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Effect of Support on Methanol Synthesis over Cu Catalyst

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The effect of metal oxides such as ZnO, Al_2O_3, ZrO_2, Ga_2O_3, and Cr_2O_3 contained in Cu-based catalysts was classified into two categories: Stabilization of the Cu^+ species by metal oxides and improvement of the Cu dispersion.

A number of mechanistic studies on methanol synthesis over Cu/ZnO-based catalysts have been conducted for over 20 years.[1-3] There have been controversies as to the active species of copper and the synergetic effect of the support. Chinchen et al. have reported that the activity of a Cu-based catalyst is proportional to the surface area of metallic copper, indicating that the active species for methanol synthesis is metallic copper and ZnO has no special role in the activity.[4] On the other hand, Burch et al. have shown that the addition of Al_2O_3, ZrO_2, Ga_2O_3 or ZnO to Cu/SiO_2 catalysts results in an increase in the rate of methanol synthesis per unit area of copper, suggesting a synergy between the metal oxide and Cu. Most apparent is the synergy between Cu and ZnO, which has been explained by the role of ZnO acting as a reservoir for atomic hydrogen which spillovers onto the surface of Cu and promotes the hydrogenation processes.[5,6] The synergetic effect, however, may be related to the presence of a Cu^+ species which has been regarded as an active site for methanol formation as reported by King et al. who have shown by XPS studies that the catalytic activity increased with the amount of Cu^+ species for alkali-doped Cu catalysts.[7,8] Thus, we have tried to examine the correlation between the catalytic activity for methanol synthesis and the amount of surface Cu^+ species during the hydrogenation of CO_2 over Cu catalysts containing various metal oxides, such as ZnO, Al_2O_3, ZrO_2, Ga_2O_3, Cr_2O_3, La_2O_3, and SiO_2. To estimate the amount of Cu^+ bound to oxygen atoms, we measured the oxygen coverage on the surface of Cu for the post-reaction catalysts by the adsorption of N_2O. In addition, we examined the correlation between the surface area of Cu and the catalytic activity for methanol formation. In this letter, we report on the effect of metal oxides contained in a Cu/ZnO-based catalyst, which can be classified into two factors according to their role in the catalytic activity: stabilization of Cu^+ and improvement of the Cu dispersion.

All catalysts were prepared by a coprecipitation method as described elsewhere.[9] The catalyst fixed in a reactor was reduced in a gas mixture of H_2 (10%) and He (90%) at 523 K with a total pressure 5.0 MPa. The hydrogenation of CO_2 was then carried out at 523 K in a flow reactor by feeding a gas mixture of H_2 and CO_2 with a mole ratio of H_2/CO_2=3. The total pressure of H_2 and CO_2 was 5.0 MPa. The typical reaction time was 2 h. The reaction products were analyzed by gas chromatographs directly connected to the reactor. After the methanol synthesis reaction, CO_2 and H_2 were depressurized and swept out from the reactor, and the post-

reaction catalyst was exposed to a stream of helium at near ambient temperature. A N_2O/He (2.5% N_2O) gas stream was then fed over the catalyst to estimate the surface area of metallic copper ($Cu_{react.}$) during methanol synthesis. The amounts of N_2 formed by the reaction between Cu and N_2O were measured with a thermal conductivity detector at 333 K. The total copper surface area of each catalyst after the reaction (Cu_{total}) was also determined by the N_2O reaction technique after re-reducing the post-reaction catalysts with H_2 at 523 K. The following equation was used to calculate the oxygen coverage (Θ_O).

$\Theta_O=(Cu_{total} - Cu_{react.}) / (Cu_{total} \times 2)$

Here, we assumed that a N_2O molecule reacts with two Cu atoms, which was in agreement with surface science data[10,11]; that is, the saturation coverage of O_a on the low index plane of copper was $\Theta_O \approx 0.5$, where $\Theta_O=1$ corresponded to the number of copper surface atoms.

To elucidate the role of metal oxides in Cu-based catalysts, methanol synthesis from CO_2 and H_2 was performed at 523 K over Cu catalysts containing various metal oxides such as ZnO, Al_2O_3, ZrO_2, Ga_2O_3, Cr_2O_3, and SiO_2. Figure 1 shows the specific activities of the catalysts for methanol formation, i.e. mass time yield per total Cu surface area, as a function of oxygen coverage for the post-reaction Cu surfaces determined by the reaction with N_2O. Excellent correlation between the specific activity and the oxygen coverage was obtained for the Cu catalysts containing different metal oxides, where the specific activity increased linearly with the oxygen coverage below $\Theta_O=0.16$ and then decreased above $\Theta_O= 0.18$. The presence of oxygen on the Cu surface formed during the reaction is indicative of the presence of Cu^+ species bound to the surface oxygen; therefore, the results shown in Fig. 1 indicate that the specific activity is controlled by the ratio of Cu^+/Cu^0, and that both Cu^+ and Cu^0 species are necessary for catalyzing methanol synthesis from CO_2 and H_2. For the catalysts in the absence of ZnO such as Cu/SiO_2, Cu/Al_2O_3, and Cu/ZrO_2, the oxygen coverage was as small as $\Theta_O=0.1$, which is less than that for Cu/ZnO ($\Theta_O=0.23$). Accordingly, the synergy between ZnO and Cu is ascribed to the role in the stabilization of Cu^+, which is probably formed in the vicinity of ZnO_X moieties (x=0-1) on the Cu surface. Recently, we have obtained evidence that the ZnO_X moieties in Cu/ZnO_X migrate onto the Cu surface,

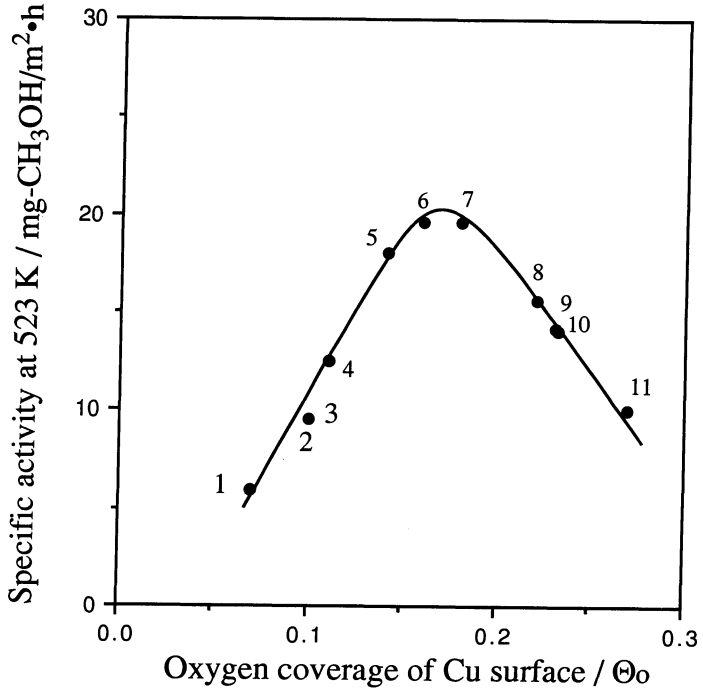

Fig. 1. Specific activity at 523 K as a function of oxygen coverage of Cu surface.

Reaction conditions: H2/CO2=3, Feed gas rate=300 cc/min, Total pressure=5.0 MPa, Catalyst weight=1.0 g.
Catalysts composition (wt%): 1; Cu/SiO2 (30/70), 2; Cu/Al2O3 (50/50), 3; Cu/ZrO2 (50/50), 4; Cu/Cr2O3 (50/50), 5; Cu/ZnO/Cr2O3 (50/40/10), 6; Cu/ZnO/Ga2O3 (50/25/25), 7; Cu/Ga2O3 (50/50), 8; Cu/ZnO/Al2O3 (50/45/5), 9; Cu/ZnO (50/50), 10; Cu/ZnO/ZrO2 (50/25/25), 11; Cu/ZnO/La2O3 (50/40/10).

suggesting that the ZnO_x stabilizes the Cu^+ species by creating a Cu-O-Zn site. [12] It is also found that the maximum specific activity was obtained for $Cu/ZnO/Ga_2O_3$ (50/25/25) and $Cu/ZnO/Cr_2O_3$ (50/45/5), indicating that the addition of Ga_2O_3 or Cr_2O_3 regulates and optimizes the ratio of Cu^+/Cu^0 on the Cu surface.

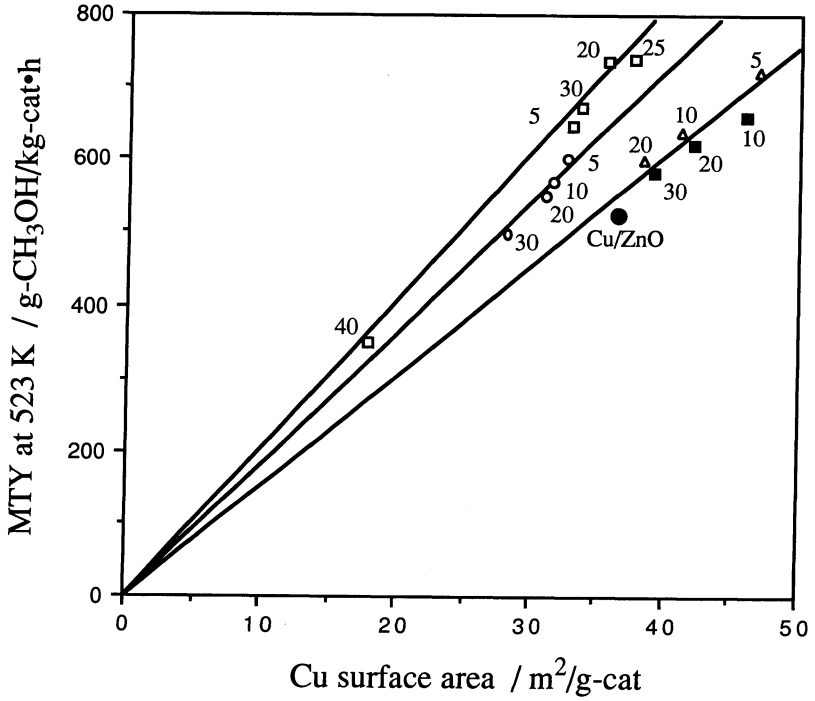

Fig. 2. Methanol synthesis activity (MTY) at 523 K as a function of Cu surface area.
Reaction conditions: H2/CO2=3, Feed gas rate=300 cc/min, Total pressure=5.0 MPa, Catalyst weight=1.0 g.
The contents (wt%) of metal oxides in the Cu/ZnO-based catalysts are indicated in the figure. Cu content of the catalysts is 50 wt%.
□; Cu/ZnO/Ga2O3, ○; Cu/ZnO/Cr2O3, △; Cu/ZnO/Al2O3, ■; Cu/ZnO/ZrO2, ●; Cu/ZnO (50/50).

The effect of metal oxides on the dispersion of Cu in a Cu/ZnO catalyst was then examined by careful measurements of the Cu surface area and the catalytic activity. Figure 2 shows the catalytic activity for the methanol synthesis, mass time yield, over Cu/ZnO-based catalysts containing Al_2O_3, ZrO_2, Ga_2O_3, and Cr_2O_3 on varying the content from 5 to 40 wt%, as a function of total Cu surface area. For each metal oxide contained in the Cu catalysts, linear relationships between the yield and the surface area were seen, indicating that the specific activity is identical for each metal oxide even if the content of a metal oxide in the Cu/ZnO-based catalysts is varied. The specific activities for the Cu/ZnO catalysts containing Ga_2O_3 or Cr_2O_3 are greater than that of a Cu/ZnO catalyst by factor of 40% and 30%, respectively. A $Cu/ZnO/Ga_2O_3$ catalyst with a weight ratio =50/25/25 showed the highest yield (10.8%) of methanol at 523 K, the CO_2 conversion and selectivity being 21.5 and 50.2% at 523 K, respectively. On the other hand, the specific activity is not altered by the addition of Al_2O_3 or ZrO_2, though these metal oxides play a role in increasing the surface area of Cu. This indicates that the addition of Al_2O_3 or ZrO_2 improves the dispersion of Cu/ZnO without changing the Cu^+/Cu^0 ratio, while Ga_2O_3 and Cr_2O_3 are not effective for increasing the dispersion but are effective for optimizing the

Cu^+/Cu^0 ratio. Although Chinchen et al. [4] have reported that the catalytic activity of Cu/ZnO catalysts containing Al_2O_3, MgO, MnO, and SiO_2 can be explained simply by the surface area of Cu, the present study definitely shows the additional effect of metal oxide control the Cu^+/Cu^0 ratio, leading to the change in the specific activity.

In summary, the present study clearly showed that the role of the metal oxide contained in a Cu/ZnO catalyst is classified into two categories:

1) to control the ratio of Cu^+/Cu^0 on the surface of Cu catalysts, which is optimized by addition of Ga_2O_3 or Cr_2O_3.

2) to increase the dispersion of Cu particles by addition of Al_2O_3 or ZrO_2.

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