The difference in the active sites for CO_2 and CO hydrogenations on Cu/ZnO-based methanol synthesis catalysts

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The effect of Zn in copper catalysts on the activities for both CO_2 and CO hydrogenations has been examined using a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ and a Zn-containing Cu/SiO_2 catalyst or $(Zn)Cu/SiO_2$. Reduction of the physical mixture with H_2 at 573–723 K results in an increase in the yield of methanol produced by the CO_2 hydrogenation, while no such a promotion was observed for the CO hydrogenation, indicating that the active site is different for the CO_2 and CO hydrogenations. However, the methanol yield by CO hydrogenation is significantly increased by the oxidation treatment of the $(Zn)Cu/SiO_2$ catalyst. Thus it is concluded that the Cu–Zn site is active for the CO_2 hydrogenation as previously reported, while the Cu–O–Zn site is active for the CO hydrogenation.

KEY WORDS: Cu/ZnO catalyst; methanol synthesis; CO_2 and CO hydrogenations; effect of ZnO; active site

1. Introduction

Cu/ZnO-based catalysts are well known to be active for methanol synthesis from a $CO/CO_2/H_2$ mixture gas [1–4]. The active site, the role of ZnO, and the reaction mechanism for this reaction are still subjects to considerable controversy, even though efforts have been made in order to obtain consensus by considering the experimental conditions [5,6]. It is accepted that methanol can be synthesized from both CO and CO_2 over Cu-based catalysts [1]. On Cu/ZnO catalysts, the reaction rate of methanol synthesis by the hydrogenation of CO_2 is greater than that by the hydrogenation of CO at the normal industrial temperatures of 450–550 K [4]. At higher reaction temperatures, the rate of the CO hydrogenation is comparable with that of the CO_2 hydrogenation [7]. However, the rate of hydrogenation of CO_2 vs. CO depends on reaction conditions, especially the CO/CO_2 and $H_2/(CO + CO_2)$ ratios and the reaction pressure, and clearly different results have been obtained by different researchers [8–11]. Thus the controversial issues concerning the methanol synthesis should be separately discussed for the CO_2 hydrogenation and the CO hydrogenation.

As for the CO_2 hydrogenation, the proposals concerning the active site and the role of ZnO can be divided into three models: (i) the morphology model proposed by the Topsøe [12,13], Campbell [14], and Waugh [15] groups in which wetting–nonwetting of the copper particles on ZnO significantly influence the methanol synthesis activity. Note that the particles size of the copper should also be taken into consideration because the morphology effect was reported at the low loading of Cu or the high dispersion of Cu as 1–5 wt% Cu/ZnO by Topsøe et al. [12], although high Cu-loading catalysts of 50–70 wt% Cu/ZnO are generally used in industrial methanol synthesis processes [1]; (ii) the Cu–Zn active site model proposed by Fujitani and Nakamura et al. [16–22] in which the Cu–Zn surface alloy and Cu metals cooperate to catalyze the methanol synthesis. The role of the Cu–Zn site is to activate the hydrogenation of the formate species. They changed the active site model from the Cu–O–Zn site to the Cu–Zn site in 1996 based on surface science studies as repeatedly described [19,22–24]; and (iii) the interfacial active site between Cu and ZnO, as reported by Poels et al. [18]. On the other hand, surface science studies on Cu(111) [26], Cu(110) [14,27], and Cu(100) [27,28] have clearly shown that metallic copper has some catalytic activity for methanol synthesis by the hydrogenation of CO_2. The point in the controversy is the promotional effect of ZnO or Zn on the methanol synthesis on Cu.

An important question arises as to whether or not the active site and the role of ZnO for the CO_2 hydrogenation are the same as those for the CO hydrogenation. Many researchers have reported that a Cu^+ species is responsible for the methanol synthesis activity from CO and H_2 in the absence of CO_2, in contrast to the reports for the CO_2 hydrogenation, as mentioned above, although the models of the active sites are different from each other. Originally, Klier and Herman and coworkers [29,30] have reported that the Cu^+ ion dissolved in the ZnO matrix is the active component of the Cu/ZnO-based catalysts. Sheffer and King [31,32] have reported that the differences in the promotional effect of the Group IA elements (Na, K, Rb, Cs) on unsupported copper catalysts for methanol synthesis by CO hydrogenation were attributable to differences in the concentration of the Cu^+ species at the surface. Nonneman and Ponec [33] have reported that a pure Cu catalyst is inactive for methanol

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synthesis from CO and H_2, while small amounts of contamination such as alkali promote Cu to produce methanol. They concluded that the promoter stabilized the Cu^+ active center. Robinson and Mol [34] have reported that no correlation is obtained between the methanol synthesis activity from CO/H_2 and the surface area of Cu, in contrast to the well-known linearity for the methanol synthesis from $CO/CO_2/H_2$ or CO_2/H_2. These reports cited above are consistent in that the active site of the Cu catalysts for methanol synthesis by CO hydrogenation includes the Cu^+ species, which is different from that for CO_2 hydrogenation.

Recently, Spencer [6] discussed the role of surface oxygen on Cu in methanol synthesis catalysts, in which strongly adsorbed oxygen bonded to both copper and zinc atoms is important for the methanol synthesis catalysts. He considered that the surface zinc is provided by the Zn-containing Cu particles (α-brass or Cu–Zn alloy). The alloy formation in Cu particles for Cu/ZnO and a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ upon high-temperature reduction was proved by Fujitani and Nakamura et al. [17]. Thus it is likely that the role of ZnO for the CO hydrogenation is to stabilize Cu^+ on Cu particles by ZnO. On the other hand, Spencer [5] and Burch et al. [35] have reported evidence for the spillover effect of hydrogen as a synergy effect of Cu and ZnO for the methanol synthesis by CO hydrogenation. They found that a physical mixture of Cu/SiO_2 and ZnO/SiO_2 is more active than Cu/SiO_2 for the CO hydrogenation without high-temperature reduction treatments. This seems to be different from the result of Fujitani and Nakamura et al. [17] in which the high-temperature reduction of the physical mixture lead to an increase in the methanol synthesis activity by CO_2 hydrogenation. This difference can be ascribed to the CO and CO_2 hydrogenations.

In this study, we compared the catalytic activities for both the CO_2 and CO hydrogenations over a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ catalyst and a Zn-containing Cu/SiO_2 catalyst depending on the reduction and oxidation treatments. We thus report the difference in the active sites and the role of ZnO for both reactions.

2. Experimental

The Cu/SiO_2 and the ZnO/SiO_2 were prepared by the impregnation and alkoxide methods, respectively. The preparation methods of the Cu/SiO_2 and ZnO/SiO_2 catalysts are the same, as previously reported [16,36]. The loading of Cu in Cu/SiO_2 was 30 wt%, and the loading of ZnO in ZnO/SiO_2 was 80 wt%. The particle sizes of Cu/SiO_2 and ZnO/SiO_2 were <150 μm and 150–250 μm, respectively. The catalysts were physically mixed in a weight ratio of $Cu/SiO_2 : ZnO/SiO_2 = 0.25$ g : 0.25 g, then 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 migration of Zn species from ZnO/SiO_2 onto the Cu/SiO_2, as previously reported [17].

Reactions were carried out at 523 K and 50 atm with a H_2/CO_2 molar ratio of 3 or a H_2/CO molar ratio of 2. The reaction gas consisted of a mixture of H_2/CO_2 or H_2/CO flowing at 75 cm^3/min. The CO/H_2 was passed through a molecular sieve trap for iron carbonyl removal. In some experiments, we used a Zn-containing Cu/SiO_2 catalyst separated from the physical mixture using a 150 μm sieve, which was abbreviated (Zn)Cu/SiO_2 [19]. The collected (Zn)Cu/SiO_2 catalyst was set in the flow reactor and re-reduced with H_2 at 523 K and 50 atm. The weight of the (Zn)Cu/SiO_2 catalyst used for reaction was 0.25 g. The reaction conditions were the same as those of the physical mixture catalysts. The oxidation treatment of the catalysts was conducted in air flowing at 100 cm^3/min at 1 atm and 623 K for 3 h.

The reaction products were analyzed using gas chromatographs with a thermal conductivity detector and a flame ionization detector. Catalytic activities were evaluated in terms of the yield of methanol (%) and the mass time yield (MTY) defined as the weight of the product molecules per catalyst weight per time (g-molecule/kg-cath) for the Arrhenius plot of the reaction rate. In the case of the physically mixed catalyst, the calculated MTY was based on the weight of Cu/SiO_2. Methane is formed as a by-product of the methanol synthesis by the CO hydrogenation. The maximum yield of methane was 0.06%. As for the CO_2 hydrogenation, the amount of methane was negligibly small. The copper surface areas of the catalyst were measured using N_2O/He (2.54% N_2O) gas by reactive frontal chromatography, as previously reported [17]. The Cu surface area ($\sim$1.3 m^2/g-Cu/SiO_2) of the Cu/SiO_2 catalysts was almost the same, independent of the reduction temperature [36]. The particle size of the powder catalyst was calculated to be about 150 nm based on the measurement of the Cu surface area.

3. Results and discussion

We have reported that the Cu–Zn site is active for the methanol synthesis by CO_2 hydrogenation [16–22]. We first examined whether or not the Cu–Zn site operates as the active site for CO hydrogenation. Figure 1 shows the yield of methanol by the CO_2 and CO hydrogenations as a function of the reduction temperature of the physical mixture and the promoted (Zn)Cu/SiO_2 catalysts. The yield of methanol produced by the CO_2 hydrogenation over the physical mixture catalysts increased with increasing reduction temperature. This result has been reproduced in previous results [17,36]. That is, the methanol synthesis activity by CO_2 hydrogenation was promoted by the creation of the Cu–Zn active site by migration of Zn from ZnO onto the Cu particles upon the H_2 reduction treatment. On the other hand, no such increase was observed for the yield of methanol by CO hydrogenation upon reduction treatment. These results indicate that the Cu–Zn site does not operate as the active site for the methanol synthesis by CO hydrogenation. That is, the active sites are different for the CO_2 and CO hydrogenations. At the reduction temperature of 523 K, the yield of methanol is slightly greater than that of the Cu/SiO_2 catalysts. This

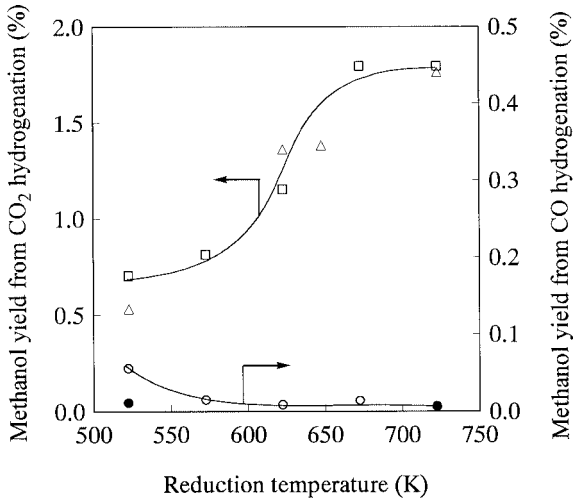

Figure 1. The yield of methanol produced by CO_2 and CO hydrogenations over a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ as a function of reduction temperature. The CO_2 hydrogenation was carried out at $P(H_2)/P(CO_2) =$ 37.5 atm/12.5 atm and 523 K. The CO hydrogenation was carried out at $P(H_2)/P(CO) = 33.3$ atm/16.7 atm and 523 K. Cu/SiO_2 : $ZnO/SiO_2 =$ 0.25 g : 0.25 g. CO_2 hydrogenation (□) and CO hydrogenation (○) over the physical mixture catalyst. CO hydrogenation over Cu/SiO_2 (●). CO_2 hydrogenation over $(Zn)Cu/SiO_2$ (△).

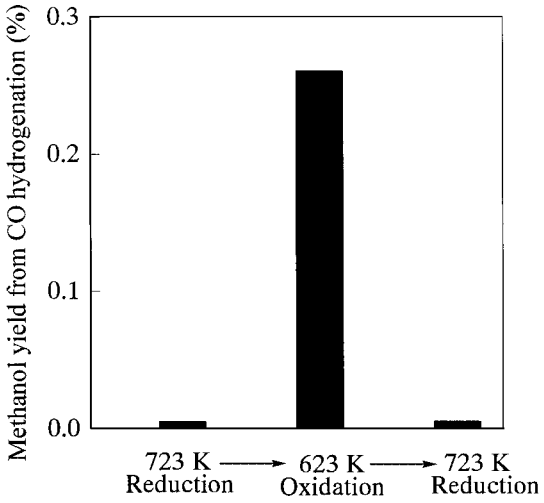

Figure 2. Effect of reduction–oxidation treatments on the methanol yield by CO hydrogenation over a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ catalyst at 523 K. $P(H_2)/P(CO) = 33.3$ atm/16.7 atm.

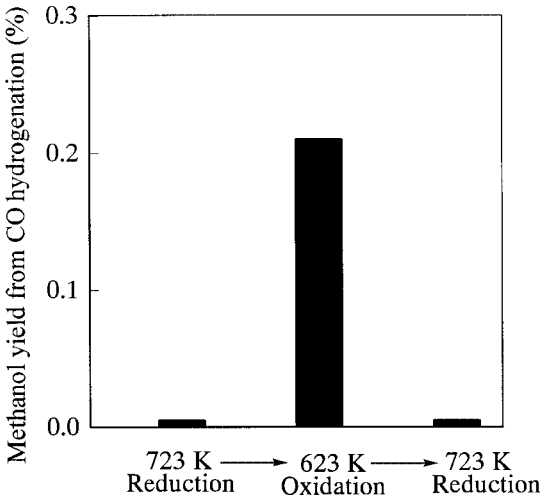

Figure 3. Effect of reduction–oxidation treatments on the methanol yield by CO hydrogenation over a $(Zn)Cu/SiO_2$ catalyst at 523 K. $P(H_2)/P(CO) =$ 33.3 atm/16.7 atm.

suggests that ZnO itself promotes the methanol synthesis activity from CO hydrogenation. The spillover effect was also observed in this work, as shown in figure 1. The methanol yield of the physical mixture catalysts was six times more active than that of the Cu/SiO_2 catalyst at the reduction temperature of 523 K. This result is in good agreement with the report by Spencer and Burch et al. [35] in that the physical mixture is seven times more active than Cu/SiO_2. However, the oxidation-treatment effect is much greater than the spillover effect.

We then postulate that the oxidation state of the Cu–Zn site may influence the formation of the active site for CO hydrogenation. Thus we examined the effect of the oxidation state of the migrated Zn on the Cu particles on the methanol synthesis activity by CO hydrogenation using the physical mixture catalyst. As shown in figure 2, the methanol yield by CO hydrogenation was very little when the physical mixture catalyst was reduced at 723 K. However, the oxidation treatment of the reduced physical mixture at 623 K with air for 3 h resulted in an increase in the methanol synthesis activity for CO hydrogenation. The methanol yield was again decreased by the successive reduction at 723 K. These results indicate that the oxidation state of the Cu–Zn site plays an important role in the formation of the active site for CO hydrogenation. No such promotion was observed by the oxidation treatment of the physical mixture without prior reduction.

We then examined whether or not ZnO itself had a promotion effect of the methanol synthesis for CO hydrogenation using the $(Zn)Cu/SiO_2$ catalyst, which was separated from the physical mixture catalysts using the sieve after reduction at 723 K, as described in section 2. The same experiment for the oxidation and reduction treatments as that shown in figure 2 was performed. As shown in figure 3, the results are in good agreement with that of the physical mixture catalyst. The methanol yield on $(Zn)Cu/SiO_2$ decreased by about 0.05% compared to that for the physical mixture catalyst, suggesting that the difference in the methanol yield was the additional effect of ZnO/SiO_2, because the activity gap between Cu/SiO_2 and the physical mixture catalyst is about 0.05% at the reduction temperature of 523 K, as shown in figure 1. This means that the promotion of the methanol synthesis activity was not due to ZnO/SiO_2, but due to the Zn migrated onto Cu particles.

In order to clarify that the methanol synthesis activity was enhanced by the oxidation of Zn migrated onto Cu particles, we measured the methanol synthesis activity of the physical mixture by changing the quantity of the migrated Zn. This means that the Zn quantity that migrated over the Cu par-

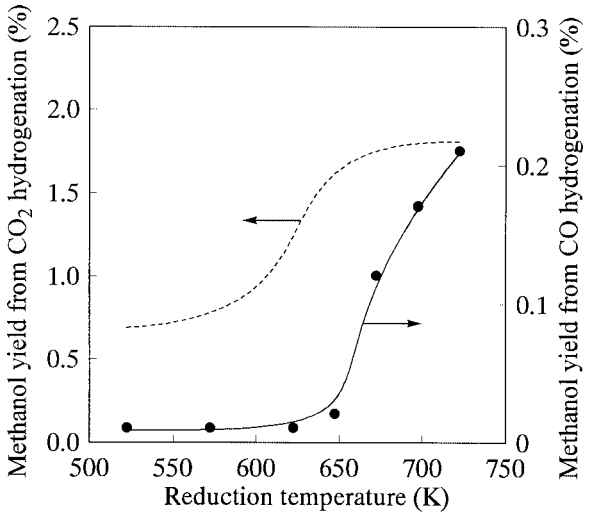

Figure 4. Methanol yield over a (Zn)Cu/SiO_2 catalyst as a function of reduction temperature. After the reduction of Cu/SiO_2 + ZnO/SiO_2, the Cu/SiO_2 was separated from the physical mixture and was oxidized at 623 K. Then CO hydrogenation was carried out at $P(H_2)/P(CO)$ = 33.3 atm/16.7 atm and 523 K. The dashed line shows the previous results of CO_2 hydrogenation over the (Zn)Cu/SiO_2 [36].

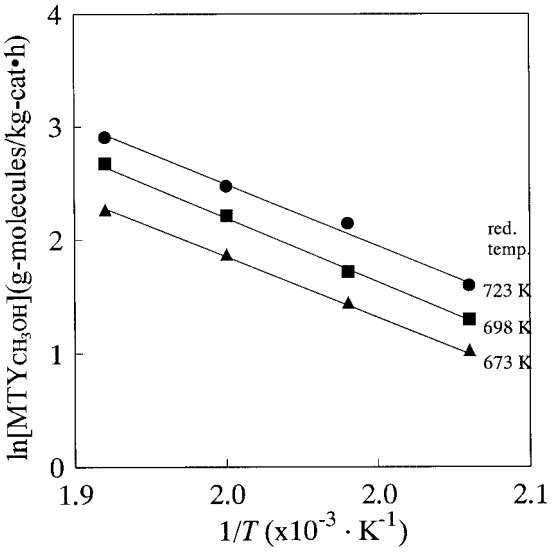

Figure 5. Arrhenius plots of the mass time yield (MTY) for CH_3OH formation by CO hydrogenation over the (Zn)Cu/SiO_2 prepared by the reduction at 673 (▲), 698 (■), and 723 K(●) followed by oxidation at 623 K. $P(H_2)/P(CO)$ = 33.3 atm/16.7 atm.

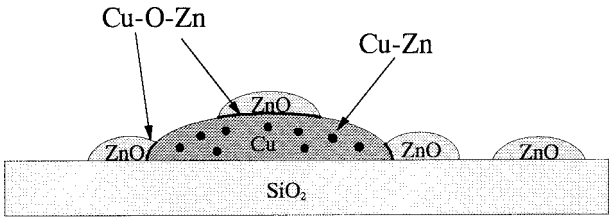

Figure 6. A proposed model of active sites for CO_2 and CO hydrogenations.

ticles was controlled by varying the reduction temperature between 523 and 723 K, as previously reported. Figure 4 shows the methanol yield by CO hydrogenation as a function of reduction temperature of the physical mixture, where the catalyst was oxidized in air for 3 h at 1 atm and 623 K after the reduction. The result of CO_2 hydrogenation shown in figure 1 is also presented in figure 4 for comparison. The methanol yield by the CO hydrogenation significantly increased around the reduction temperature of 650 K. The reduction temperature corresponds to the temperature at which the Zn quantity dissolving into the Cu particles becomes the dissolution limit. We have already reported the formation of the Cu–Zn alloy by the H_2 reduction treatment of a physical mixture by EDX-TEM and XRD [17]. The reproducible results were obtained for the Cu–Zn alloy formation. From the literature value [37], the average contents of Zn in the Cu particle were estimated to be 13–15 at%. That is, the active site for the CO hydrogenation forms at the dissolution limit. The excess Zn over the dissolution limit in the Cu particles is present as an oxidized form of ZnO_x on the Cu particles due to the oxidation treatment. This result is consistent with the surface science result of a Zn-deposited Cu(111) model catalyst [38]. The deposited Zn on Cu(111) exists as a metallic Zn below the Zn coverage of 20 at%, while Zn was oxidized during the reaction over the 20 at%. Accordingly, Zn over the dissolution limit remained in oxidized form during the reaction, leading to the creation of active sites. This indicates that the active site for CO hydrogenation is a Cu–O–Zn site formed at the interface between the ZnO species and Cu particles. That is, the Cu^+ combined with ZnO is the active oxidation state.

Finally, we measured the apparent activation energy for methanol synthesis by CO hydrogenation in order to examine the qualitative and quantitative changes in the Cu–O–Zn active site created on the oxidized (Zn)Cu/SiO_2 catalysts depending on the reduction temperatures. As carried out in the experiments shown in figure 4, the physical mixture of Cu/SiO_2 + ZnO/SiO_2 was first reduced at 673, 698, and 723 K, and then the resultant (Zn)Cu/SiO_2 was oxidized by air at 623 K. Figure 5 shows the Arrhenius plots of MTY for the methanol synthesis over the oxidized (Zn)Cu/SiO_2. The lines of the Arrhenius plot are almost parallel, indicating no dependence of the activation energy (86–96 kJ/mol) on the reduction temperature. Thus it is clear that the quality of the active site did not change, but the quantity of the active site increased with increasing reduction temperature. That is, the number of Cu–O–Zn active site increased with the increasing number of zinc atoms that migrated onto the Cu particles from ZnO upon reduction.

The active site model of the (Zn)Cu/SiO_2 catalyst for the CO and CO_2 hydrogenations is schematically shown in figure 6. The Zn that dissolved into the Cu particles creates the Cu–Zn surface alloy, which operates as the active site for the CO_2 hydrogenation. The Zn over the dissolution limit in the Cu particles becomes ZnO by an oxidation treatment, and forms the Cu–O–Zn site at the interface with the Cu particles, and it operates as the active site for the CO hydrogenation.

4. Conclusions

(i) The active site for the methanol synthesis by CO hydrogenation is the Cu–O–Zn site, which differs from that (Cu–Zn alloy) for the CO_2 hydrogenation.

(ii) The Cu–Zn alloy in the Cu particles is important for creating the Cu–O–Zn site on the Cu surface.

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