (24) also are based on the mechanism, and furthermore they discussed the oxidation of methanol into methylformate. According to the mechanism by Busca (24), the formation of meth-

ylformate requires another site for the esterification, probably on TiO_2 support. The TOF of methylformate in the present study revealed a maximum at low concentrations of molybdenum, where the surface of tin oxide remained sufficiently exposed; therefore, the present study supported the mechanism of methylformate formation on the surface of support. As for the supported catalysts, Iwasawa and Tanaka (25) found dimolybdenum compound immobilized on SiO_2 to have higher activity than that of monomeric species; this study with the inorganic complex immobilized catalyst also revealed the high activity of adjacent molybdenum cations.

Ai reported a significant influence of the acidity of mixed SnO_2–MoO_3 on the catalytic activity of methanol oxidation (5). Ono et al. also reported the acidic properties of ZrO_2–MoO_3 using IR spectroscopy, and correlated it with the catalytic activity for the oxidation of alcohol and olefin (9). Strong acid sites, however, appeared at high concentrations of MoO_3 where the TOF for methanol oxidation was constant. The acidity profile was not correlated with those of catalyst activity at all. The dependence of the catalytic activity upon the acidity can thus be disregarded.

The monolayer with 100% coverage is an ideal structure to investigate the activity of loaded oxide. We could have insight into structural dependence and interface interaction based upon the simple structure. Present investigation dealt with the molybdenum oxide monolayer of ca. 75% of the coverage, and revealed the intimate relationship between structure and activity. Mixed oxide of SnO_2 and MoO_3, on the other hand, was analogous to the supported catalyst from the viewpoint of not only the surface condition but also the turnover frequency. The surface conditions on the mixed oxide catalyst, at high concentrations of molybdenum oxide, were different from those of the monolayer, but still somewhat resembled them. Based upon

these considerations, the conclusions from the supported catalyst may be applicable to the mixed oxides.

Molybdena forms monolayers not only on SnO_2 but also on Al_2O_3 and TiO_2 (6–10), and thus a similar structure can be anticipated. However, values of TOF are different, and all of them are much larger than on unsupported MoO_3. Either a subtle change of structure of surface molybdate or different effects induced by basal oxides may result in differences in the enhanced activity. Geometric factors such as distances of adjacent Mo–Mo atoms (25, 26) or degree of reduction of molybdenum cations (3, 20, 23, 27) are to be investigated.

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