The synergy between Cu and ZnO in methanol synthesis catalysts

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The hydrogenation of CO_2 over physically-mixed Cu/SiO_2 and ZnO/SiO_2 was carried out to clarify the synergetic effect between Cu and ZnO in Cu/ZnO methanol synthesis catalysts. The activity of the physical mixtures significantly increased with increasing reduction temperature in the range of 573–723 K. TEM-EDX results definitely showed that ZnO_x moieties migrated from ZnO/SiO_2 particles onto the surface of Cu particles when the physical mixtures were reduced at high temperatures above 573 K. Upon the migration of the ZnO_x species, the oxygen coverage on the surface of Cu, measured after the hydrogenation of CO_2, increased with the reduction temperature. The results clearly showed that the synergetic effect of ZnO in the physical mixtures can be ascribed to the creation of active sites such as Cu^+ which the ZnO_x moieties stabilize on the Cu surface. Further, XRD results showed that the migrated ZnO_x species partly dissolved into the Cu particles to form a Cu–Zn alloy.

Keywords: methanol synthesis; Cu/ZnO catalyst; effect of reduction temperature; oxygen coverage; physical mixture; Cu–Zn alloy

1. Introduction

Methanol is produced on an industrial scale from gas mixtures containing carbon monoxide, carbon dioxide and hydrogen. The plants usually operate at pressures of 5–10 MPa and temperatures of 503–573 K. It is known that Cu/ZnO-based catalysts are very active for the hydrogenation of CO and CO_2 to methanol. Although a large number of studies have been done concerning the role of ZnO, the valence state of copper, and the reaction mechanism, it is still very controversial at present. In particular, opinions on the active species of Cu are divided into two categories: one insists that the methanol synthesis occurs over the metallic Cu surface [1–6], while the other insists that there is a special site such as Cu^+ species [7–11]. Chinchen et al. [1–3] have reported that the methanol synthesis reaction occurs exclusively on the surface of metallic copper, and that ZnO has no special role with respect to copper except as a carrier to prevent the sintering of copper particles. In surface science studies, Chorkendorff et al. [4,5] and Campbell et al. [6] have carried out methanol synthesis on clean Cu(100) or poly-Cu surfaces, and they concluded, based on kinetic analyses, that the metallic copper is active for methanol formation. On the other hand, Sheffer and King [7,8] have shown that the methanol synthesis activity increased with the amount of Cu^+ on the surface of alkali-doped unsupported Cu catalysts. Similarly, Ponec et al. [9] and Goodman et al. [10] have reported that Cu^+ is the active species. In our series of studies on methanol synthesis from CO_2, Fujitani et al. [11] have shown that Cu^+ and Cu^0 species are both essential for methanol formation and the ratio (Cu^+/Cu^0) determines the specific activity. Further, Kanai et al. [12] have shown evidence for the migration of ZnO_x species from ZnO to Cu in a Cu/ZnO catalyst during the methanol synthesis reaction, leading to the formation of active sites such as Cu^+–O–Zn. Recently, Nakamura et al. [13] have carried out methanol synthesis over Zn-deposited polycrystalline Cu and Cu(111) surfaces, and have shown the significant promotional effect of Zn on the activity, while no promotional effect was observed for the reverse water–gas shift (RWGS) reaction. Thus, we have considered that the role of ZnO in Cu/ZnO catalysts is to create active sites such as Cu^+–O–Zn. Here, we report that ZnO_x migration definitely occurs in a physical mixture of Cu/SiO_2 and ZnO/SiO_2 leading to the formation of active sites on the Cu surface.

2. Experimental

The employed catalysts, Cu/SiO_2 and ZnO/SiO_2, were prepared by the alkoxide method described by

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Ueno et al. [14]. Copper nitrate or zinc nitrate was dissolved in ethanol at 300 K, followed by the addition of tetraethyl silicate with stirring at 353 K. When the mixed solution became homogeneous, water was added to 10 times the number of moles of tetraethyl silicate to form a clear gel. The gel was dried in an oven at 383 K for 24 h. The obtained powder was calcined at 673 K for 2 h in air. The Cu/SiO_2 and ZnO/SiO_2 powders were sieved to collect the 500–1000 μm portion, and then mixed in different volume ratios. The loadings of Cu and ZnO for the prepared Cu/SiO_2 and ZnO/SiO_2 were 30 and 70 wt%, respectively.

The catalytic hydrogenation of CO_2 was carried out in a high-pressure stainless-steel tubular reactor by feeding a gas mixture of H_2 and CO_2 in the molar ratio of $H_2/CO_2 = 3$. Prior to the activity measurements, the catalysts were reduced in the reactor with hydrogen at the desired temperatures for 5 h. The reaction was performed at 523 K with a total pressure of 5 MPa and a space velocity of 33 000 h^{-1}. The flow rate was controlled by a mass flow controller. The effluent gases were analyzed by an on-line gas chromatograph with thermal conductivity and flame ionization detectors. A routine and reproducible measurement of the copper surface area is available by monitoring the reaction of N_2O with copper atoms [11,15–17]. The most convenient form of this method for in situ applications is called reactive frontal chromatography (RFC) [2,18], which is readily employed in a microreactor for assessing the copper surface area. 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 the metallic copper (Cu_{react}) during methanol synthesis. The amounts of N_2 formed by the reaction between Cu and N_2O at 333 K were measured with a thermal conductivity detector. The total copper surface area of each catalyst after the reaction (Cu_{total}) was also determined by the RFC 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):

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

Here, we assumed that oxygen atoms left after the reaction were bonded to two Cu atoms on the basis of surface science data [19,20]. 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. The specific activity for methanol formation was calculated using the metallic Cu surface area measured by N_2O chemisorption.

X-ray diffraction (XRD) measurements were done using a Rigaku RINT 2000 equipped with a nickel-filtered Cu Kα radiation source at 40 kV and 40 mA. The lattice constant of the metallic copper was estimated from the Cu(111) reflection using the Bragg equation. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-2000FX2 microscope operated at 200 kV. The sample was first ground in an agate mortar and then suspended in ethanol using supersonic waves. A portion of the finest parts of the suspension was pipetted onto a molybdenum micro-grid covered with collodion film (400 mesh). Micrographs were obtained with an instrumental magnification of 10^5. Energy-dispersive X-ray spectroscopy (EDX) was used for elemental analyses of local sites (spot size 100 Å) in the catalysts, where the composition on the probe area was calculated from the intensity of the Cu Kα (8.04 keV) and Zn Kα (8.63 keV) radiations.

3. Results

The hydrogenation of CO_2 was performed over the physical mixtures of Cu/SiO_2 and ZnO/SiO_2 at 523 K and a total pressure of 5 MPa. The ratio of Cu/SiO_2 and ZnO/SiO_2 was varied as 1 : 0.5, 1 : 2, and 1 : 3 by volume. The catalysts were reduced with H_2 at the desired temperature after mixing Cu/SiO_2 with ZnO/SiO_2 and then used for the reaction at 523 K. The main products of the hydrogenation were methanol, carbon monoxide, and water. Fig. 1 shows the methanol synthesis activity of Cu/SiO_2 and the physical mixtures of $Cu/SiO_2 + ZnO/SiO_2$ with various ratios of the content by volume as a function of reduction temperature. Although the activity of Cu/SiO_2 was constant regardless of the reduction temperature, the activity of the physical mixtures significantly increased with increasing reduction temperature in the range of 573–723 K. The increase in activity was more remarkable at higher contents of ZnO/SiO_2 (1 : 3) in the physical mixtures, which was three times more active than that of Cu/SiO_2 after

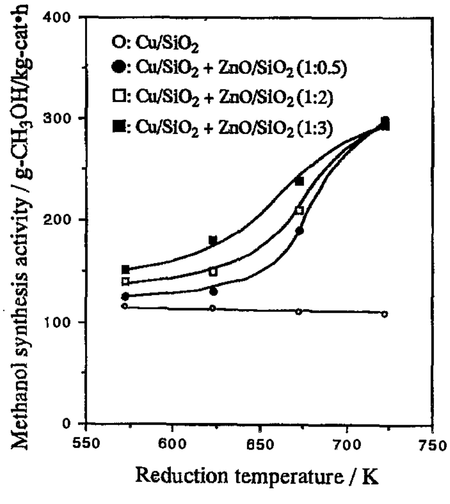

Fig. 1. Methanol synthesis activity for the hydrogenation of CO_2 over Cu/SiO_2 and physical mixtures of Cu/SiO_2 and ZnO/SiO_2 with various volume ratios as a function of reduction temperature. $Cu/SiO_2 : ZnO/SiO_2$: 1 : 3 (■), 1 : 2 (□), and 1 : 0.5 (●); Cu/SiO_2 (O).

reduction at 723 K. The promotional effect is considered to be due to the migration of the ZnO_x species from ZnO particles onto the Cu surface, because we have found that the migration occurs in a Cu/ZnO catalyst [12].

To directly confirm the migration of ZnO_x onto Cu particles, elemental analyses of the physical mixtures were performed using TEM coupled with EDX, which can analyze a local site with a resolution of 100 Å. Figs. 2 and 3 show the TEM micrographs of the physical mixtures of $Cu/SiO_2 + ZnO/SiO_2$ (1 : 0.5) which were reduced at 723 K before and after the mixing, respectively. The results of the elemental analysis on spots A–G by EDX are also shown in figs. 2 and 3. Copper, zinc, silicon, and oxygen atoms were detected as well as carbon and molybdenum, which are due to the materials of the microgrid and collodion film. For spots A, B and C, no zinc was detected, but copper was detected, indicating that spots A, B and C correspond to the Cu/SiO_2 particles and no migration of ZnO_x onto the Cu particles occurred when Cu/SiO_2 and ZnO/SiO_2 were separately reduced at 723 K and then physically mixed. On the ZnO/SiO_2 particles, zinc was detected at different points, but no Cu was detected together with Zn. On the other hand, the coexistence of Zn with Cu was observed in spots D, E and F on the sample reduced at 723 K in the presence of both Cu/SiO_2 and ZnO/SiO_2. The atomic contents of Zn, Zn/(Cu + Zn), for the spots D, E and F are estimated to be 37.2, 33.7 and 35.7%, respectively, based on the elemental sensitivity for the yield of X-ray fluorescence. The results clearly indicate that the migration of ZnO_x definitely occurred upon reducing the mixture of Cu/SiO_2 and ZnO/SiO_2 with H_2 at 723 K. Thus, it is considered that the increase in methanol synthesis activity can be ascribed to the migration of the ZnO_x species onto the Cu surface. However, the content of Zn in the bulk of a Cu particle is probably overestimated because the size of a spot (~ 100 Å) analyzed by TEM is larger than that of a Cu particle, and the ZnO_x moieties on SiO_2 in the vicinity of the Cu particles might be involved in the analysis spots. However, it is clearly shown that the migration of ZnO_x species takes place from ZnO/SiO_2 to Cu/SiO_2 particles.

To characterize the surface of Cu, which is responsible for the catalytic activity in the reduced mixtures of $Cu/SiO_2 + ZnO/SiO_2$, the oxygen coverage on the Cu surface during the hydrogenation of CO_2 was estimated by the dissociative adsorption of N_2O in the same way as

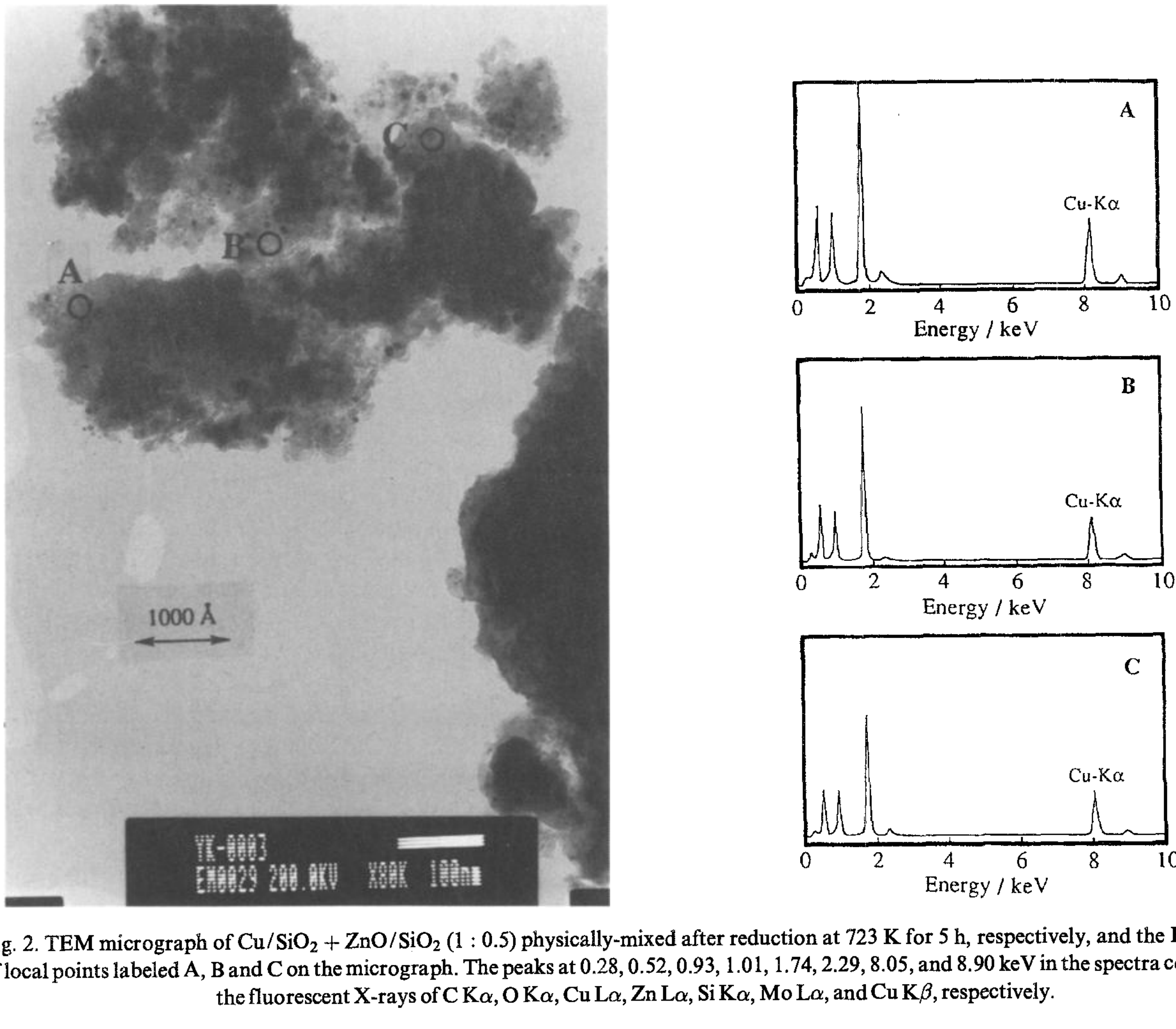

Fig. 2. TEM micrograph of $Cu/SiO_2 + ZnO/SiO_2$ (1 : 0.5) physically-mixed after reduction at 723 K for 5 h, respectively, and the EDX spectra of local points labeled A, B and C on the micrograph. The peaks at 0.28, 0.52, 0.93, 1.01, 1.74, 2.29, 8.05, and 8.90 keV in the spectra correspond to the fluorescent X-rays of C Kα, O Kα, Cu Lα, Zn Lα, Si Kα, Mo Lα, and Cu Kβ, respectively.

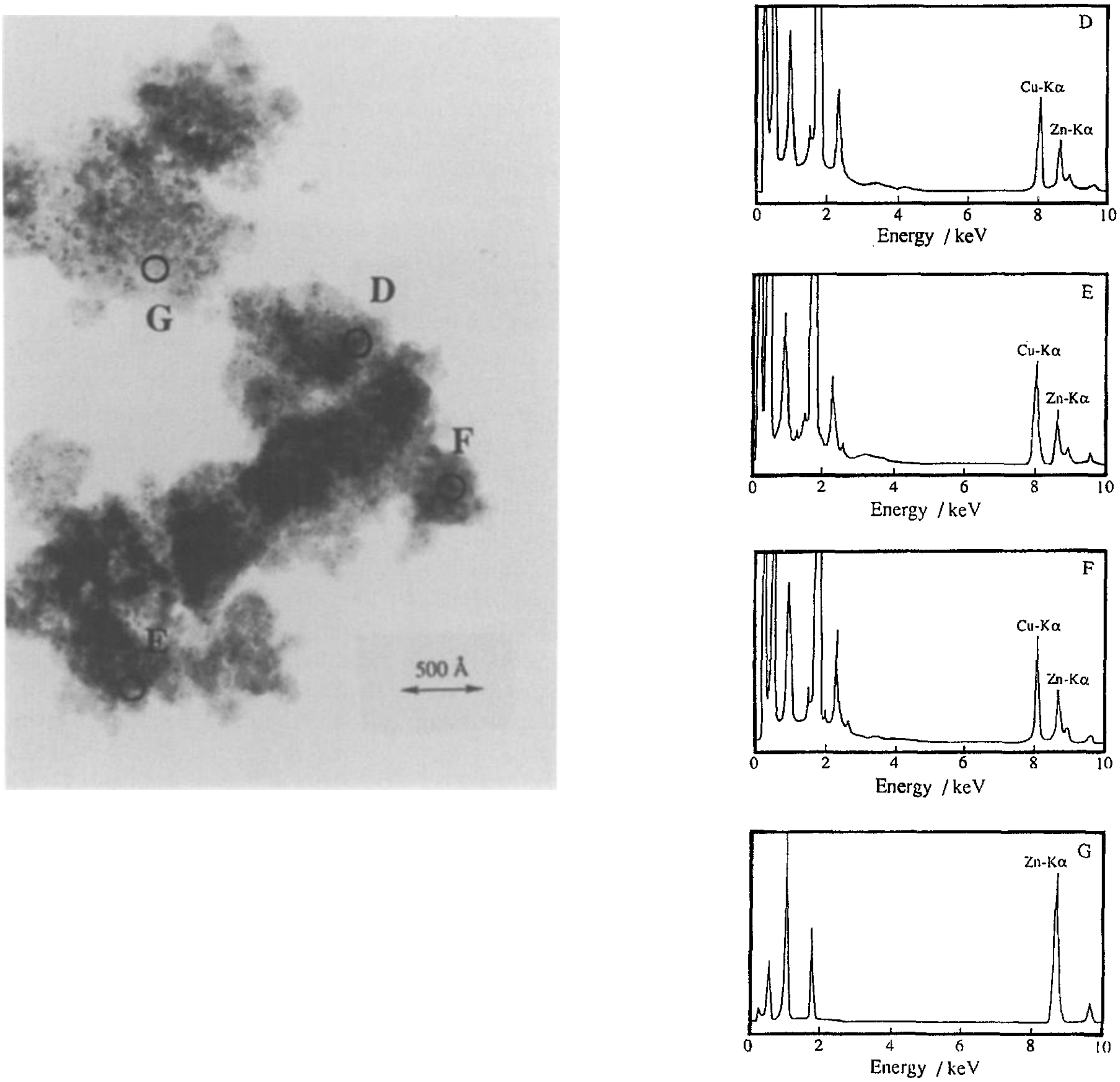

Fig.3. TEM micrograph of $Cu/SiO_2 + ZnO/SiO_2$ (1 : 0.5) reduced at 723 K for 5 h after physical-mixing, and the EDX spectra of local points labeled D, E, F and G on the micrograph. The peaks at 0.28, 0.52, 0.93, 1.01, 1.74, 2.29, 8.05, 8.64, 8.90, and 9.57 keV in the spectra correspond to the fluorescent X-rays of C Kα, O Kα, Cu Lα, Zn Lα, Si Kα, Mo Lα, Cu Kα, Zn Kα, Cu Kβ, and Zn Kβ, respectively.

previously carried out [11]. The oxygen adsorbed on the Cu surface was completely removed by the reduction with H_2 at 523 K and 5 MPa. Here, $\Theta_O = 0$ corresponds to a state of the Cu surface after the reduction at 523 K. Fig. 4 shows the oxygen coverage as a function of the reduction temperature for Cu/SiO_2 and the physical mixtures of Cu/SiO_2 and ZnO/SiO_2 with the ratio of 1 : 3. Clearly, the oxygen coverage for the physical mixtures increased from $\Theta_O = 0.08$ to 0.15 with increasing reduction temperature, while no change in the oxygen coverage upon reduction was observed for Cu/SiO_2, and the oxygen coverage of $\Theta_O = 0.07$ was less than those of the physical mixtures. The increase in the oxygen coverage was also observed for the other physical mixtures with different $Cu/SiO_2 : ZnO/SiO_2$ ratios. We have reported that the oxygen coverage is correlated to the catalytic activity for methanol formation [11]. That is, a volcano-shaped correlation between the oxygen coverage and the specific activity, shown in fig. 5, was obtained for the Cu catalysts containing various metal oxides, indicating that Cu^+ and Cu^0 spcies are both essential for methanol formation. Here, it is considered that the role of the metal oxides is to stabilize the Cu^+ species bound to metal oxides. In fig. 5, the open and closed circles represent the previous and present data, respectively. The present data is found to be well fitted to the correlation curve for the Cu-based catalysts, indicating that the effect of ZnO/SiO_2 in the physical mixtures on the catalytic activity is essentially identical to the effect for the Cu-based catalysts prepared by the coprecipitation method. Thus, the results in fig. 5 strongly suggest that ZnO_x moieties formed by the high temperature reduction of ZnO/SiO_2 migrate onto the surface of Cu of the Cu/SiO_2 particles and create active sites such as Cu^+–O–Zn.

The bulk of the Cu particles in Cu/SiO_2 and the physi-

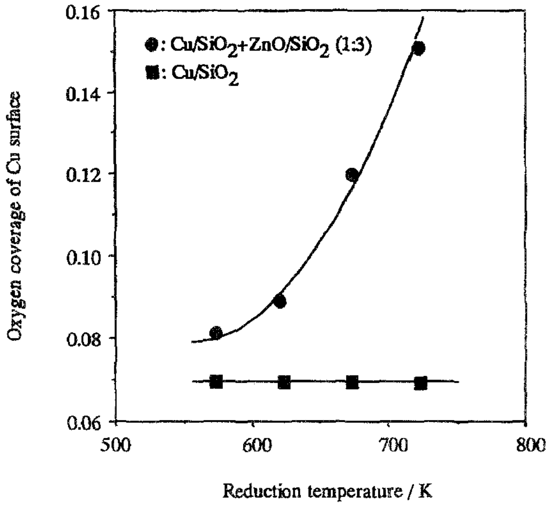

Fig.4. Oxygen coverage of a Cu surface for Cu/SiO_2 (■) and a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ with the volume ratio of 1 : 3 (●) as a function of reduction temperature.

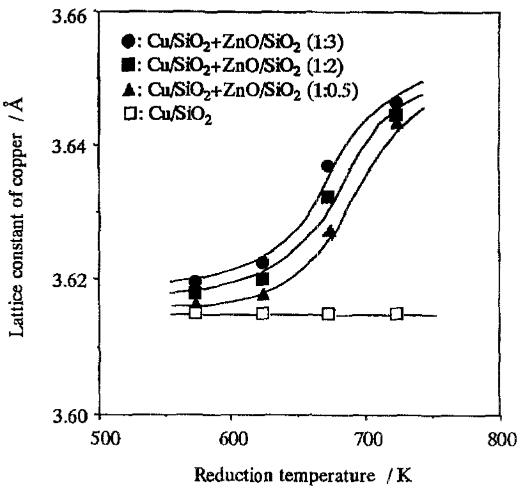

Fig.6. Lattice constant of the metallic copper in physical mixtures of $Cu/SiO_2 + ZnO/SiO_2$ with various volume ratios and Cu/SiO_2 as a function of reduction temperature. The lattice constants were calculated from the position of the Cu(111) line after Kα-2 elimination. $Cu/SiO_2 : ZnO/SiO_2$: 1 : 3 (●), 1 : 2 (■), and 1 : 0.5 (▲); Cu/SiO_2 (□).

cal mixtures of $Cu/SiO_2 + ZnO/SiO_2$ reduced at different temperatures were characterized by XRD. A peak appeared at around $2\Theta = 43°$ in XRD patterns for Cu/SiO_2 and the physical mixtures reduced at 573–723 K, which corresponds to the (111) line of metallic copper. From the position, the lattice constant of Cu was determined using the Bragg equation after Kα-2 elimination. The lattice constant of Cu for the physical mixture increased from 3.62 to 3.64 Å with reduction temperature, while no change in the lattice constant of Cu was observed for Cu/SiO_2 based on reduction temperature, as shown in fig. 6. The increase of the lattice constant can be attributed to the formation of Cu–Zn alloys, because it is known that there is a linear relationship between the lattice constant of Cu and the content of Zn in a Cu–Zn alloy at Zn contents less than 20% [21]. It is considered that ZnO_x species migrate onto the surface of Cu and dissolve into the Cu particle to form a Cu–Zn alloy. From the literature value [21], the average contents of Zn in the Cu particle for the physical mixture, $Cu/SiO_2 + ZnO/SiO_2$, reduced at 723 K were estimated to be 13–15 at% for the three mixtures with different ZnO/SiO_2 contents. The lattice constant of Cu for Cu/SiO_2 was exactly the same as the literature value of 3.615 Å for pure copper [21].

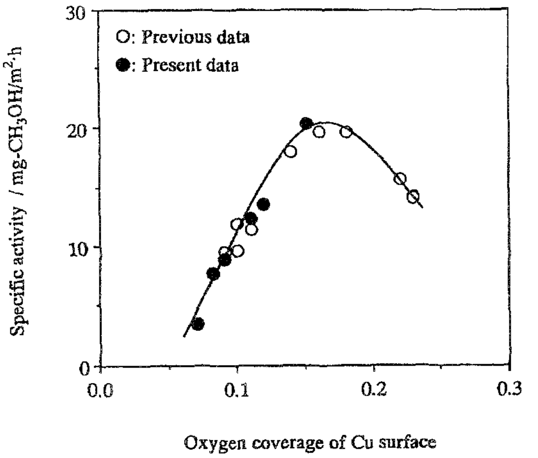

Fig.5. Specific activity for methanol formation as a function of oxygen coverage of a Cu surface for a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ with the volume ratio of 1 : 3 and Cu-based catalysts containing various metal oxides. Present data obtained using a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ (●); and previous data obtained using various Cu-based catalysts (O) [11].

4. Discussion

There is still no agreement on the synergetic effect of Cu and ZnO in Cu/ZnO catalysts on the activity for methanol synthesis. Burch et al. [22–25] have already shown the synergetic effect, where the activity of $Cu/SiO_2 + ZnO/SiO_2$ physical mixtures was higher than the sum of individual activities of Cu/SiO_2 and ZnO/SiO_2. The promotional effect was explained by a hydrogen-spillover mechanism: ZnO acts as a reservoir for atomic hydrogen. They speculated that hydrogen atoms migrate from ZnO to the Cu surface and promote hydrogenation of formate species. On the other hand, our previous data have shown that the specific activity of Cu-based catalysts supported by more than ten kinds of metal oxides is determined by the Cu^+/Cu^0 ratio on the surface of the Cu particles [11]. That is, an excellent volcano-shaped curve was obtained between the specific activity for methanol formation and the coverage of oxygen formed on the Cu surfaces during the hydrogenation of CO_2, where the activity increased with oxygen coverage below $\Theta_O < 0.16$ and then decreased above $\Theta_O > 0.18$. Thus, we have concluded that the role of ZnO in a Cu/ZnO catalyst is to stabilize Cu^+ species by creating a site such as Cu^+–O–Zn species. Although the hydrogen spillover may occur between Cu and ZnO particles, we have considered that the spillover is not responsible for the synergetic effect on the methanol synthesis activity.

In this paper, the migration of the ZnO_x species onto the Cu surface and the creation of active sites were confirmed based on the characterization of the Cu/SiO_2 and ZnO/SiO_2 physical mixtures reduced at various temperatures by EDX-TEM, XRD, and oxygen coverage measurements. The synergy model of the physical mixture is schematically shown in fig. 7, in which the ZnO_x species migrate from ZnO/SiO_2 onto the Cu particles at high reduction temperatures, and then partly cover the surface creating the active species such as Cu^+–O–Zn as well as dissolving into the Cu particles forming a Cu–Zn alloy. Currently, we speculate that the migration occurs through the gas phase in a state of metallic Zn because when Cu/ZnO catalysts were reduced at the high temperature of 723 K, the reactor was coated with metallic films, which should be Zn. A similar migration of Zn in a Cu/ZnO catalyst has been reported by Herwijnen et al. [26]. Note that the results obtained here are consistent with those of the model catalysts [13,27], i.e., Zn-deposited poly-Cu and Cu(111) studied by surface science methods. It has been clearly shown that the vapor deposition of Zn on poly-Cu or Cu(111) by heating a zinc wire promotes the methanol synthesis by an order of magnitude at optimal Zn coverage. The phenomena should be essentially the same as the present results for the powder catalysts of the physical mixtures ($Cu/SiO_2 + ZnO/SiO_2$). We consider that the role of the active sites created by introducing Zn on the Cu surface is to stabilize formate species, which are crucial intermediates related to the rate-determining step of methanol synthesis.

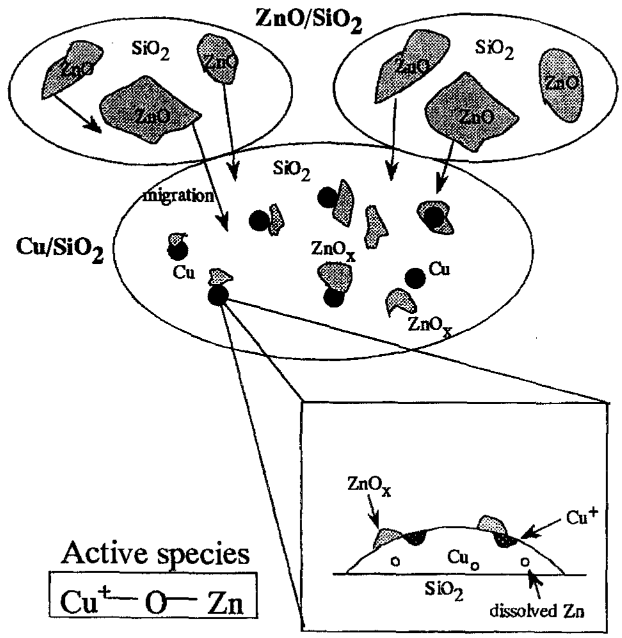

Fig.7. Synergy model for the methanol synthesis over a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$.

5. Conclusions

(1) The methanol synthesis activity of the physical mixtures of Cu/SiO_2 and ZnO/SiO_2 significantly increased with increasing reduction temperature in the range of 573–723 K, while no such change was observed for Cu/SiO_2.

(2) Migration of ZnO_x species from ZnO/SiO_2 particles onto the surface of Cu particles upon reduction in H_2 was confirmed by EDX-TEM, XRD and oxygen coverage measurements, where the migration was more significant at higher temperatures. The ZnO_x species that migrated onto the Cu surface partly covers the Cu surface leading to the creation of active species such as Cu^+–O–Zn, and partly dissolve into the Cu particles forming a Cu–Zn alloy.

(3) The synergy between Cu and ZnO in methanol synthesis catalysts is ascribed to the creation of active species on the Cu surface.

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