[Review Paper]

Enhancement of the Catalytic Performance and Active Site Clarification of Cu/ZnO Based Catalysts for Methanol Synthesis by CO₂ Hydrogenation

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The active site and the role of ZnO in Cu/ZnO-based catalysts for methanol synthesis from CO₂ and H₂ were investigated using both classical catalytic and surface science techniques. The active site model in which Zn species present on the Cu surface promotes methanol synthesis is proposed based on the findings for the powder catalysts such as a physical mixture of Cu/SiO₂ and ZnO/SiO₂. Zn promotion was confirmed with a model catalyst of a Zn-deposited Cu(111) surface. The mechanism and kinetics of methanol synthesis over Zn/Cu(111) as well as the structure of the active site were studied. Metallic Cu–Zn surface alloy acts a catalytically active species for the methanol synthesis from CO₂ and H₂. Furthermore, we describe the improvement of catalyst performance and development of catalytic processes based on these findings.

Keywords

Methanol synthesis, Copper catalyst, Zinc oxide support, Active site, Reaction mechanism

1. Introduction

The concentration of carbon dioxide (CO₂) in the atmosphere has increased by about 100 ppm over the past 20 years, which is mainly attributed to the consumption of large amounts of fossil fuels. This higher CO₂ concentration in the atmosphere is a major cause of global warming. Climate change caused by global warming is feared to have a major impact on the entire ecosystem on the earth. Therefore, we must develop new technologies that can contribute to the suppression of global warming, such as the reduction of emissions or effective utilization of CO₂.

Suppression of CO₂ emissions can be achieved by direct reduction of CO₂ emissions by achieving lower fuel consumption, energy saving, and greater use of renewable energy, or by recovery of CO₂ from the emissions of power plants, steelworks, or chemical factories for conversion into useful chemicals.

Many chemicals can be produced by hydrogenation of CO₂, such as CO, methane, alcohols, light hydrocarbons, dimethyl ether, formic acid, and derivatives¹⁾. Different chemicals can be produced by changing the type of catalyst and reaction conditions. Many of these products are basic chemicals, which can be converted into various more complex chemicals. Therefore, by considering CO₂ as a carbon resource

reacted with hydrogen to produce useful chemicals for reuse, a carbon resource circulation system can be constructed. Such a system can produce chemicals derived from non-fossil fuels and reduce fossil fuel usage.

The most conventional catalytic hydrogenation reaction is methanol synthesis from CO₂ using the hydrogenation reaction²⁾.

This reaction involves the catalytic transformation of CO₂ based on the high activity of Cu/ZnO-based catalyst. Activation and hydrogenation of CO₂ on the catalyst surface involve several elementary reactions, but no consensus has yet been reached concerning the active site and reaction mechanism. This review describes the active site and reaction mechanism of methanol synthesis by CO₂ hydrogenation over Cu/ZnO-based catalysts, and discusses the improvement of catalyst performance and development of catalytic processes based on these fundamental findings.

2. Formation of the Active Site on Cu/ZnO Catalyst

Cu/ZnO-based catalysts are well known for excellent characteristics in methanol synthesis by CO₂ hydrogenation. Extensive research has been conducted on methanol synthesis, but the active site and the role of ZnO are not fully understood. Therefore, we studied the effect of ZnO in a physically-mixed Cu/SiO₂ and ZnO/SiO₂ catalyst on the methanol synthesis activity^{3),4)}.

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Reaction conditions: 523 K, 5 MPa, $H_2/CO_2 = 3$, $SV = 33,000 \text{ h}^{-1}$.

Fig. 1 Methanol Synthesis Activities of Cu/SiO₂ and Cu/SiO₂ + ZnO/SiO₂ Catalysts as a Function of Reduction Temperature⁴⁾

Hydrogenation of CO₂ was carried out over physical mixtures of Cu/SiO₂ and ZnO/SiO₂ reduced at 573 K. The main products of the hydrogenation were methanol, carbon monoxide, and water. The methanol synthesis activities of the physical mixtures increased with the ZnO/SiO₂ content. The activity of 100 % Cu/SiO₂ exceeded that of ZnO/SiO₂ by a factor of 100, whereas the activity of the 1 : 3 Cu/SiO₂ and ZnO/SiO₂ mixture was higher than that of Cu/SiO₂ by 30–40 %, demonstrating that ZnO/SiO₂ physically mixed with Cu/SiO₂ has a synergistic effect on the catalytic activity for methanol formation. In contrast, the activities of the physical mixtures of Cu/SiO₂ + pure SiO₂ were almost constant regardless of the SiO₂ content.

Next, we examined the influence of reduction temperature of the physical mixtures of Cu/SiO₂ and ZnO/SiO₂ on the methanol synthesis activity. **Figure 1** shows the methanol synthesis activities of the physical mixtures with various ratios as well as Cu/SiO₂ as a function of reduction temperature. The activity of Cu/SiO₂ remained constant regardless of the reduction temperature, whereas the activities of the physical mixtures significantly increased with higher reduction temperature in the range of 573 to 723 K. The increase in activity was more remarkable at higher contents of ZnO/SiO₂ in the physical mixtures, to three times higher activity than that of Cu/SiO₂. This result shows that higher reduction temperature enhances the synergy between Cu and ZnO.

To investigate the mechanism of the effect of reduction temperature, Cu/SiO₂ and the physical mixtures reduced at different temperatures were characterized by

Fig. 2 Lattice Constant of Metallic Copper in Cu/SiO₂ and Cu/SiO₂ + ZnO/SiO₂ Catalysts as a Function of Reduction Temperature⁴⁾

X-ray diffraction (XRD). **Figure 2** shows the lattice constants of copper in Cu/SiO₂ and the physical mixtures as a function of reduction temperature. The lattice constant of Cu was determined from the peak position of the Cu[111] line using Bragg's equation. The lattice constant for the physical mixture increased from 3.62 to 3.64 Å ($1 \text{ Å} = 10^{-10} \text{ m}$) with higher reduction temperature, whereas the lattice constant of Cu in Cu/SiO₂ showed no change. The increase in the lattice constant was greater with higher content of ZnO/SiO₂. These results indicate that reduction of the physical mixtures at high temperatures above 573 K resulted in migration of Zn species formed by the reduction of ZnO onto the surface of Cu followed by dissolution into the Cu particle to form Cu–Zn alloy. The lattice constant of Cu has a linear relationship with the content of Zn for Cu–Zn alloy at less than 20 atomic% Zn. Therefore, the average contents of Zn in the Cu particle for the physical mixture reduced at 723 K could be estimated at 13–15 atomic% for mixtures with different ZnO/SiO₂ contents. The lattice constant of Cu for Cu/SiO₂ was exactly the same as the reported value of 3.615 Å for pure copper.

These XRD results strongly suggest that the Zn species migrates to the Cu particles in the physical mixtures. To directly confirm the migration of Zn species onto Cu particles, elemental analysis of the physical mixtures was performed using transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDX), which can analyze local sites with a resolution of 100 Å. **Figures 3 and 4** show the TEM micrographs of the physical mixtures of Cu/SiO₂ + ZnO/SiO₂ (1 : 0.5) reduced at 723 K before and after mixing, respectively. The results of the ele-

Fig. 3 TEM Micrograph of Physically Mixed $\text{Cu/SiO}_2 + \text{ZnO/SiO}_2$ (1 : 0.5) after Reduction at 723 K for 5 h, and EDX Spectra of Local Points Labeled A, B, and C on the Micrograph⁴⁾

Fig. 4 TEM Micrograph of Physically Mixed $\text{Cu/SiO}_2 + \text{ZnO/SiO}_2$ (1 : 0.5) Reduced at 723 K for 5 h, and EDX Spectra of Local Points Labeled D, E, F, and G on the Micrograph⁴⁾

mental analysis on spots A-G are also shown in Figs. 3 and 4. Cu/SiO₂ and ZnO/SiO₂ particles can be discriminated by measuring more than 10 sites with EDX for each TEM measurement. Copper, zinc, silicon, and oxygen atoms were detected as well as carbon and molybdenum, which are materials of the microgrid and collodion film. Copper but no zinc was detected at spots A, B and C, indicating that spots A, B and C correspond to the Cu/SiO₂ particles, and no migration of ZnO onto the Cu particles occurred if Cu/SiO₂ and ZnO/SiO₂ were separately reduced at 723 K and then physically mixed. Zn was detected at different points on the ZnO/SiO₂ particles, but no Cu was detected together with Zn. On the other hand, Zn with Cu was observed in spots D, E and F on the sample of the mixture of Cu/SiO₂ and ZnO/SiO₂ reduced at 723 K. These results clearly indicate that migration of Zn definitely occurred during reduction of the mixture of Cu/SiO₂ and ZnO/SiO₂ with H₂ at 723 K. The combined findings of XRD, TEM, and EDX showed that Zn formed by reduction of ZnO at high temperature migrated onto the surfaces of Cu particles, and Zn dissolved into the bulk of copper to form Cu-Zn alloy, which formed the active sites for methanol synthesis.

3. Role of Active Sites

3.1. Hydrogenation of CO₂ over Zn/Cu(111) Model Catalysts

To prove that the Cu-Zn alloy sites act as the active sites for methanol formation, we adopted an extremely effective surface science approach. Specifically, we studied a model catalyst surface based on a single crystal surface using X-ray photoelectron spectroscopy (XPS) combined with a high-pressure reactor. The model catalyst surface was prepared by depositing Zn on Cu(111).

First of all, it is important to establish that the model surface reproduces the turnover frequency (TOF) of actual catalyst for methanol synthesis. **Figure 5** shows the TOF for methanol formation as a function of the Zn coverage (θ_{Zn}). The TOF increased linearly with Zn coverage below $\theta_{\text{Zn}} = 0.19$ and decreased above $\theta_{\text{Zn}} = 0.20$. No activity for methanol formation was observed above $\theta_{\text{Zn}} = 0.5$. These results clearly indicate that the Zn deposited on the Cu surface directly promoted methanol synthesis in the range of $0 < \theta_{\text{Zn}} < 0.4$. The optimum TOF obtained at $\theta_{\text{Zn}} = 0.19$ was thirteen-fold larger than that of the Zn-free Cu(111) surface. The TOF for Zn/Cu(111) ($\theta_{\text{Zn}} = 0.19$) was consistent with that for Cu/ZnO powder catalyst measured under the same conditions. Furthermore, the apparent activation energies were estimated to be 83.7 ± 3.9 kJ/mol from the Arrhenius plots for methanol formation over Zn/Cu(111) ($\theta_{\text{Zn}} = 0.19$), which is close to that of the Cu/ZnO powder catalyst⁶⁾. Therefore,

Reaction conditions: 523 K, 1.8 MPa, H₂/CO₂ = 3, Flow rate = 100 cm³/min.

Fig. 5 Turnover Frequencies (TOF) for Methanol Formation as a Function of Zn Coverage (θ_{Zn}) on the Zn/Cu(111) Model Catalyst⁶⁾

Reaction conditions: 523 K, 1.8 MPa, H₂/CO₂ = 3, Flow rate = 100 cm³/min.

Fig. 6 Turnover Frequencies (TOF) for CO Formation as a Function of Zn Coverage (θ_{Zn}) on the Zn/Cu(111) Model Catalyst⁶⁾

Zn-deposited Cu(111) is appropriate as a model catalyst for methanol formation over Cu/ZnO catalysts because the TOF and the apparent activation energy of Zn/Cu(111) showed good agreement with those for Cu/ZnO catalysts.

The reverse water-gas shift (RWGS) reaction also occurred on the Zn-free and Zn-deposited Cu(111) surfaces. **Figure 6** shows the TOF for the RWGS reac-

Fig. 7 Zn 2p_{3/2} and O 1s XP Spectra of the Zn/Cu(111) Surface after (a) and before (b) Reaction⁶⁾

tion as a function of θ_{Zn} . The TOF for CO formation started to decrease at $\theta_{\text{Zn}} = 0.10$ and reached zero at $\theta_{\text{Zn}} = 0.5$. Thus, Zn had no promotional effect for the RWGS reaction. CO formation by the RWGS reaction mainly occurs over metallic Cu⁷⁾. Therefore, these results indicated that the deactivation of CO formation with higher θ_{Zn} is due to covering of the surface Cu atoms by the deposited Zn. In spite of the decrease in the number of surface Cu atoms, methanol formation over Cu(111) was promoted by the deposited Zn. The increase in the catalytic activity for methanol synthesis indicates the formation of very active sites. The sharp decrease in the TOF observed at $\theta_{\text{Zn}} = 0.15$ – 0.20 was attributed to a change in the oxidation state of Zn (from Zn to ZnO), which will be described below.

3. 2. Surface Analysis by XPS

Surface analysis by XPS was carried out after Zn deposition and hydrogenation of CO₂. After the reaction, the sample was cooled to 373 K in the presence of the reaction mixture, and then the reaction mixture was evacuated. Consequently, surface species stably adsorbed on the post-reaction surface at 373 K can be detected.

Figure 7 shows the XP spectra of Zn 2p_{3/2} and O 1s for the Zn/Cu(111) surfaces ($\theta_{\text{Zn}} = 0.07, 0.15, 0.19, 0.30$) taken before and after the reaction. The Zn 2p_{3/2} peak, representing the Zn initially deposited on Cu(111), appeared at 1021.1 eV regardless of Zn coverage, but no oxygen was detected on the surfaces, indicating that the Zn was in metallic form. However, the Zn 2p_{3/2} peak shifted to higher binding energies with increasing Zn coverage on the post-reaction surfaces. At $\theta_{\text{Zn}} = 0.30$, the Zn 2p_{3/2} peak was observed at 1021.8 eV, and the full-width at half maximum of Zn 2p_{3/2} was larger than that of the initially deposited Zn (1.25 eV) by ~ 0.6 eV. The O 1s spectra of the post-reaction Zn/

Cu(111) surfaces detected peaks at ~ 532 eV and 530.4 eV, which were assigned to formate species and oxygen combined with Zn as previously described^{5),8)}.

The surface chemistry apparently changes significantly at $\theta_{\text{Zn}} = 0.15$. At low Zn coverages below $\theta_{\text{Zn}} = 0.15$, the O 1s peak was observed only at ~ 532 eV, and the Zn 2p_{3/2} peak slightly shifted to higher binding energies. These results suggest that Zn is partially oxidized by formate species because no other oxygen species were present on the post-reaction surface. At higher Zn coverages ($\theta_{\text{Zn}} > 0.15$), the O 1s peak at 530.4 eV was significantly larger with higher θ_{Zn} . Concomitantly, the Zn 2p_{3/2} peak further shifted to higher energies. Therefore, the Zn was mainly oxidized to ZnO_x during the hydrogenation of CO₂. The formate species was still present on the Zn-deposited Cu(111) surfaces at high Zn coverages. Thus, the ZnO_x species is a mixture of ZnO and Zn-formate as will be described later.

The C 1s spectra detected no carbon species on the Zn-deposited Cu(111) before the hydrogenation of CO₂. However, two peaks at 284.5 eV and 289.0 eV were observed after the reaction, which were attributed to graphitic carbon deposited during the reaction and the formate species, respectively. The coverage of graphitic carbon was estimated to be $\theta_{\text{C}} = 0.15$, and could not be further reduced in our experiments. Graphitic carbon should act as a catalyst poison for methanol synthesis, but deactivation probably accounted for $< 20\%$ of the true catalytic activity as previously discussed⁸⁾. The O 1s and C 1s peaks for the formate species formed on the post-reaction surfaces shifted in similar ways to higher binding energies with higher θ_{Zn} . That is, the peaks shifted to higher energies below $\theta_{\text{Zn}} = 0.15$, then indicated constant binding energy at $0.15 < \theta_{\text{Zn}} < 0.30$, and again started to shift at $\theta_{\text{Zn}} = 0.30$. These results suggest that the chemical characteristics of the formate species, such as reactivity or stability, depend on the Zn coverage.

The coverages of oxygen and carbon were estimated from the areas of the O 1s and C 1s peaks at ~ 532 ($\theta_{\text{O,HCOO}}$) eV and ~ 289 eV ($\theta_{\text{C,HCOO}}$) on the post-reaction Zn/Cu(111) surfaces. The ratio of $\theta_{\text{O,HCOO}}/\theta_{\text{C,HCOO}}$ was almost two regardless of Zn coverage, strongly supporting the suggestion that the O 1s and C 1s peaks at 532 eV and 289 eV were due to the formate species. Both $\theta_{\text{O,HCOO}}$ and $\theta_{\text{C,HCOO}}$ linearly increased with Zn coverage between $\theta_{\text{Zn}} = 0$ and 0.15, and then slightly decreased above $\theta_{\text{Zn}} = 0.15$. A $\theta_{\text{HCOO}}/\theta_{\text{Zn}}$ ratio of 0.43 was obtained from the slope at $\theta_{\text{Zn}} < 0.15$. TOF and θ_{Zn} had a linear relationship at $\theta_{\text{Zn}} < 0.15$ (Fig. 5), so a linear relationship was established between θ_{HCOO} and TOF, which is important for the role of Zn in the reaction mechanism. The linear relationship between θ_{HCOO} and θ_{Zn} indicates that the formate species formed during the reaction is directly combined with Zn at $\theta_{\text{Zn}} < 0.15$.

Fig. 8 Coverage of ZnO-oxygen and Formate-oxygen with O 1s peaks at 530.4 eV and ~ 532 eV on the Post-reaction Zn/Cu(111) Surface, Respectively, as a Function of Zn Coverage (θ_{Zn})⁶⁾

Figure 8 shows the coverage of oxygen species with O 1s peaks at 530.4 eV ($\theta_{\text{O,ZnO}}$) and ~ 532 eV ($\theta_{\text{O,HCOO}}$) on the post-reaction Zn/Cu(111) surfaces as a function of the Zn coverage. As described above, formate coverage increased with Zn coverage below $\theta_{\text{Zn}} = 0.15$ and then decreased above $\theta_{\text{Zn}} = 0.20$. In contrast, the oxygen coverage as ZnO was very low at Zn coverages below $\theta_{\text{Zn}} = 0.15$, but increased at higher Zn coverages ($\theta_{\text{Zn}} > 0.20$). This finding indicates that the surface chemistry of Zn-deposited Cu(111) changes at $\theta_{\text{Zn}} = 0.15$ – 0.20 , which corresponds to the optimum coverage for catalysis of methanol synthesis (**Fig. 5**). The coverage of oxygen for ZnO was almost equal to the Zn coverage in the range between $\theta_{\text{Zn}} = 0.4$ and 0.7 , indicating the formation of ZnO species during the CO_2 hydrogenation reaction. The promotional effect of Zn on the TOF for methanol synthesis occurred in the range of $\theta_{\text{Zn}} = 0$ – 0.19 . ZnO species was absent on the post-reaction surface. Therefore, Zn is an active site that stabilizes the formate species as a reaction intermediate. However, Cu atoms other than the active sites are necessary for several hydrogenation steps during methanol synthesis.

3.3. Reaction Intermediates

The role of Zn in the mechanism of methanol synthesis as well as the local structure of the active site were investigated. Formate synthesis over the clean Cu(111) surface was examined by infrared reflection absorption (IRA) spectroscopy⁹⁾. Three vibrational peaks due to formate species were observed in the IRA spectra for the Cu(111) surface exposed to a CO_2/H_2 gas mixture at 760 Torr (1 Torr = 133.322 Pa) and 353 K. The peaks at 1324 – 1326 cm^{-1} and 2850 – 2864 cm^{-1} were identified as the symmetric OCO

Fig. 9 *In-situ* IRA Spectra of Formate Species on Clean Cu(111) (a) and Zn-deposited Cu(111) ($\theta_{\text{Zn}} = 0.15$) (b) Surfaces during Hydrogenation of CO_2 at 760 Torr and 353 K¹⁴⁾

stretching ($\nu_s(\text{OCO})$) and CH stretching bands characteristic of the bridging bidentate formate species on copper^{10)–13)}. The other peak at 2938 – 2946 cm^{-1} was assigned to the combination band of the asymmetric OCO stretching ($\nu_a(\text{OCO})$) and the in-plane CH bending modes^{11,13)}. These frequencies agreed with those obtained for formate species formed by the adsorption of HCOOH or synthesized from CO_2/H_2 on Cu(100)^{10)–12)} and Cu(110)¹³⁾.

Formate synthesis was performed over a Zn/Cu(111) surface¹⁴⁾. **Figure 9** shows the *in-situ* IRA spectra of formate species synthesized from CO_2 and H_2 at 760 Torr and 353 K on (a) a clean Cu(111) surface and (b) a Zn-deposited Cu(111) surface ($\theta_{\text{Zn}} = 0.15$). The peak due to the $\nu_s(\text{OCO})$ band of the formate species on copper was observed on both surfaces at ~ 1330 cm^{-1} . Two new peaks at 1350 cm^{-1} and 1585 cm^{-1} were observed only on the Zn/Cu(111) surface. The peak at 1585 cm^{-1} was assigned to the $\nu_a(\text{OCO})$ band of the formate species¹⁵⁾. Adsorption of a bidentate formate species on the Cu surface should not result in the $\nu_a(\text{OCO})$ band with a vibration parallel to the surface. Therefore, the $\nu_a(\text{OCO})$ peak in **Fig. 9** indicates that a formate species inclined toward the surface was present on the Zn/Cu(111) surface. We showed that Zn deposited on Cu(111) is not oxidized to ZnO by atomic oxygen during methanol synthesis from CO_2 and H_2 at θ_{Zn} below 0.15 . Furthermore, STM has shown that Zn/Cu(111) contains a Cu–Zn surface alloy formed by substituting Zn atoms with Cu surface atoms^{16,17)}. Thus, we conclude that the $\nu_a(\text{OCO})$ peak at 1585 cm^{-1} is due to a bridging bidentate formate species adsorbed on a Cu–Zn site. The shoulder peak at 1350 cm^{-1} was ten-

Catalysts and contents of metal oxides are indicated in the figure. Copper content of the catalysts was 50 wt%. Reaction conditions: 523 K, 5 MPa, $H_2/CO_2 = 3$, $F/W = 18,000$ mL-feed (g-cat h) $^{-1}$.

Fig. 10 Methanol Synthesis Activity (MTY) of Various Cu/ZnO-based Ternary Catalysts as a Function of Copper Surface Area¹⁹⁾

tatively assigned to the $\nu_s(OCO)$ band of the formate species on the Cu-Zn site. Furthermore, the C-O stretching band of the methoxy species was observed around 1080 cm^{-1} on Zn/Cu(111)¹⁴⁾. On the other hand, no methoxy peak was observed on the clean Cu(111) surface. These results clearly indicate that only the formate species adsorbed on Cu-Zn alloy sites was hydrogenated to the methoxy species. Therefore, the function of the Cu-Zn site is to promote the hydrogenation of formate species.

4. Development of Practical Catalysts for Methanol Synthesis

Approaches to improve the performance of Cu/ZnO-based catalysts were assessed based on the findings of the active site and reaction mechanism^{18),19)}. As a first step, the effects of various metal oxides contained in Cu/ZnO-based ternary catalysts (Cu/ZnO/ M_xO_y) were investigated on their activities for methanol synthesis from CO_2 and hydrogen. Al_2O_3 , Ga_2O_3 , ZrO_2 and Cr_2O_3 increased the activity of Cu/ZnO catalyst. **Figure 10** shows the methanol synthesis activity of Cu/ZnO-based ternary catalysts containing 5 to 40 wt% Al_2O_3 , Ga_2O_3 , ZrO_2 and Cr_2O_3 as a function of copper surface area. **Figure 10** strongly suggests that the metal oxides contained in Cu/ZnO-based catalysts have two effects: Al_2O_3 or ZrO_2 improves the surface area of copper, *i.e.* the dispersion of copper particles in the catalyst; and Ga_2O_3 or Cr_2O_3 increases the specific activity, *i.e.* the activity per unit Cu surface area of the catalyst.

Therefore, Cu/ZnO-based multicomponent catalysts

Catalyst: (○) Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃, (□) Cu/ZnO/ZrO₂/Al₂O₃, (▲) Cu(50)/ZnO(45)/Al₂O₃(5), (●) Cu(50)/ZnO(50). Reaction conditions as shown in Fig. 10.

Fig. 11 Activities of Various Cu/ZnO-based Catalysts as a Function of Treatment Temperature in the Stream of Hydrogen¹⁹⁾

were designed by selecting the optimum metal oxides on the basis of these findings. **Figure 11** shows the activities of the multicomponent catalysts (Cu/ZnO/ZrO₂/Al₂O₃ and Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃), a Cu/ZnO/Al₂O₃ catalyst and a Cu/ZnO catalyst as a function of the pretreatment temperature in hydrogen ranging from 523 to 723 K. **Figure 11** clearly indicates that the multicomponent catalysts were more active than the ternary or binary catalysts. Furthermore, the multicomponent catalysts remained highly active even after treatment in flowing hydrogen at 723 K, indicating that their thermal stabilities are extremely high.

Many studies have tried to improve the long-term stability of Cu/ZnO-based multicomponent catalysts during methanol synthesis^{20),21)}. A small amount of silica incorporated into the catalysts by adsorption of colloidal silica on the precipitates prepared by coprecipitation greatly improves long-term stability. Calcining the catalyst at high temperatures around 873 K is also important for obtaining stable activity^{21),22)}. A Cu/ZnO/ZrO₂/Al₂O₃ catalyst containing 0.6 wt% of silica and calcined at 873 K lost 10 % of its initial activity in 40 h of methanol synthesis, but subsequently no significant decrease in activity was observed until 500 h, as shown in **Fig. 12**. On the other hand, the activity of a catalyst without silica decreased monotonously and did not become stable by 500 h.

Cu/ZnO/ZrO₂/Al₂O₃ catalysts without silica and containing 0.6 wt% of silica were examined by XRD. The XRD peaks assigned to ZnO in the catalyst without silica increased greatly with longer time on stream, whereas those peaks in the catalyst containing 0.6 wt% of silica hardly changed. Furthermore, the effect of

Catalyst: (Δ) without SiO_2 , calcined at 873 K; ($\blacktriangle$) without SiO_2 , calcined at 623 K; ($\circ$) with 0.6 wt% SiO_2 , calcined at 873 K; ($\bullet$) with 0.6 wt% SiO_2 , calcined at 623 K. Reaction conditions: 523 K, 5 MPa, $\text{CO}_2/\text{CO}/\text{H}_2 = 22/3/75$, $\text{SV} = 10,000 \text{ h}^{-1}$.

Fig. 12 Effect of Small Amount of Silica Added to a $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3$ Catalyst on Long-term Stability during Methanol Synthesis¹⁹⁾

silica on the stability of a $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst was similar to that for a $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3$ catalyst, although the activity of the $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst was around 20 % lower than that of the $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3$ catalyst. These findings strongly suggest that catalyst deactivation in methanol synthesis results from crystallization of the metal oxides contained in the catalyst, especially ZnO , leading to reductions in the surface area and copper surface area. These findings clearly indicate that silica added to the catalyst can suppress the crystallization of ZnO in the catalyst to improve the long-term stability of the catalyst during methanol synthesis from CO_2 and hydrogen.

Addition of a larger amount of silica gave slightly different results. The initial decrease in the activity of a $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3$ catalyst containing 2.2 wt% of silica during methanol synthesis was much greater than that for the catalyst containing 0.6 wt% of silica. In addition, the surface area of the catalyst containing 2.2 wt% of silica did not change during methanol synthesis for 160 h, whereas the copper surface area and the activity of the catalyst decreased by 31 % and 38 %, respectively. These findings suggest that some silica might migrate and block the active sites on the copper surface resulting in the large initial decrease in the activity with no change in the surface area of the catalyst. This mechanism could also explain the initial decrease in the activity of the catalyst containing 0.6 wt% of silica during the first 40 h of methanol synthesis, as shown in Fig. 12. The optimum amount of silica in the catalyst was determined to be 0.5 to 0.9 wt%²²⁾.

Finally, we found that $\text{Cu/ZnO/ZrO}_2/\text{Al}_2\text{O}_3$ catalyst containing 0.6 wt% of SiO_2 has remained very stable during long-term (about 1 year) operation for methanol synthesis from a feed gas containing a small amount of water and CH_3OH .

5. Summary

The active site and reaction mechanism of Cu/ZnO catalyst for methanol synthesis by hydrogenation of CO_2 were examined in detail using both classical catalytic and surface science techniques. Cu-Zn acts as the active site, and promotes the hydrogenation of formate species in the methanol synthesis reaction. A high-performance practical Cu/ZnO -based multicomponent catalyst was developed based on these findings.

However, recently debate about active sites has been renewed. Therefore, the detailed mechanism of the methanol synthesis catalyst must be determined through detection of reaction intermediates and evaluation of reactivity.

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要 旨

二酸化炭素水素化によるメタノール合成用銅亜鉛系触媒の活性点構造の解明と高性能化

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Cu/ZnO 触媒上での二酸化炭素の水素化によるメタノール合成における活性種, ZnO の役割および反応機構を触媒化学および表面科学的手法を駆使して研究を行った。Cu/SiO₂およびZnO/SiO₂の物理的混合触媒を用いた研究から, Cu 表面に金属状態の Zn がマイグレートして活性点を形成するモデルを提案した。この活性点モデルを表面科学的手法により検証した。Cu(111) 単結晶に Zn を蒸着することで Cu/ZnO 触媒のモデル触

媒表面を作製し, 活性点構造, Zn の役割および反応機構について詳細に検討した。その結果, Cu/ZnO 系触媒上でのメタノール合成における活性点は Cu-Zn 表面合金であり, Zn の役割は反応中間体のフォルメート種の水素化の促進であることを明らかにした。さらに, これらの発見に基づいて, 触媒性能の改善と触媒プロセスの開発を検討した結果についても説明する。