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Creation of the active site for methanol synthesis on a Cu / SiO_2 catalyst

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The effect of ZnO / SiO_2 in a physical mixture of Cu / SiO_2 and ZnO / SiO_2 on methanol synthesis from CO_2 and H_2 was studied to clarify the role of ZnO in Cu / ZnO-based catalysts. An active Cu / SiO_2 was prepared by the following procedure: the Cu / SiO_2 and ZnO / SiO_2 catalysts with a different SiO_2 particle size were mixed and reduced with H_2 at 523–723 K, and the Cu / SiO_2 was then separated from the mixture using a sieve. The methanol synthesis activity of the Cu / SiO_2 catalyst increased with the reduction temperature and was in fairly good agreement with that previously obtained for the physical mixture of Cu / SiO_2 and ZnO / SiO_2. These results indicated that the active site for methanol synthesis was created on the Cu / SiO_2 upon reduction of the physical mixture with H_2. It was also found that ZnO itself had no promotional effect on the methanol synthesis activity except for the role of ZnO to create the active site. The active site created on the Cu / SiO_2 catalyst was found not to promote the formation of formate from CO_2 and H_2 on the Cu surface based on in situ FT-IR measurements. A special formate species unstable at 523 K with an OCO asymmetric peak at $\sim 1585\ cm^{-1}$ was considered to be adsorbed on the active site.

Keywords: methanol synthesis, Cu / ZnO catalyst, hydrogenation of CO_2, role of Zn, in situ FT-IR

1. Introduction

Although Cu / ZnO-based catalysts are well known to be active for the methanol synthesis by hydrogenation of CO or CO_2, the reaction mechanism, the active species, and the role of ZnO are still ambiguous and controversial. The issue of the role of ZnO has been roughly classified into three categories. (i) ZnO itself directly plays a role in catalyzing methanol synthesis, (ii) the ZnO support changes the morphology of Cu particles leading to an active Cu surface such as Cu(110), and (iii) an active site is created on the surface of Cu in the presence of ZnO.

Concerning the proposed role (i), Burch et al. [1–3] have reported that ZnO behaves as a reservoir for atomic hydrogen needed for the hydrogenation steps on the Cu surface. On the other hand, adsorbates such as formate or methoxy formed on ZnO surfaces have been reported to be the intermediate during methanol synthesis. Fujita et al. [4,5] have shown that the methoxy species adsorbed on a ZnO catalyst is readily hydrolyzed to methanol by water. Recently, several papers have been published on the morphology of Cu particles on ZnO surfaces, or the role (ii). Yoshihara and Campbell [6] have suggested that the role of ZnO is to maintain ultrathin Cu islands that have (110)-like behavior. Ovesen et al. [7] have carried out a dynamic micro-kinetic analysis of the methanol synthesis including the changes in the particle morphology of Cu based on EXAFS data [8]. Hadden et al. [9] have also studied the morphological changes of the Cu surface of a Cu / ZnO / Al_2O_3 catalyst by CO TPD.

We have studied the role of ZnO in the methanol synthesis by the hydrogenation of CO_2 over Cu catalysts using both surface science techniques and powder catalysts [10–16]. The results obtained so far have definitely indicated the creation of an active site in the presence of ZnO, namely (iii) in the above categories. It has been found that Zn deposited on Cu(111) significantly promotes the methanol synthesis activity, but does not promote the reverse water–gas shift reaction [12–14]. This is evidence for the presence of a special species that promotes the methanol synthesis. The results obtained from the surface science studies are consistent with those of the powder catalysts such as a physical mixture of Cu/ SiO_2 + ZnO / SiO_2 [14–16]. That is, the ZnO_x species in the physical mixture was found to migrate from the ZnO particles onto the Cu particles upon H_2 reduction at 523–723 K, leading to the creation of active sites on the Cu surface.

The objective of the present study is to clarify the following two points:

(i) We tried to prepare the active species on the Cu/

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SiO_2 catalyst by excluding the ZnO/SiO_2 particles from the mixture of Cu/SiO_2 and ZnO/SiO_2 after reducing the mixture with H_2. At the same time, we determined whether or not the ZnO/SiO_2 itself in the physical mixture of Cu/SiO_2 and ZnO/SiO_2 has any promotional effect such as the hydrogen spillover or the conversion of the adsorbates on ZnO to methanol.

(ii) In this study, we divided the methanol synthesis into two parts, before and after the formation of the formate intermediate. We then examined which part is promoted by the creation of the active site.

2. Experimental

The Cu/SiO_2 and ZnO/SiO_2 catalysts were prepared by the alkoxide method [17] using $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Si(OCH_2CH_3)_2$ as previously reported [16]. The loading of Cu and ZnO in the Cu/SiO_2 and ZnO/SiO_2 catalysts was 30 and 70 wt%, respectively. After drying the catalyst gel at 383 K for 24 h, the catalyst was calcined at 623 K for 2 h in air. The obtained Cu/SiO_2 and ZnO/SiO_2 catalysts were then sieved to collect the catalyst particles with sizes of $< 200\ \mu m$ and $> 250\ \mu m$, respectively. The catalysts were physically mixed with a weight ratio of $Cu/SiO_2 : ZnO/SiO_2 = 2 : 1$, and the mixture was reduced with H_2 in a flow reactor for 2 h at 523–723 K and 50 atm. This leads to the preparation of the active site on the Cu/SiO_2. After the reduction, the Cu/SiO_2 was separated from the physical mixture using a 200 μm sieve. The collected Cu/SiO_2 catalyst was set in the flow reactor and reduced with H_2 at 523 K and 50 atm. The weight of the catalyst was 2 g. The hydrogenation of CO_2 was then carried out at 50 atm with a H_2/CO_2 ratio of 3. The flow rate was 300 cm^3/min, and the typical reaction time was 2 h. The reaction products were analyzed using gas chromatographs with a thermal conductivity detector and a flame ionization detector.

For an in situ FT-IR study, a Fourier transform infrared spectrometer (JIR-6500, Jeol) was connected to a flow reactor (Spectra Tech model 0030-102) to observe the behavior of adsorbates during the methanol synthesis. The windows of the reactor were made of ZnSe. The samples were placed in a sample cup without further dilution. A thermocouple was inserted in the reaction cell, which reached the catalyst bed. Typically, before the FT-IR measurements, catalysts were reduced with H_2 at 523 K and 1 atm for 0.5 h in the flow reactor.

3. Results and discussion

3.1. Creation of active species

We have previously shown [16] that ZnO_x species migrates from ZnO/SiO_2 particles onto the Cu/SiO_2 surface in a physical mixture of $ZnO/SiO_2 + Cu/SiO_2$ upon H_2 reduction at 523–723 K as mentioned in the introduction. The migration of the ZnO_x species has been considered to create active sites for the methanol synthesis on the surface of Cu. However, it was not clear whether or not ZnO/SiO_2 itself had any activities for methanol synthesis. To answer this question, we tried to prepare a ZnO_x-promoted Cu/SiO_2 catalyst by excluding ZnO/SiO_2 particles using the following procedure; we first prepared Cu/SiO_2 ($< 200\ \mu m$) and ZnO/SiO_2 (250–500 μm) catalysts supported by SiO_2 with different particle sizes, then reduced the mixture with H_2, and finally separated the Cu/SiO_2 from the mixture using a 200 μm sieve (see section 2). Figure 1 shows the catalytic activity of the separated Cu/SiO_2 catalyst at 50 atm and 523 K as a function of the reduction temperature, together with the previous results of the physical mixture of $ZnO/SiO_2 + Cu/SiO_2$ and non-treated Cu/SiO_2 [16]. It is clear that the activity increased with increasing reduction temperature for both the separated Cu/SiO_2 and physical mixture. The results indicated that the ZnO_x species that migrated onto the Cu surface created active sites for methanol synthesis and that ZnO/SiO_2 possesses no appreciable activity for methanol formation. The results also indicated that the methoxy or formate species probably formed on the ZnO particles, which were reported to be intermediates of methanol formation [4,5], do not contribute to the promotional effect observed in the physical mixture of $Cu/SiO_2 + ZnO/SiO_2$. From now on, we will abbreviate the separated Cu/SiO_2 to $(Zn)Cu/SiO_2$.

To confirm the migration of Zn species onto the Cu/SiO_2, XRD measurements were made for the $(Zn)Cu/SiO_2$ reduced at different temperatures as previously carried out for $Cu/SiO_2 + ZnO/SiO_2$ [16]. Figure 2 shows the lattice constant of Cu estimated from the XRD meas-

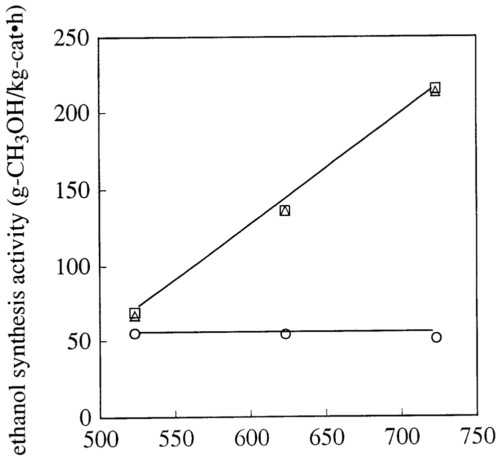

Figure 1. Methanol synthesis activity for the hydrogenation of CO_2 over the separated Cu/SiO_2 ((△) $(Zn)/Cu/SiO_2$) as a function of reduction temperature, together with the previous data for the physical mixture ((□) $Cu/SiO_2 + ZnO/SiO_2$) and non-treated Cu/SiO_2 ((○) Cu/SiO_2) catalysts.

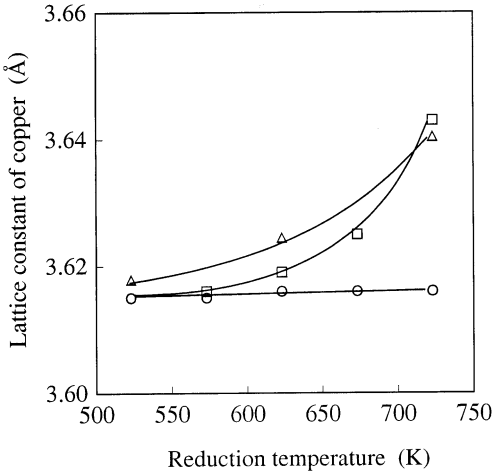

Figure 2. The lattice constant of Cu estimated from the XRD measurements of the (Zn)Cu/SiO$_2$ (($\triangle$) (Zn)/Cu/SiO$_2$) as a function of reduction temperature, together with the previous data for the physical mixture (($\square$) Cu/SiO$_2$ + ZnO/SiO$_2$) and non-treated Cu/SiO$_2$ (($\bigcirc$) Cu/SiO$_2$) catalysts.

urements of the (Zn)Cu/SiO$_2$, together with Cu/SiO$_2$ and Cu/SiO$_2$ + ZnO/SiO$_2$ [16] data, as a function of reduction temperature. As reported earlier, a XRD peak appeared at $2\theta = 43.3^\circ$ for Cu/SiO$_2$ regardless of the reduction temperature, from which the lattice constant of Cu for Cu/SiO$_2$ was found to be the same as that for pure copper (3.615 å) [18]. In contrast, the lattice constant of Cu for the (Zn)Cu/SiO$_2$ increased with increasing reduction temperature as shown in figure 2, which is similar to the behavior of the Cu/SiO$_2$ + ZnO/SiO$_2$ mixture. The lattice constant of Cu for the (Zn)Cu/SiO$_2$ reduced at 723 K was estimated to be 3.64 å, from which the average content of Zn in the Cu particles for the (Zn)Cu/SiO$_2$ reduced at 723 K was estimated to be about 13% based on the literature data [18]. The results indicate the migration of Zn species from the ZnO particles to the Cu particles upon reduction at high temperature.

The results in figure 1 are comparable with those obtained from the surface science study using the Cu(111) model catalyst. We have found that the deposition of Zn on Cu(111) enhances the methanol synthesis activity by an order of magnitude [12–14]. At the promotional regime of Zn coverage ($0 < \Theta_{Zn} < 0.2$), the Zn species was found to be metallic during the reaction, and it was suggested that Zn atoms are substituted with Cu atoms leading to a Cu–Zn surface alloy. That is, the active species is not composed of ZnO, but metallic Zn. Thus, it is suggested that the active site newly created on the Cu/SiO$_2$ upon reduction in the presence of ZnO is the Zn atom in the Cu–Zn surface alloy. The recent surface science results of the Zn-deposited Cu(111) thus indicated [12,13] that the Cu–Zn site and Cu^0 are both active species for methanol synthesis, although our previous studies using the powder catalysts suggested that Cu$^+$ and Cu^0 species co-work to catalyze methanol synthesis [15,19]. Currently, we considered that the model of the Cu–Zn active site is correct, and the Cu$^+$ species proposed in the powder catalyst are probably due to the decomposition of formate intermediates upon evacuation of the reaction mixture at 523 K.

3.2. Formate synthesis

A question arises as to which elementary step is promoted by the creation of active species on the (Zn)Cu/SiO$_2$ catalyst. It has been accepted that methanol is produced through formate and methoxy intermediates [20–22]. We were first interested in which elementary step before or after the formation of the formate intermediate is promoted by the Zn species. To examine the effect of the Zn species on the formation of formate, we measured the reaction rate of the formate synthesis on the Cu/SiO$_2$ and (Zn)Cu/SiO$_2$ catalysts using in situ FT-IR by exposing CO$_2$ and H$_2$ (1 : 3) to them at 373 K and 1 atm. Figure 3 shows the peak intensity of the OCO symmetric stretching of formate at 1350 cm^{-1} as a function of exposure time. The formation rate of the formate species was the same for both Cu/SiO$_2$ and (Zn)Cu/SiO$_2$, indicating that the newly created active site upon Zn migration does not promote the formation process of formate species from CO$_2$ + H$_2$.

The results in figure 3 are consistent with our surface science results concerning the formation of formate on Cu(111) and Zn/Cu(111) [13,22,23]. That is, no promotional role of Zn in the formation of formate from CO$_2$ + H$_2$ was observed over a Zn-deposited Cu(111) surface ($\Theta_{Zn} = 0.09$). Here, the saturation coverage of formate on a clean Cu(111) surface was estimated to be $\Theta_{HCOO} = 0.25$, where $\Theta = 1$ corresponded to the number of surface Cu atoms. Assuming that the saturation coverage of formate in figure 3 is 0.25, the initial formation rate of formate over the Cu/SiO$_2$ was estimated to be 1.7×10^{-3} molecules/(site s) at 373 K. This value was

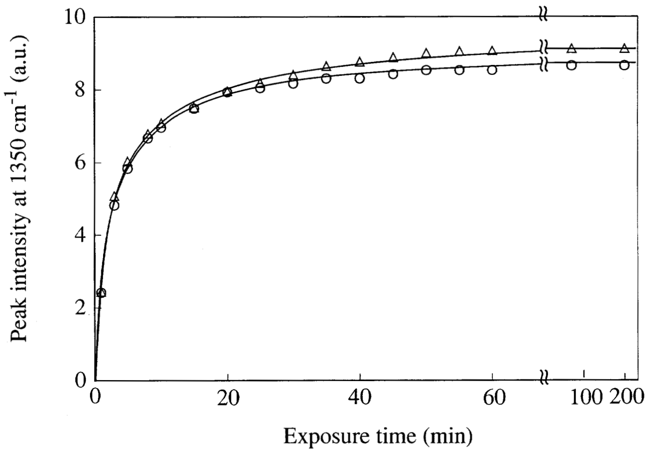

Figure 3. The intensity of the IR peak at 1350 cm^{-1} due to formate species as a function of exposure time at 373 K and 1 atm. ($\triangle$) (Zn)Cu/SiO$_2$, ($\bigcirc$) Cu/SiO$_2$.

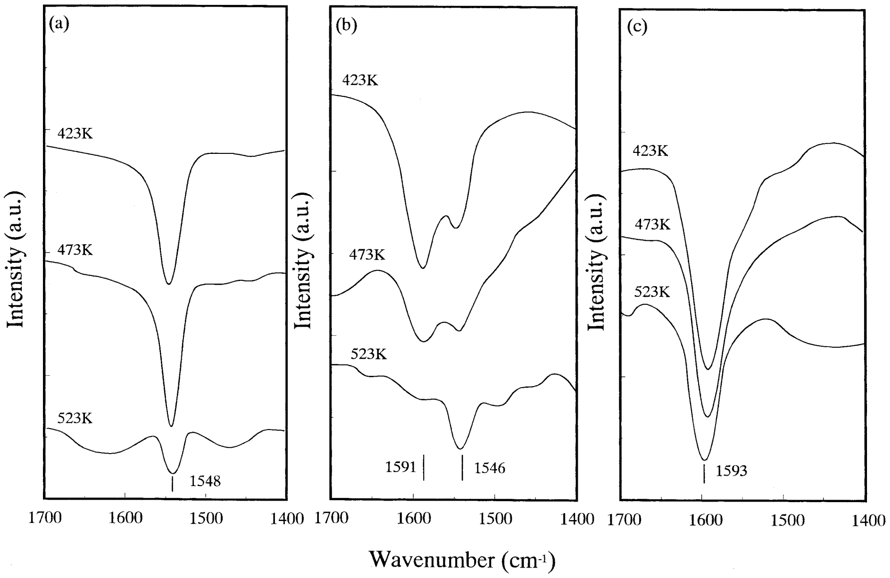

Figure 4. In situ FT-IR spectra of formate species formed during the hydrogenation of CO_2 at 423–523 K and 1 atm. (a) Cu/SiO_2, (b) $(Zn)Cu/SiO_2$, (c) $Cu/SiO_2 + ZnO/SiO_2$.

comparable with that measured for the clean Cu(111) surface (7.6×10^{-4} molecules/(site s)), although the H_2/CO_2 ratio (= 3) in the powder experiment was different from that (= 1) in the surface science experiment. The results in figure 3 indicate that the Zn active species promote a hydrogenation process after the formation of formate. This is consistent with the literature which has reported that the rate-determining step of methanol synthesis over Cu catalysts is hydrogenation of the formate [20,21,24] or dioxymethylene (H_2COO) species [25].

3.3. Special formate species

Differences among Cu/SiO_2, $(Zn)Cu/SiO_2$, and the physical mixture observed in the in situ FT-IR measurements were the peak position of the OCO asymmetric stretching due to formate species and the behavior varying with reaction temperature. Figures 4a–4c show the in situ FT-IR spectra of the OCO asymmetric stretching during the hydrogenation of CO_2 at 423–523 K and 1 atm.

For Cu/SiO_2, a single peak due to the asymmetric stretching of the formate species was observed at 1546–1548 cm^{-1}, characteristic of formate on the metallic Cu surface, whose intensity increased with decreasing reaction temperature. As for $(Zn)Cu/SiO_2$, a peak at 1585–1591 cm^{-1} appeared in addition to the peak of the Cu-formate at ~1550 cm^{-1}. The peak at ~1590 cm^{-1} was also seen for the physical mixture of $Cu/SiO_2 + ZnO/SiO_2$, whereas its intensity was relatively large and the temperature dependency was quite different from that for the peak at ~1585 cm^{-1} for $(Zn)Cu/SiO_2$. That is, the peak at 1585 cm^{-1} for the physical mixture was seen at a high temperature of 523 K without decomposition, while the peak observed for $(Zn)Cu/SiO_2$ disappeared at 523 K. It has been reported that the formate species adsorbed on ZnO is stable up to 600 K [26,27]. On the other hand, formate species on metallic Cu surface starts to significantly decompose around 450 K [28–30]. Thus, the peak at ~1585 cm^{-1} seen for the physical mixture was assigned to the formate species adsorbed on ZnO. On the other hand, the formate species unstable at 523 K with the peak at 1585 cm^{-1} was unique for the $(Zn)Cu/SiO_2$ and was considered to be adsorbed on the active site.

Recently, we have observed the formate species, with the OCO asymmetric peak at 1585 cm^{-1} by IRAS, on the Zn/Cu(111) surface during the hydrogenation of CO_2 at 348 K and 1 atm. The Zn/Cu(111) had no atomic oxygen and was considered to be the Cu–Zn surface alloy as already mentioned. We currently regard that the formate species bound to the Cu–Zn active site shown in figure 5 is the pivotal intermediate of methanol synthesis.

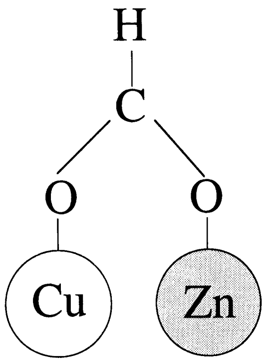

Figure 5. Proposed model of the special bidentate formate adsorbed on the Cu–Zn site.

4. Conclusions

(i) The active species for methanol synthesis was successfully prepared on the Cu/SiO_2 catalyst by reduction of the physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ with H_2 at 523–723 K followed by the separation of Cu/SiO_2 from the mixture by a sieve.

(ii) Formate or methoxy species on the ZnO surface is not an intermediate of the methanol synthesis reaction over the physical mixture catalyst under the reported reaction conditions. The ZnO itself in the physical mixture has no promotional effect on the methanol synthesis activity.

(iii) The Zn active species created on the Cu surface of the $(Zn)Cu/SiO_2$ catalyst does not promote the formation of formate species from CO_2 and H_2 on the Cu surface. The reaction rate on the Cu/SiO_2 catalyst is comparable with that measured on Cu(111).

(iv) A special formate species unstable at 523 K with an OCO asymmetric peak at $\sim 1585\ \mathrm{cm}^{-1}$ is observed for the $(Zn)Cu/SiO_2$ catalyst, which is probably bound to the Zn active species.

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