Adsorbed species of methanol on zirconia support and molybdenum oxide monolayer. Its role in the methanol oxidation

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Methanol was strongly adsorbed on ZrO_2 support as dioxymethylene and carbonate species, both of which were adsorbed on the basic sites as the intermediate for complete oxidation. On the molybdenum oxide monolayer, it was adsorbed as methoxide species to form formaldehyde. Upon elevating the temperature, however, the methoxide species turned into formate ion, from which CO was finally desorbed. Adsorption of methoxide species readily takes place only on the loaded molybdenum oxide monolayer, and the acid sites seem to accommodate the species.

KEY WORDS: methanol; adsorbed intermediate; ZrO_2; MoO_3 monolayer; IR; TPD

1. Introduction

Methanol oxidation into formaldehyde occurs selectively on MoO_3 loaded on such weak basic supports as SnO_2, Fe_2O_3 and ZrO_2, among which SnO_2 has the most prominent effect [1]. The effect by the support on the activity is an interesting chemical aspect to understand the role of support on the metal oxide. A lot of investigations on the prominent effect by the support have been reported in the literature [2–4]. In our previous study [5], it was concluded that acidity was a key parameter to control the activity for methanol oxidation. Molybdenum oxide was readily spread on the surface of tin oxide in less than 6 $\mathrm{Mo\,nm^{-2}}$, and about one fifth of the exposed molybdenum atoms showed the solid acidity on the monolayer. The generated acid sites, possibly Brønsted acid sites, played an important role in the selective oxidation of methanol into formaldehyde. From the temperature-programmed desorption experiment of methanol, the role of acid sites for the oxidation of methanol was estimated. Methanol was adsorbed strongly on the tin oxide support, while it was weakly adsorbed on the molybdenum oxide monolayer on tin oxide, and formaldehyde was formed only from the latter adsorbed species. This means that the acid sites do not enhance the methanol adsorption; rather, these accommodate the adsorbed species to form formaldehyde selectively. Further discussion on the reaction mechanism was impossible on the tin-oxide-based catalyst, because an infrared study to observe the reaction intermediate was not available due to the low transmittance. In this investigation, therefore, ZrO_2 is used as support in place of SnO_2, and IR observation of the reaction intermediate will be carried out. The purpose of the present investigation is thereby to identify the reaction intermediate for not only selective but also non-selective oxidation of methanol both on support and loaded molybdenum oxide, and on the basis of the observation the mechanism of methanol oxidation will be discussed.

2. Experimental

2.1. Catalyst preparation

Zirconium oxide was prepared from a solution of $ZrO(NO_3)_2$, to which NH_4OH was added to precipitate the hydroxide, until the pH of the solution was adjusted to 10.0. The hydroxide gel thus obtained was dried and calcined in air at 773 K for 4 h. Supported catalyst was prepared by an impregnation method. ZrO_2 was added to the solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, followed by adjusting the pH to 10 with NH_4OH. Water was evaporated on a hot plate, then the catalyst was dried at 383 K, and it was calcined in a stream of oxygen at 773 K for 3 h.

2.2. TPD of ammonia and methanol

Temperature-programmed desorption (TPD) of ammonia was measured using an all-glass apparatus with two vacuum pumps; the experimental apparatus was described in detail previously [6]. About 0.1 g of the sample was evacuated at 773 K for 1 h, and the bed temperature was cooled down to 373 K. Ammonia was then adsorbed, and evacuated; water vapor was contacted with the catalyst bed. The water vapor treatment was performed twice; in this step, water was adsorbed to replace with removable ammonia. The bed temperature was elevated with a ramp rate of 10 $\mathrm{K\,min^{-1}}$, and desorbed ammonia was detected by mass spectroscopy at m/e 16.

TPD of methanol was measured using the same apparatus as for the TPD of ammonia. The sample was first oxidized

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in a flow of oxygen at 773 K, and methanol was injected through an inlet before the sample bed to be adsorbed at 373 K. Injections were repeated to saturate the surface of the oxide with adsorbed methanol. Then, the temperature was elevated with a ramp rate of 10 K min^{-1}. Mass spectroscopy was used to detect the desorbed molecules, and m/e of 28, 30, 31 and 44 were used for CO, formaldehyde, methanol and CO_2, respectively.

2.3. Infrared study

Infrared spectra were taken with a Jasco FT/IR-5300 spectrophotometer using a compressed self-supporting disk in the quartz *in situ* cell. Before measurements, the sample was evacuated at 773 K for 2 h. Methanol was then adsorbed at 373 K, and infrared spectra were taken at room temperature after evacuation at 373–773 K.

3. Results and discussion

The BET surface area of the MoO_3 (9.6 wt%)/ZrO_2 was 48 $m^2\,g^{-1}$, and the surface concentration was 7 Mo nm^{-2}. Spreading of molybdenum oxide was measured by the BAT method [1,2], and the extent of coverage by MoO_3 was 96%. The calculated surface concentration of Mo at the 100% coverage monolayer is 4 or 7 Mo nm^{-2}, when tetrahedral or octahedral configuration of molybdenum oxide species, respectively, is assumed. It was therefore identified that the surface of the support of this catalyst was covered by the molybdenum oxide monolayer almost completely.

Solid acidity was measured by TPD of ammonia using water vapor treatment, as shown in figure 1. Although ammonia desorption was detected from ZrO_2 by a usual method of TPD, it was negligibly small by an improved TPD measurement accompanied with water vapor treatment. The water vapor treatment, however, did not affect the TPD on the molybdenum oxide monolayer catalyst, and ammonia molecules desorbed from the loaded molybdenum oxide only could be measured, as shown in figure 2. TPD of ammonia on the MoO_3/ZrO_2, measured at m/e of 16, showed two desorption peaks, at ca. 500 and 1000 K. However, the higher temperature desorption peak was not ascribable to desorbed ammonia, because the intensity at m/e 17 was not detected at the higher temperature region. The number of acid sites was thus measured from the lower temperature peak. It was 0.048 mol kg^{-1}, and the ratio of desorbed NH_3 divided by loaded Mo atoms was 0.16. The ratio of acid site against the loaded Mo was similar to those of MoO_3 on SnO_2 [5] and of WO_3 on ZrO_2 [7]. The common degree of acid site generation on the MoO_3 and WO_3 monolayers may be indicative of acid sites with a similar structure. This catalyst will be used in the following experiments of infrared and desorption profiles of adsorbed methanol.

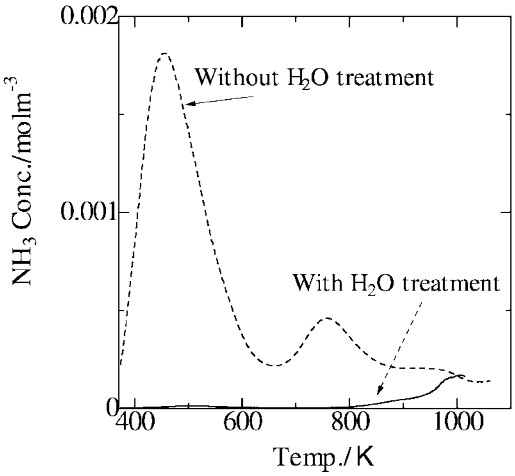


Figure 1. TPD of ammonia on ZrO_2 without (- - -) and with (—) the water vapor treatment.

Adsorption of methanol was studied on ZrO_2 support (BET surface area, 61 $m^2\,g^{-1}$). Figure 3 shows the TPD of methanol on ZrO_2. Methanol was adsorbed on the support,

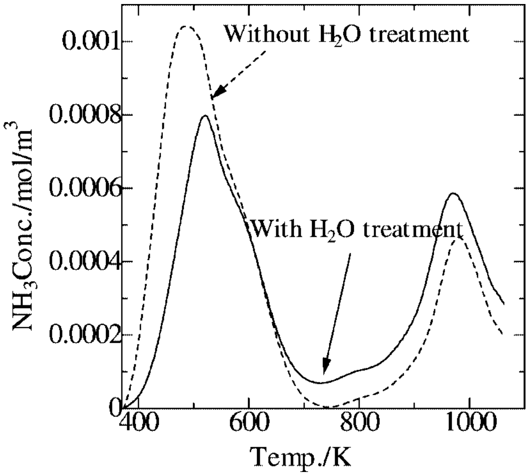


Figure 2. TPD of ammonia on MoO_3/ZrO_2 without (- - -) and with (—) the water vapor treatment.

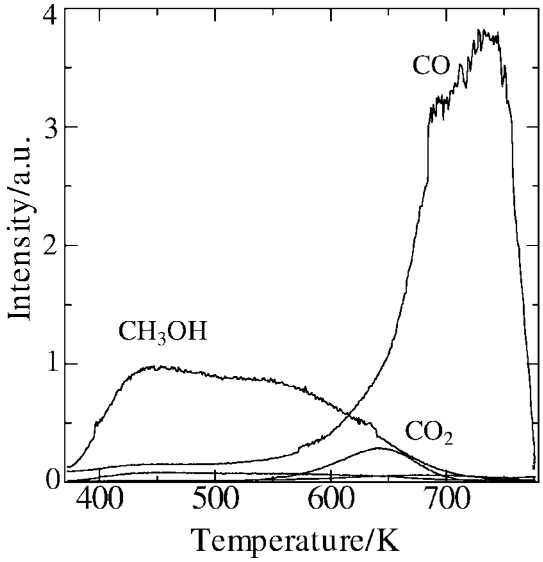


Figure 3. TPD of methanol on ZrO_2.

and it was gradually desorbed from 373 to 673 K. Above 573 K, CO was desorbed with a high intensity. Formaldehyde was not detected during the desorption experiment from ZrO_2.

Infrared spectra obtained by the same procedure of methanol adsorption and evacuation are shown in figure 4. Adsorption of methanol revealed six absorption bands, at 2924, 2815, 1564, 1444, 1158 and 1057 cm^{-1}. Evacuation of the catalyst with increasing the temperature up to 773 K showed the gradual alteration of IR bands, and from the observation, these were classified into two kinds of IR bands, i.e., 2924, 2815, 1158 and 1057 cm^{-1} bands and 1564 and 1444 cm^{-1} bands. The bands of 2924 and 2815 cm^{-1} seemed to be ascribable to asymmetric and symmetric stretching vibrations of the C–H bond in methylene, respectively. Because the band of 2815 cm^{-1} shifted to 2824 cm^{-1} on evacuation at 573 K, the species was adsorbed in different conditions depending on the concentration. The wave number of 2815–2824 cm^{-1} was, however, too low to be identified as symmetric vibration of methylene, which suggested that the species was adsorbed with a strong interaction with the surface. The unusual low wave number of the C–H bond was observed in methyl attached to such a metal as lithium [8] or in methylene next to nitrogen [9]. The bands of 1154 and 1057 cm^{-1} were identified as ν_{CO}, because these were observed in the IR spectrum of $H_2C(OCD_3)_2$ [10]. Busca et al. observed similar IR bands by the adsorption of formaldehyde on ZrO_2 [11], and assigned it to dioxymethylene species. Their observed IR bands from formaldehyde on ZrO_2 were similar to those from methanol in the present investigation, but there were some differences between them. In particular, the complex bands at 1180–965 cm^{-1} appeared in the adsorbed formaldehyde, while two simple bands at 1154 and 1057 cm^{-1} were observed in the adsorbed methanol. As pointed out by Busca et al. [11], the existence of the complex band showed the different conformer of adsorbed formaldehyde. The infrared spectrum of adsorbed methanol, on the other hand, showed its simple monomeric character unlike the adsorbed formaldehyde. Ouyang et al. also observed similar IR bands of 1153 and 1075 cm^{-1} by the adsorption of methanol on SnO_2 and identified it as dioxymethylene species [12].

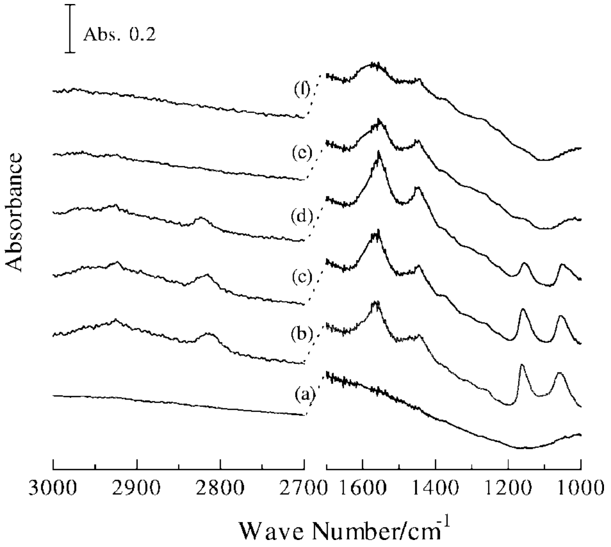


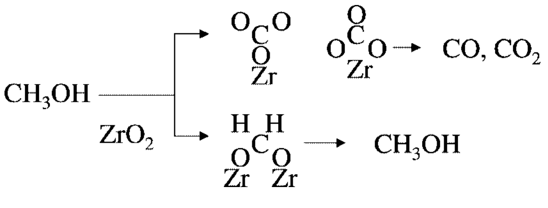
Figure 4. Infrared spectra of ZrO_2 evacuated at 773 K (a), followed by adsorption of methanol at 373 K and evacuation at 373 (b), 473 (c), 573 (d), 673 (e) and 773 K (f).

Because these IR bands were removed at 473–573 K, and the behavior was similar to that of methanol desorption in figure 3, the dioxymethylene species is the intermediate to form desorbed methanol. As indicated by Busca et al. [11] the formation of methanol from dioxymethylene species seems to be due to a Cannizzaro type reaction. Formaldehyde is thus to be accompanied with methanol, if the Cannizzaro reaction takes place. However, formaldehyde was not detected during the TPD of methanol; and, it may readily turn into another adsorbed species shown below.

The bands at 1564 and 1444 cm^{-1} were neither identified as formate nor as methoxide species, because the formate ion usually shows one more strong absorption at 1350–1380 cm^{-1}, and the methoxide must accompany with the bands at 2900–2800 and at 1150 cm^{-1}. On the other hand, infrared spectra of ZrO_2 calcined at 573 K showed two absorption bands at 1557 and 1447 cm^{-1} inherently, and these were stabilized up to 673 K (not shown). A temperature-programmed evacuation experiment on the 573 K calcined ZrO_2, which was done without the adsorption of methanol, showed desorption of CO and CO_2, at the same temperature region. Based on these experimental findings, the 1564 and 1444 cm^{-1} bands were ascribed to adsorbed carbonate ions. The bands at 1564 and 1444 cm^{-1} were identified as bidentate and unidentate adsorbed carbonate ions, respectively [13]. Because these bands were stabilized up to 673 K, removed gradually at 773 K, and the behavior was similar to CO desorbed in figure 3, CO was formed from the carbonate ion. Thus, one can summarize the adsorption of methanol and subsequent reaction, shown in scheme 1.

Methanol is readily oxidized into oxygenated products on ZrO_2, dioxymethylene and carbonate species, and these are stabilized on the basic sites of zirconia as strong adsorbed species. Dioxymethylene species may be converted into CO and CO_2 during the catalytic reaction in the presence of oxygen, though it was desorbed as methanol during the TPD of methanol. In other words, these species are intermediates for non-selective oxidation of methanol.

Adsorption and desorption of methanol were then studied on the MoO_3 monolayer on ZrO_2. As shown in figure 5, the TPD profile was different from that on ZrO_2; methanol and formaldehyde were desorbed at 420 and 450 K, respectively, and CO was desorbed at 650 K with a small amount



Scheme 1.

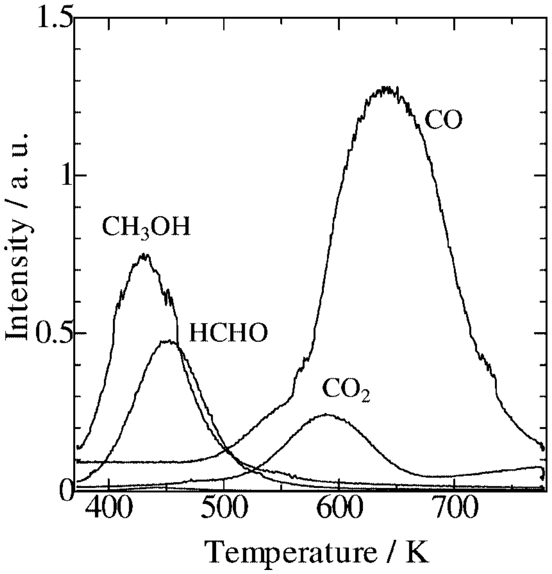


Figure 5. TPD of methanol on MoO_3/ZrO_2.

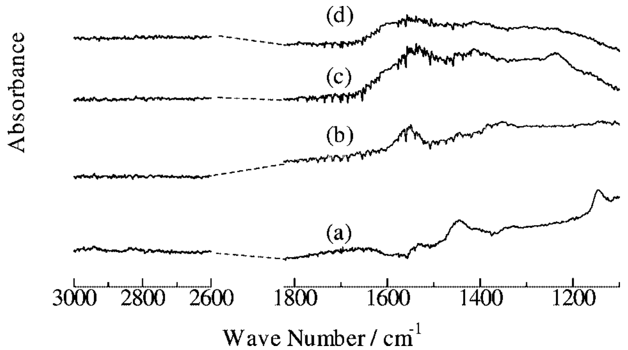
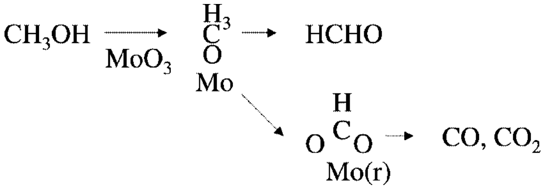


Figure 6. Infrared spectra of MoO_3/ZrO_2 evacuated at 773 K, followed by adsorption of methanol at 373 K and evacuation at 373 (a), 473 (b), 573 (c) and 673 K (d).

of CO_2. IR observation of methanol adsorbed at 373 K, in figure 6, showed bands at 1446 and 1146 cm^{-1}, accompanied with weak C–H stretching vibrations at 2943 and 2837 cm^{-1}; from these IR absorptions, the species was identified as adsorbed methoxide species. Evacuation of the catalyst with increasing the temperature decreased the intensity of methoxide bands, and gave rise to the absorptions at 1551 and 1349 cm^{-1} at 473 K. These bands shifted to 1543 and 1414 cm^{-1}, respectively, at 573 K, and lost the intensity gradually at 673 K.

The methoxide species is, most probably, the adsorbed intermediate to form formaldehyde, because it was removed by the evacuation at 473 K, and formaldehyde was desorbed at this temperature region. Methanol detected in the TPD experiment up to 473 K also may be formed from the same species. The absorptions at 1551 and 1349 cm^{-1} could be identified as the formate anion, and it was found from the IR observation that the formate ion was converted from the adsorbed methoxide species. The formate anion was not detected upon adsorption of methanol at 373 K, on the initial oxidized surface of molybdenum oxide. It is therefore speculated that the formate species on the molybdenum oxide monolayer is formed only on the reduced conditions of molybdenum oxide. Basic property is enhanced upon the reduction, and the reduced sites are favorable for the adsorption of carboxylate anion. The formate anion species may not be formed at the actual conditions of methanol oxidation. At the reaction conditions, methoxide species only may be formed on the oxidized molybdenum oxide monolayer; thus, the monolayer has the high selectivity for the formaldehyde formation.



Scheme 2.

The shifted bands at 1543 and 1414 cm^{-1} also were ascribable to formate anion or carbonates. Due to the broadness of the bands, it was difficult to assign the species clearly, and it would be indicated that more than two kinds of species were stabilized at the conditions. These IR bands, however, were ascribed to the species to form desorbed CO during the TPD of methanol, because these behaviors of infrared and TPD agreed well. Adsorption of methanol and subsequent desorption on the molybdenum oxide monolayer are summarized in scheme 2.

Methanol is adsorbed as methoxide species, and some of them are desorbed as formaldehyde. On the reduced sites of molybdenum oxide Mo(r), the formate ion may be formed, and it is removed directly or indirectly as CO and CO_2.

In the investigation on mechanism of methanol oxidation by Bennett et al. [14], two kinds of methoxide species on the terminal and bridged molybdenum oxide sites were detected. The methoxide species at 1446 cm^{-1} observed on the molybdenum oxide monolayer in the present investigation was that of identified species to be adsorbed on the Mo–□–Mo site with the anion vacancy at the bridged Mo position (□ is an anion vacancy). It was expected that the anion vacancy was created on the Mo(V) cation. The solid acid site could be formed on the reduced site as Mo(V)–OH, and by dehydroxylation the anion vacancy would be formed on the Mo(V) site. Methanol would be thus stabilized on the Mo–OH site as methoxide species of the reaction intermediate for formaldehyde formation. The expected mechanism will thereby account for the relationship between the acidity and the selective activity in the methanol oxidation.

ZrO_2 support is known to be an oxide with the weak basic property. Oxygenated products are stabilized on the surface as such species as dioxymethylene and carbonate species. Methanol undergoes the non-selective reaction on the surface of zirconia, therefore. The surface of zirconia has to be covered with the loaded molybdenum oxide in order to enhance the partial oxidation. Loaded molybdenum oxide will be strongly interacted with the basic sites, thus creating the strong acidity available for adsorption of the selective species.

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