ELSEVIER

Catalysis Today 52 (1999) 71–81

CATALYSIS TODAY

Role of the solid acidity on the MoO_3 loaded on SnO_2 in the methanol oxidation into formaldehyde

Miki Niwa*, Jyun-ya Igarashi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori 680-8552, Japan

Abstract

The selective oxidation activity of the molybdena thin layer loaded on SnO_2 which was calcined at 773–1173 K was studied. MoO_3 spread readily on SnO_2, and covered the surface of support with ca. 80% coverage at most independent of the calcination temperature of tin oxide. On the other hand, the turn-over frequency depended on the calcination temperature, i.e., the high TOF was kept on the catalyst with the SnO_2 calcined below 973 K, but it decreased with the SnO_2 calcined above 1073 K. Characterization of the catalysts revealed relations between the catalytic activity and the property, i.e., reducibility and solid acidity. In particular, the strong dependence upon the solid acidity was observed. The acid sites were generated on the molybdenum oxide loaded on tin oxide calcined below 973 K, and possibly identified as the Brønsted acid sites. Methanol was adsorbed more weakly on the acid sites than on exposed surface of SnO_2, and converted into formaldehyde selectively.

Keywords: Solid acidity; MoO_3 loaded; Methanol oxidation

1. Introduction

Oxidative dehydrogenation of methanol into formaldehyde is an important industrial reaction over the Fe_2O_3–MoO_3 catalyst. On the other hand, this reaction has been used as a test reaction to prove the activity of the MoO_3 and V_2O_5 loaded catalysts for oxidation reaction. In particular, there are many investigations on the activity and selectivity of molybdenum oxide loaded catalysts, and the reaction mechanism and the structure of active sites were proposed [1–6].

We have been studying the support effect on the loaded MoO_3 in the oxidation of methanol. In our previous papers [7–9], the activity of MoO_3 loaded on various oxides was measured, and a sequence of the activity was concluded, i.e., on SnO_2>on Fe_2O_3>on ZrO_2>on TiO_2>on Al_2O_3>unsupported MoO_3. The sequence was determined based on the turn-over frequency which was measured from the number of exposed molybdenum oxide site and the rate of oxidation. The sequence of the activity was nearly the same for all the studies, not only on MoO_3 [10–13] but also on V_2O_5 [14,15]. Wachs et al. [10–12] explain the sequence due to the reducibility of support oxide, because they considered the high activity being caused by the oxygen atom located between metal oxide and support such as M–O–M′. Their conclusion, however, is not sufficiently supported by the experimental findings. One may indicate that the interesting finding for the activity enhancement by the support remains unsolved.

---

*Corresponding author. Tel.: +81-857-31-5256; fax: +81-857-31-5256; e-mail: mikiniwa@chem.tottori-u.ac.jp

0920-5861/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(99)00064-4

When various kinds of metal oxide were used as a support, there will be many variable physico-chemical parameters, e.g., reducibility, bond strength of metal and oxygen, acid–base property, size of metal cation, electro-negativity, etc. Such a complexity will make the problem so difficult to be solved. Based on the consideration, only one kind of metal oxide, i.e., tin oxide will be utilized as a support in this study. The calcination temperature of tin oxide will be varied because of a key parameter in the preparation, and thus induced change in the activity and property will be studied in order to finally obtain the relationship between them.

2. Experimental

2.1. Preparation of SnO_2 and the supported catalyst

Tin oxide was prepared from a solution of $SnCl_2·2H_2O$ which was dissolved into the HCl solution. To the solution, NH_4OH was added to precipitate the hydroxide, which was then washed to remove the chlorine ion until the pH of the solution was adjusted to 7.0. The hydroxide gel thus obtained was dried and calcined in air at temperatures from 773 to 1123 K for 2 h.

Supported catalyst was prepared by an impregnation method. Tin oxide was added to the solution of $(NH_4)_6Mo_7O_{24}·4H_2O$, followed by adjusting the pH to 10 by NH_4OH. Water was evaporated on a hot plate, and then dried at 383 K. It was calcined in a stream of oxygen at 773 K for 3 h.

2.2. Benzaldehyde–ammonia titration (BAT), OH measurements, and IR

Benzaldehyde–ammonia titration method to know the spreading of loaded oxide was performed in a method described previously [16]. Usual pulse method was used with a 6 mm o.d. pyrex glass tube and FID gas chromatography using a silicon column. Helium carrier gas was purified by a liquid nitrogen trap prior to the reactor. Usually, 0.1 g of the sample was used and heated at 673 K for 1 h in a flow of oxygen. After cooling down to 523 K, the carrier gas was switched to He, and benzaldehyde was injected repeatedly until the saturation at 523 K. Subsequent reaction of ammonia with the adsorbed benzoate species formed benzonitrile, from which the amount of benzoate anion was determined.

Concentration of surface hydroxide on the calcined SnO_2 was measured by the reaction of a Grignard reagent, $MgCH_3I$ with surface OH to form methane at room temperature [17]. Tin oxide was evacuated at 673 K, and $MgCH_3I$ in a dimethylether solution was allowed to be reacted; the amount of evolved methane was measured volumetrically.

Infrared spectra were taken with Jasco FT/IR-5300 spectrophotometer using the compressed disk consisting of KBr and 5 wt% solid sample.

2.3. Oxidation of methanol

The catalytic reaction was performed by a continuous flow method. Methanol was fed from the saturator chilled by ice, and the composition of gas mixture was 3.4% CH_3OH, 15.2% O_2 and 81.4% N_2. The reaction temperature was 498 K, and the weight of catalyst was chosen to adjust the conversion of methanol to less than 20%. Products were analyzed by gas chromatography with a thermal conductivity cell and separation columns of Porapak Q and Molecular sieves 13 X. The catalytic activity was measured at 1 h after the reaction.

2.4. TPR, and TPD of ammonia and methanol

Temperature programmed reduction (TPR) profile was obtained using Ar–H_2 mixture (H_2, 6 vol%) as a carrier gas. Prior to the measurements, the sample was oxidized by a flow of oxygen at 773 K, and after cooling down to the room temperature, the temperature was elevated linearly up to 773 K in a rate of 10 K min^{-1}. Concentration of H_2 was monitored by a mass spectroscopy.

Temperature programmed desorption (TPD) of ammonia was measured using all-glass apparatus with two vacuum pumps; the detail of experimental apparatus was described previously [18]. About 0.1 g of the sample was evacuated at 773 K for 1 h, and the bed temperature was cooled down to the room temperature. Ammonia was then allowed to be adsorbed, and the gaseous ammonia was evacuated; after the evacuation, the bed temperature was elevated with the ramp rate of 10 K min^{-1}. Desorbed ammonia was detected by mass spectroscopy at 16 of m/e.

The water vapor treatment was performed twice in the step intermediate between adsorption of ammonia and elevation of temperature; the water vapor was adsorbed at room temperature, and replaced with removable ammonia.

TPD of methanol was measured using the same apparatus with the TPR experiment. Sample was first oxidized in a flow of oxygen at 773 K, and methanol was injected to be adsorbed at 373 K through an inlet before the sample bed. Injections were repeated to make the surface of oxide saturated with adsorbed methanol. Then, the temperature was elevated with the ramp rate of 10 K min^{-1}. Mass spectroscopy was used to detect the desorbed molecules, and 30, 31 and 44 of m/e were used for formaldehyde, methanol and CO_2. Intensity of the mass spectroscopy was calibrated with a certain amount of these molecules.

3. Results

3.1. Spreading of molybdenum oxide on tin oxide

Tin oxide was calcined at temperatures from 773 to 1173 K, and the surface area of the calcined sample was measured. It decreased gradually with the increasing calcination temperature, as shown in Table 1. Saturated concentration of benzoate anion adsorbed on the tin oxide was then measured by BAT method. It was ca. 1.8 nm^{-2} on the samples calcined below 973 K, and ca. 2.5 nm^{-2} above 1073 K, as shown in Table 1. The concentration of ca. 1.8 nm^{-2} was in agreement with the value previously reported [19].

Molybdenum oxide was loaded on these tin oxides, and not only the surface area but also the concentration of adsorbed benzoate anion on the loaded catalyst was measured. The degree of surface coverage by molybdenum oxide was then calculated, because the benzoate anion was adsorbed on the exposed surface of tin oxide only with the high concentration as mentioned above. The extent of coverage by loaded molybdenum oxide is defined as

$$\text{Coverage }(\%) = \left(1 - \frac{\beta_{\text{loadedcatalyst}}}{\beta_{\text{unloadedoxide}}}\right) \times 100,$$

where β is the concentration of adsorbed benzoate anion in nm^{-2}.

Fig. 1 shows the change of the coverage by molybdenum oxide with the concentration of Mo atoms on the surface. It increased with an increase in the surface concentration, and almost saturated at ca. 4 nm^{-2}. In the figure, two lines showing the monolayer relationship were drawn as comparisons. The monolayer relations were estimated from the surface area owned by a molybdenum oxide species with the octahedral (0.147 nm^2) or tetrahedral (0.252 nm^2) configuration. It was roughly shown that the coverage increased along with the expected monolayer relationship up to about 80% at less than 6 nm^{-2} of the concentration. The behavior of monolayer covering was not changed largely by varying the calcination temperature of tin oxide. This means that the molybdenum oxide spread all over the tin oxides readily. Above 6 Mo nm^{-2} of the surface concentration, the coverage did not increase, and arrived at the saturation. The relation between the coverage by Mo and the concentration is in agreement with the previous finding on metal oxide supports such as ZrO_2, TiO_2, Al_2O_3 [7], and Fe_2O_3 [9].

The IR spectra of the loaded catalyst showed an absorption of the surface molybdenum oxide at 960 cm^{-1} at more than 2.4 Mo nm^{-2} (not shown). However, this band which would be ascribable to

Table 1
Characterization data of tin oxide

Calcination temperature (K)	BET surface area ($m^2\,g^{-1}$)	Benzoate anion concentration (nm^{-2})	Hydroxide concentration (nm^{-2})	Adsorbed ammonia concentration (nm^{-2})
773	25.8	1.84	11	1.02
873	20.2	1.77	10	1.10
973	14.7	1.91	9.6	1.04
1073	9.5	2.76	6.6	1.20
1173	7.6	2.35	6.0	0.79

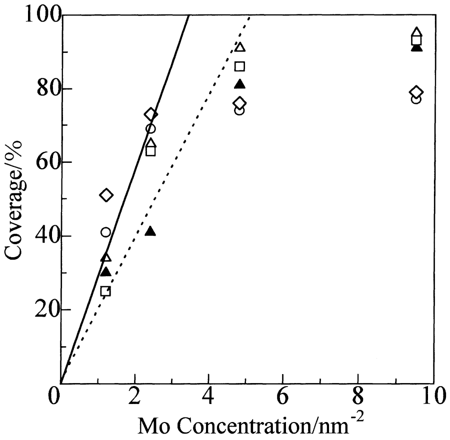

Fig. 1. Coverage by molybdenum oxide against the concentration of molybdenum oxide loaded on SnO_2 which were calcined at different temperatures: 773 (○), 873 (△), 973 (▲), 1073 (□) and 1173 (◇) K. Solid and dotted lines show the relationship expected from the formation of molybdenum oxide monolayer with octahedral and tetrahedral configurations, respectively.

surface molybdate species was not observed on the MoO_3 loaded on the SnO_2 calcined at 1173 K. At 9.5 Mo nm^{-2} loaded on SnO_2 calcined at 973 and 1073 K, another band appeared at 991 cm^{-1}, which was ascribable to free MoO_3. The highly spreading of molybdenum oxide at the low concentration was thus supported by the IR observation.

Concentration of surface OH on SnO_2 was then measured to examine the change in surface conditions by the calcination. As shown in Table 1, the concentration of surface OH was 11–10 nm^{-2} on the tin oxide calcined below 973 K. This value was nearly in agreement with that previously reported by Harrison and Guest [20] from the gravimetric measurements. The concentration decreased by the calcination above 1073 K to 7–6 nm^{-2}. It seems that there is a complementary relation between concentrations of benzoate anion and hydroxide, as shown in Table 1. Because the benzoate anion is stabilized on a coordination unsaturated site (CUS site; M–O$^-$) formed by the dehydroxylation, the complementary relation would be easily understood.

XRD of the SnO_2 showed the rutile structure. The intensity increased with an increase in the calcination temperature. The XRD proved only the sintering of metal oxide, but did not show any change in the structure.

3.2. *Activity for methanol oxidation*

Catalytic activity of the MoO_3 loaded on SnO_2 for the methanol oxidation was measured. The conversion of methanol was adjusted to less than 20% in order to determine the activity in the differential conditions. The selectivity to form formaldehyde was so high that other products could be neglected. The rate of formaldehyde formation was measured, and the turn-over frequency (TOF) was determined from the rate of formation and the number of molybdenum atom exposed on the surface which was determined from the surface area occupied by the molybdenum oxide.

Fig. 2 shows the plot of the TOF thus determined against the surface concentration of loaded Mo atom. As shown in the figure, the values of TOF were roughly divided into two groups, i.e., the high TOF on tin oxide calcined below 973 K and the low TOF on tin oxide calcined above 1073 K. In other words, the catalytic activity on an active site was kept high by the calcination of tin oxide up to 973 K, but it decreased significantly above 1073 K.

The TOF was very small at the low Mo concentration, and then increased almost linearly with the concentration of Mo. The behavior is again in agreement with that previously reported.

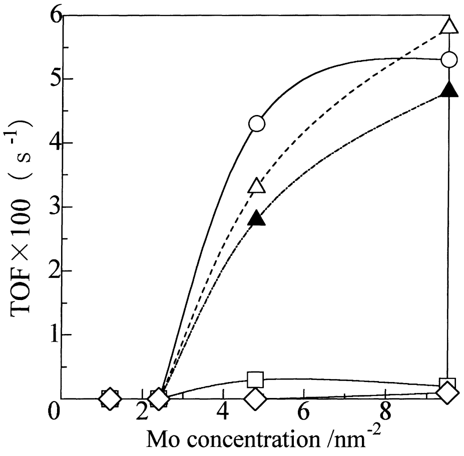

Fig. 2. Turn-over frequency for the methanol oxidation into formaldehyde on the MoO_3 loaded on SnO_2 calcined at 773 (○), 873 (△), 973 (▲), 1073 (□) and 1173 (◇) K.

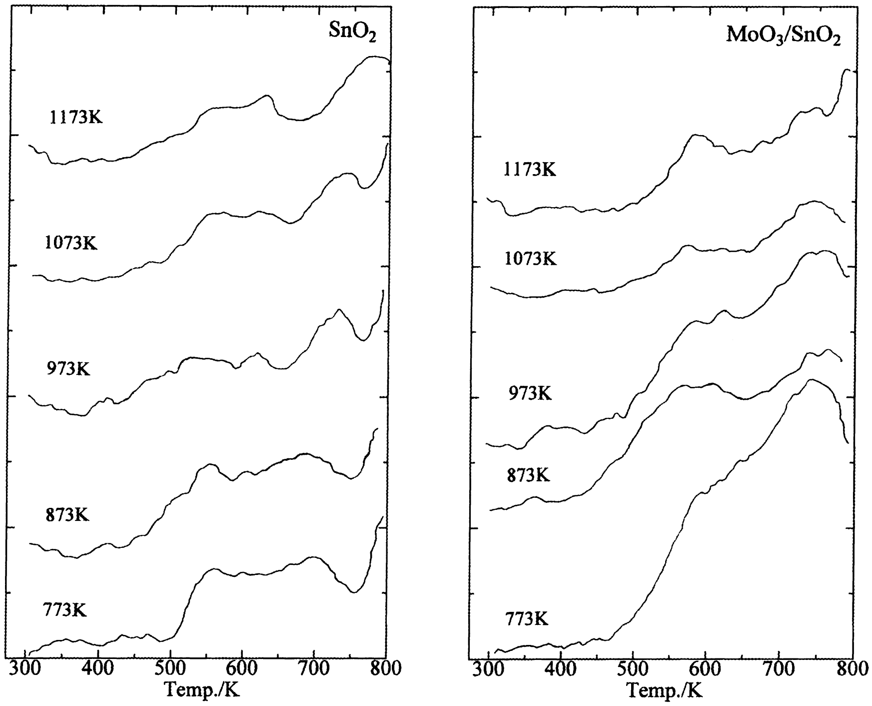

Fig. 3. TPR using H_2 on SnO_2 and on MoO_3 (9.5 Mo nm^{-2})/SnO_2 calcined at different temperatures.

3.3. TPR using H_2

In order to understand the change of activity by the calcination of support, the catalysts were characterized using temperature programmed reduction and desorption techniques.

First, the reducibility of the catalyst was studied by a TPR technique with H_2 as a reductant. The experiments were performed on, not only the loaded catalysts but also on support tin oxide, as shown in Fig. 3. Reduction of tin oxide occurred at about 473 K, and continued up to 773 K. Two broad peaks of hydrogen consumption were observed at 550 and 700 K. The total amount of consumed hydrogen was plotted against the calcination temperature, as shown in Fig. 4.

By varying the calcination temperature, the reduction behavior of SnO_2 changed small, and the total amount of H_2 required for the reduction until 773 K was kept almost a constant. On the other hand, the amount of consumed H_2 increased by the loading of MoO_3 on the SnO_2 calcined at 773–973 K. On the catalysts containing SnO_2 calcined at 1073 and 1173 K, however, it was decreased or unchanged. The change of consumed amount of hydrogen by the loading of MoO_3 is thus similar to that observed for the variation in catalytic activity. The amount of H_2 molecule divided by loaded Mo atom was 2.5–4.3 on

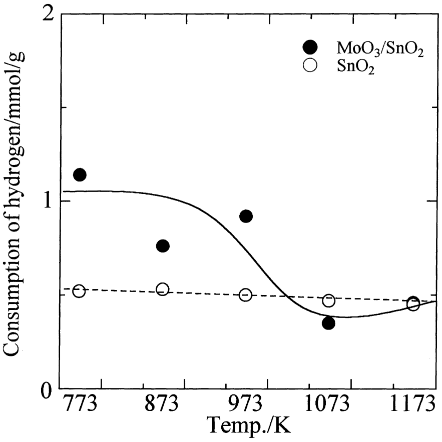

Fig. 4. Amount of H_2 required for the reduction of SnO_2 and MoO_3 (9.5 Mo nm^{-2})/SnO_2 until 773 K.

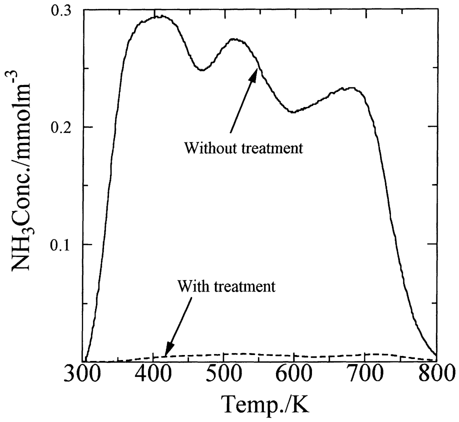

Fig. 5. TPD of ammonia on SnO_2 with and without the water vapor treatment.

the catalysts with the SnO_2 calcined at 773–973 K, and larger than 1 which was expected from the reduction to MoO_2.

3.4. TPD of ammonia

Acidic property of the catalyst was then measured by the TPD of ammonia. As shown in Fig. 5, the TPD profile on SnO_2 showed three desorption peaks of ammonia at ca. 400, 520 and 680 K, and ammonia was desorbed completely at 800 K. The temperature of ammonia desorption was so high that the desorption peak could be identified as ammonia strongly adsorbed on acid sites on SnO_2. The concentration of adsorbed ammonia was ca. 1 nm^{-2}, and did not largely change by the calcination up to 1173 K, as shown in Table 1. However, the water vapor treatment, which was made at room temperature after the ammonia adsorption, deleted the ammonia peak almost completely. In this case, water was found to be desorbed in place of ammonia. It was thereby clear that water was adsorbed to be replaced with adsorbed ammonia which would be desorbed during the TPD experiment without the water vapor treatment.

On the other hand, the TPD on MoO_3 loaded on 773 K calcined SnO_2 with 8 Mo nm^{-2} of the concentration showed a broad desorption peak with the peak maximum at 390 K, as shown in Fig. 6. The treatment by water vapor had only a small effect on the TPD profile; the intensity did not change, and the peak temperature was shifted to high by ca. 30 K only. Consequently, ammonia adsorbed on the loaded MoO_3 was not replaced by water. Thus, the water vapor treatment resulted in the contrastive behaviors on SnO_2 and MoO_3/SnO_2.

In Fig. 7 are summarized the desorption profiles on the MoO_3 loaded on 773 K calcined SnO_2, which was obtained after the water vapor treatment. Intensity of the desorption peak increased with increasing the amount of loading, and became outstanding at more than 8 Mo nm^{-2}. Fig. 8 shows the TPD on the MoO_3 (8 nm^{-2}) loaded on SnO_2 calcined at different temperatures. The peak maximum temperature shifted small to the high temperature with increasing the calcination temperature. The amount of desorbed

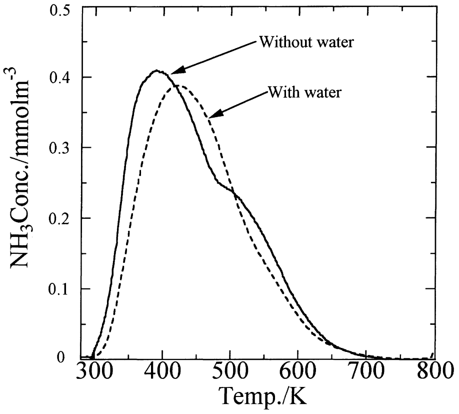

Fig. 6. TPD of ammonia on MoO_3 (8 Mo nm^{-2} of the concentration)/SnO_2 (calcined at 773 K) with and without the water vapor treatment.

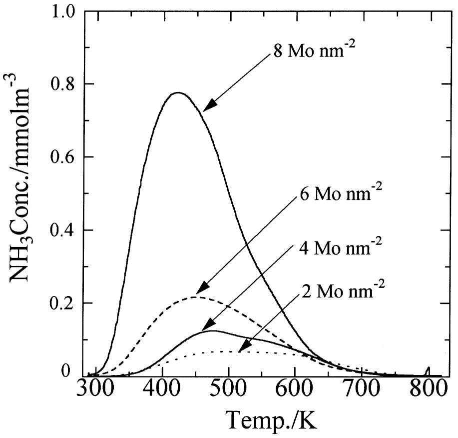

Fig. 7. TPD of ammonia on MoO_3 loaded on 773 K calcined SnO_2 with different concentrations of Mo.

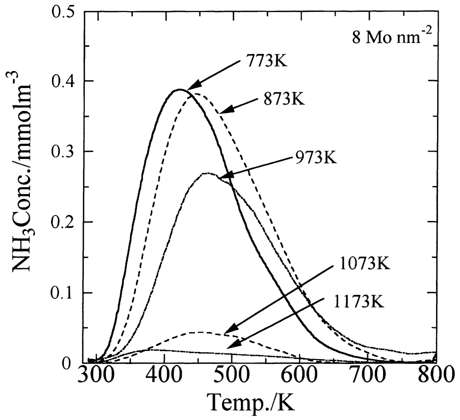

Fig. 8. TPD of ammonia on MoO_3 loaded on SnO_2 calcined at different temperatures with the concentration of 8 Mo nm^{-2}.

ammonia decreased greatly upon calcination at temperatures above 1073 K.

Amount of ammonia desorbed was summarized in Table 2, where its ratio divided by the loaded Mo was shown. It was revealed that 17–20% of molybdenum loaded on the SnO_2 which was calcined at 773–973 K with the concentration of 8 Mo nm^{-2} showed the solid acidity. In other words, about one fifth of the Mo atom showed the solid acidity, but it decreased either by the calcination at such high temperatures as 1073 and 1173 K or by the loading of less than 6 Mo nm^{-2} of the concentration. Solid acidity was therefore created, when molybdenum oxide was loaded on the SnO_2 calcined below 973 K at the concentration of the full coverage monolayer or a little excess.

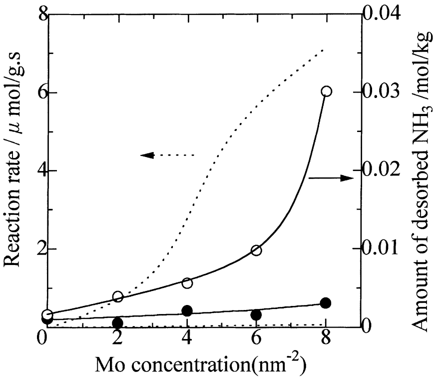

Fig. 9. Comparison between rate of methanol oxidation into formaldehyde (dotted line) and the desorbed ammonia (○, ●) as obtained by varying the concentration of molybdenum loaded on SnO_2 calcined at 773 (○) and 1173 (●) K.

Figs. 9 and 10 show the comparison between the catalytic activity and amount of desorbed ammonia. Good agreements were observed between them in not only the comparison for the loaded molybdenum concentration but also for the calcination temperature of SnO_2. However, there was a deviation in Fig. 9 at such a high concentration as 8 Mo nm^{-2}, because the amount of ammonia desorbed increased steeply with the concentration of Mo, while the reaction rate did not.

3.5. *TPD of methanol*

Adsorption of methanol was studied on SnO_2 and MoO_3 loaded catalyst using the TPD of methanol, as

Table 2
Ratio of desorbed ammonia against the loaded Mo

Calcination temperature of SnO_2 (K)	Concentration of Mo (nm^{-2})	NH_3/Mo
Upon loading of 8 Mo nm^{-2} on SnO_2 calcined at different temperatures		
773		0.17
873		0.20
973		0.19
1073		0.09
1173		0.05
Upon loading on SnO_2 calcined at 773 K		
	2	0.07
	4	0.05
	6	0.06
	8	0.17

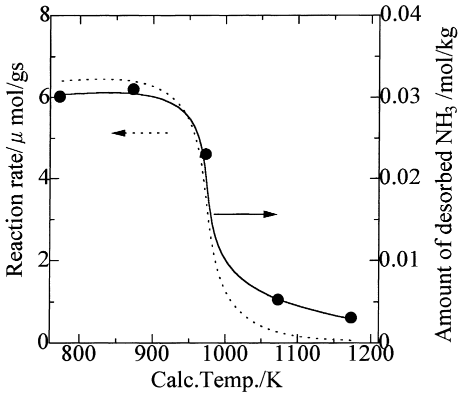

Fig. 10. Comparison between rate of methanol oxidation into formaldehyde (dotted line) and desorbed ammonia (●) as obtained by varying the calcination temperature of SnO_2.

shown in Fig. 11. In this experiment, the catalyst with 8 Mo nm^{-2} of the concentration was selected in order to know the adsorption behavior on the surface which was almost covered with the loaded molybdenum oxide.

Desorption profile was summarized in Fig. 11, and the amount of desorbed molecule in a unit of surface concentration was shown in Table 3. On the MoO_3 loaded on 773 K calcined SnO_2, methanol and formaldehyde were desorbed at 420 K, and CO_2 at 560 K. The desorption temperature for formaldehyde was close to the temperature at which formaldehyde was formed in the catalytic reaction. On the other hand, very small amount of formaldehyde was detected on the 773 K calcined SnO_2, and methanol and CO_2 were desorbed at 490 and 550 K, respectively. On the SnO_2

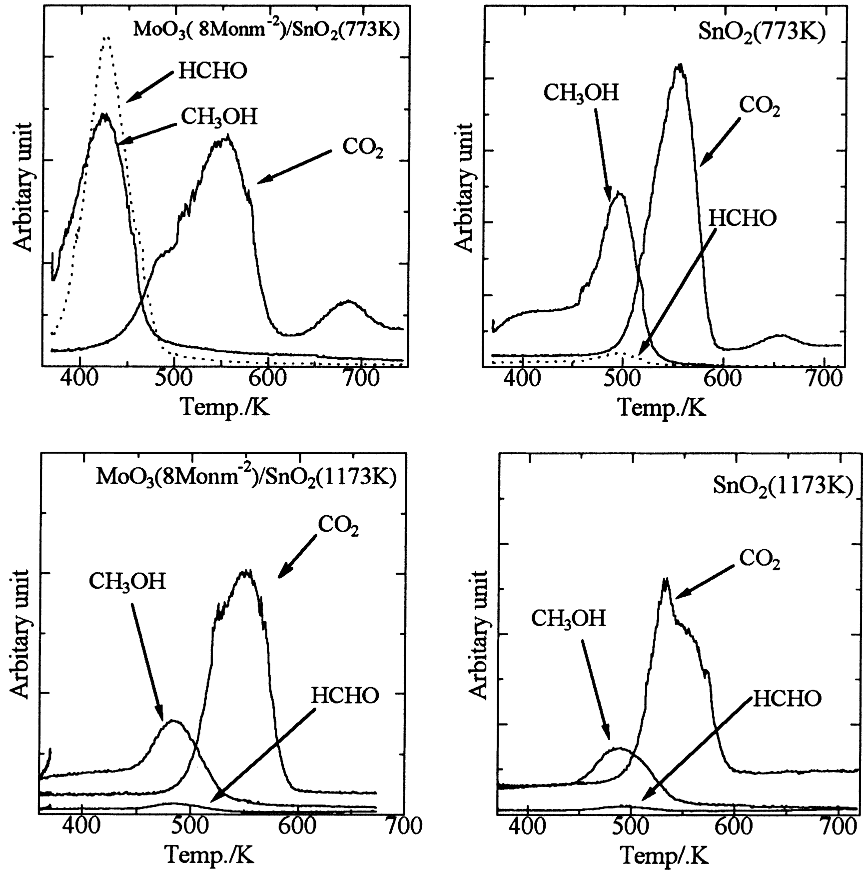

Fig. 11. TPD of methanol: (a) on MoO_3 loaded on SnO_2 calcined at 773 K; (b) on SnO_2 calcined at 773 K; (c) on MoO_3 loaded on SnO_2 calcined at 1173 K; (d) on SnO_2 calcined at 1173 K.

Table 3
Surface concentration of adsorbed molecule measured by TPD of methanol (nm^{-2})

Sample	CH_3OH	HCHO	CO_2
SnO_2 (773 K calc.)	0.18	0.06	3.83
MoO_3 (8 Mo nm^{-2})/SnO_2 (773 K calc.)	0.21	0.27	2.55
SnO_2 (1173 K calc.)	0.15	0.019	11.9
MoO_3 (8 Mo nm^{-2})/SnO_2 (1173 K calc.)	0.10	0.002	8.36

calcined at 1173 K with and without MoO_3, few of HCHO was desorbed, and methanol and CO_2 were desorbed at 490 and 540 K, respectively. It was thus found that only the MoO_3 on 773 K calcined SnO_2 which had the selective activity showed a different behavior about the desorption of CH_3OH and HCHO. It was noteworthy that methanol was adsorbed on any catalysts studied, but it was desorbed from the selective catalyst at lower temperature than from others. In other words, a different scheme of methanol adsorption was suggested only on the selective catalyst, and the close relation with solid acidity was able to be indicated.

4. Discussion

Molybdenum oxide readily spread on the tin oxide which was calcined at the temperatures from 773 to 1173 K. The readily spreading of MoO_3 on these metal oxides is expected to be due to the different properties of MoO_3 and tin oxide support. As observed previously [21], the basic property of support and the acidic property of loaded metal oxide form a strong interaction, and enable the loaded Mo highly spread on tin oxide. On the other hand, the turn-over frequency for the methanol oxidation into formaldehyde depended upon the calcination temperature of tin oxide. Different reactivity of the loaded molybdenum oxide is due to the different property of support which was prepared at different temperatures. In the present investigation, our focus is thus directed to understanding the catalyst property from viewpoints of reducibility and solid acidity. Discussion will be made at first on these properties, and then on the reactivity of the loaded catalyst which is related to the reaction mechanism.

4.1. *Reducibility*

The agreement of the experimental finding in reducibility and reactivity indicates that the reducibility measured from TPR with hydrogen may affect the activity in methanol oxidation. Temperature for the reduction did not change largely by loading of molybdenum oxide, but the amount of hydrogen required for the reduction of metal oxide was enhanced by the loading of molybdenum oxide on tin oxide calcined at lower temperatures. The amount of H_2 molecule divided by loaded Mo atom on the catalysts with the SnO_2 calcined at 773–973 K was larger than 1.0 which was expected from the reduction of MoO_3 into MoO_2. The temperature for reduction and the stoichiometry which correspond to qualitative and quantitative profiles of reduction, respectively, indicate that tin oxide support also is reduced in the TPR experiments. It is therefore suggested that the oxygen atom on the surface and in the bulk of tin oxide can participate in the oxidation. However, the oxygen was used for the reduction of H_2 at the temperatures quite different from the reaction temperature of methanol oxidation. Thereby, the TPR does not assure the participate of reducible oxygen in the reaction completely.

4.2. *Solid acidity of oxide*

TPD of ammonia on this catalyst system has previously been reported by us [8]. However, the TPD spectrum was measured with a thermal conductivity detector, and identification of the peak was impossible. On the other hand, in this investigation, mass spectroscopy was used to identify the desorption peak. In addition, an improved method of water vapor treatment has been undertaken in the present investigation. With this method, not only the number of acid site is precisely determined, but also the quality of acid site can be estimated. As indicated previously by Bagnasco [22], the water vapor treatment is a method to improve the selectivity of ammonia adsorption. He indicated that Brønsted and Lewis type acid sites might have different adsorption abilities to water and ammonia, and their strengths to the probe seemed to be ordered in a different way, i.e., water>ammonia for the Lewis type acid site, and ammonia>water for the Brønsted type acid site. Another explanation is however possible based on a concept of the ligand field stabilization energy [23]. Water is not stabilized as aquo ligand on the Sn^{4+} cation with d^0 configuration so that it undergoes the hydration to form the hydroxide. Adsorbed ammonia is thus replaced with subsequently admitted water molecule. It is therefore concluded that the site on the SnO_2 adsorbs water to make the hydroxide easily. The adsorption site for ammonia could be ascribed to the exposed site of Sn^{4+} cation as a Lewis type acid. Although the adsorbed ammonia species on SnO_2 could not be identified by infrared spectroscopy due to the low transmittance, the species adsorbed on ZrO_2 has been identified as NH_3 on the Lewis acid site [24]. No infrared absorption ascribable to NH_2 was observed on ZrO_2. Both SnO_2 and ZrO_2 having the similar property, the desorbed ammonia molecules from SnO_2 are to be identified as those on the Lewis acid site of SnO_2, and the strong acidity of tin oxide is estimated.

On the other hand, it may be possible to identify the adsorption site on the MoO_3 loaded catalyst as the Brønsted acid site, because the water vapor treatment did not affect the desorption profile largely, unlikely on SnO_2. The high probability for the loaded molybdenum to show the acidity, i.e., ca. 1/5 is of interest. There are now two kinds of explanation for the generation of acid site on the surface of loaded molybdenum oxide. This would be explained by the idea that the $Mo^{6+}{=}O$ could be reduced into $Mo^{5+}{-}OH$. We have already studied Mo^{5+} cation by electron spin resonance, and found the relationship between number of Mo^{5+} cation and catalytic activity on the SnO_2–MoO_3 mixed catalyst [25]. Thereby, the previous observation adds support to the estimation of generation of acid site by the reduction. Another idea to explain the mechanism of acid site generation is the formation of a clustered molybdenum anion species on the surface of support. Some protons would be formed on the anion to compensate for the excess electron. The latter mechanism of clustered species would explain the probability to create the acid site on the loaded MoO_3, 1/4–1/5, if 5–7 molybdenum atoms containing species forms the mono- or di-valent anion.

The generation of acid sites is strongly related with the calcination temperature of tin oxide, as mentioned above. Obviously, the physico-chemical property of tin oxide surface affects the formation of acid sites on the loaded molybdenum oxide. Among various measured properties, the concentration of surface hydroxide of tin oxide may be related with the formation of solid acidity, because its concentration is high up to 973 K of the calcination temperature of tin oxide. From the correlation, it could be possibly explained that the surface hydroxide of tin oxide has a role of creating the acid site of the loaded molybdenum oxide. However, more detailed study is required to prove not only the generation of acid sites but also the role of support.

4.3. *Mechanism of methanol oxidation on the loaded molybdenum oxide*

The turn-over frequency of methanol oxidation depended strongly on the concentration of the loaded Mo. It was very low in the low Mo concentration, and increased almost linearly with the loaded Mo at more than ca. 2 Mo nm^{-2}. The linear increase of TOF seems to suggest the structure of active site, because this means the two neighboring Mo atoms working as the active site, i.e., one for adsorption of methoxide and another for oxidative abstraction of hydrogen from the adsorbed methoxide. This mechanism of methanol oxidation is in agreement with that previously proposed by many researchers [1,3,4,6]. However, the solid acidity was created by the loading, and the generation of acidity also depended on the concentration of Mo, as mentioned above. Because the generated acidity may induce the adsorption of selective species of methanol, the concentration of loaded Mo affects the rate of methanol oxidation doubly, i.e., the formation of dual active site of Mo and the formation of acid sites. A complex dependence of the TOF on the concentration of Mo could thus be explained.

In order to catalyze the partial oxidation of methanol, therefore, two kinds of property, i.e., adsorption of methanol and oxidation activity, has to be optimized.

In this investigation, the acidity and reducibility were characterized, and these were correlated with the activity. The solid acidity was however found to be correlated more closely to the activity for oxidation of methanol than the reducibility.

Adsorption and desorption of methanol on these oxides provide us information to estimate the reaction mechanism. On SnO_2, and MoO_3 loaded on SnO_2 calcined at higher temperature, methanol was adsorbed strongly, and only CO_2 was formed. On the other hand, methanol was adsorbed weakly on the MoO_3 loaded on SnO_2 calcined at lower temperature, and yielded formaldehyde. Most probably, the Brønsted acid sites are generated by the loading of MoO_3 on SnO_2 calcined below 973 K. Methanol may be adsorbed on the acid site to form methoxide, and then the methoxide species finally yields formaldehyde. On the other hand, methanol seems to be strongly adsorbed on SnO_2 as another type species.

Ai [26] studied the influence of the acidity upon the oxidation activity in various cases of reaction and catalyst. He used the dehydration of isopropyl alcohol to characterize the acidity of catalyst, and found a lot of relations. However, he did not indicate exactly how the solid acidity affected the reaction. On the other hand, it was found in the present study that the acid site of catalyst affected the adsorption of methanol to form formaldehyde selectively, i.e., the acid site does not enhance the adsorption of methanol, but it has a role of adsorption site for the species to form formaldehyde selectively.

References

[1] J.M. Tatibouet, J.E. Germain, J.C. Volta, J. Catal. 82 (1983) 240.
[2] Y.C. Liu, G.L. Griffin, S.S. Chan, I.E. Wachs, J. Catal. 904 (1985) 108.
[3] Y. Iwasawa, K. Asakura, H. Ishii, H. Kuroda, Zeit. Phys. Chem. (NF) 144 (1985) 1005.
[4] E.M. McCarron, A.W. Sleight, Polyhedron 5 (1986) 129.
[5] T.-J. Yang, J.H. Lunsford, J. Catal. 103 (1987) 55.
[6] J.S. Chung, R. Miranda, C.O. Bennett, J. Catal. 114 (1988) 398.
[7] Y. Matsuoka, M. Niwa, Y. Murakami, J. Phys. Chem. 94 (1990) 1477.
[8] M. Niwa, H. Yamada, M. Sano, Y. Murakami, J. Catal. 134 (1992) 331.
[9] H. Yamada, M. Niwa, Y. Murakami, Appl. Catal. 96 (1993) 113.
[10] D.S. Kim, I.E. Wachs, K. Segawa, J. Catal. 146 (1994) 268.
[11] H. Hu, I.E. Wachs, J. Phys. Chem. 99 (1995) 10911.
[12] I.E. Wachs, G. Deo, J.-M. Jehng, D.S. Kim, H. Hu, in: B.K. Warren, S.T. Oyama (Eds.), Heterogeneous Hydrocarbon Oxidation, ACS Symposium Series, vol. 638, American Chemical Society, Washington, DC, 1996, p. 292.
[13] W. Zhang, A. Desikan, S.T. Oyama, J. Phys. Chem. 99 (1995) 14468.
[14] G. Deo, I.E. Wachs, J. Catal. 129 (1991) 307.
[15] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323.
[16] M. Niwa, S. Inagaki, Y. Murakami, J. Phys. Chem. 89 (1985) 2550.
[17] J.J. Fripiat, J. Uytterhoeven, J. Phys. Chem. 66 (1962) 800.
[18] N. Katada, H. Igi, J.H. Kim, M. Niwa, J. Phys. Chem. B 101 (1997) 5969.
[19] M. Niwa, K. Suzuki, M. Kishida, Y. Murakami, Appl. Catal. 67 (1991) 297.
[20] P.G. Harrison, A. Guest, J. Chem. Soc., Faraday Trans. I 83 (1987) 3383.
[21] M. Niwa, Y. Matsuoka, Y. Murakami, J. Phys. Chem. 91 (1987) 4519.
[22] G. Bagnasco, J. Catal. 159 (1996) 249.
[23] F.A. Cotton, G. Wilkison, Advanced Inorganic Chemistry, Wiley, New York, 1980.
[24] N. Naito, N. Katada, M. Niwa, Abstracts of the Third Tokyo Conference on Advanced Catalytic Science and Technology, Catalysis Society of Japan, Tokyo, 1998, p. 330.
[25] M. Niwa, M. Mizutani, M. Takahashi, Y. Murakami, J. Catal. 70 (1981) 14.
[26] M. Ai, J. Catal. 40 (1975) 327.