

The role of ZnO in Cu/ZnO methanol synthesis catalysts

J. Nakamura ^{a,*}, T. Uchijima ^a, Y. Kanai ^b, T. Fujitani ^c

^a Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

^b Research Institute of Innovative Technology for Earth, Tsukuba, Ibaraki 305, Japan

^c National Institute for Resources and Environment, Tsukuba, Ibaraki 305, Japan

Abstract

The methanol synthesis by the hydrogenation of CO_2 over Cu-based catalysts and Zn-deposited Cu(111) model catalysts was studied using XRD, TEM-EDX, reactive frontal chromatography, and surface science techniques such as XPS and AES. For the powder catalysts, a volcano-shaped relation between the oxygen coverage on the Cu surface and the specific activity for methanol formation was obtained, suggesting that a Cu^+/Cu^0 ratio on the surface control the catalytic activity. Experiments using a physical mixture of Cu/SiO_2 and ZnO/SiO_2 showed that ZnO_x species migrated from the ZnO particles onto the Cu surface upon reduction with H_2 , leading to the formation of the Cu^+ active species in the vicinity of the ZnO_x species on Cu. This model was proven by the surface science studies using partially Zn-deposited Cu(111), where the ZnO_x species on the Cu(111) surface promoted the catalytic activity of methanol formation, and a volcano-shaped relation between the Zn coverage on the Cu surface and the catalytic activity was obtained. The results definitely contradict the model of single Cu^0 active sites for methanol formation because the activity increased with decreasing Cu^0 surface area. On the other hand, the activity for the reverse water–gas shift reaction decreased with increasing Zn coverage.

Keywords: Zinc oxide; Copper; Methanol synthesis

1. Introduction

The synthesis of methanol from syngas ($\text{CO}-\text{H}_2-\text{CO}_2$) over Cu/ZnO-based catalysts is an important industrial process and one of the most investigated catalytic reactions. Despite a number of mechanistic studies conducted over some decades, there are still controversies concerning the active species of Cu and the role of ZnO promoting the catalytic activity [1]. Evidence that Cu^{n+} is the pivotal catalytic species for

methanol formation has been presented, based on the surface science studies using a Cu(100) model catalyst [2] and X-ray photoelectron spectroscopy (XPS) studies [3] of the alkali promoted Cu catalysts, while some researchers claim that metallic Cu is the active species for methanol synthesis [4–7]. The reason for the synergistic effect between Cu and ZnO is also ambiguous [8–10]. In this paper, we report that ZnO_x species on the Cu surface directly create active sites such as Cu^+ and promote the catalytic activity for methanol formation. This is proven by the experiments using both powder catalysts and Cu single crystal surfaces [11–13].

* Corresponding author.

2. Experimental

All the powder catalysts were prepared by a co-precipitation method using a mixed aqueous solution of metal nitrates (total metal concentration, 1 mol/l) and an aqueous solution of Na_2CO_3 (1.1 mol/l). The catalyst, fixed in a flow reactor, was reduced by flowing a gas mixture of H_2 (10%) and He (90%) at 523 K with a total pressure of 5.0 MPa. The hydrogenation of CO_2 was then carried out at 523 K by feeding H_2 and CO_2 ($\text{H}_2/\text{CO}_2 = 3$) at a total pressure of 5.0 MPa. The reaction products were analyzed by gas chromatographs directly connected to the reactor. Measurements of the copper surface area were carried out by monitoring the reaction of N_2O with Cu metal atoms: reactive frontal chromatography (RFC). The copper surface area during CO_2 hydrogenation (Cu_{react}) was also measured by the RFC technique just after the reaction without exposure to air. The coverage of oxygen (Θ_{O}) formed on the Cu surface during the reaction was estimated by the following equation:

$$\Theta_{\text{O}} = (\text{Cu}_{\text{total}} - \text{Cu}_{\text{react}}) / (\text{Cu}_{\text{total}} \times 2)$$

Here, we assumed that oxygen atoms left after the reaction are bonded to two Cu atoms and that $\Theta = 1$ corresponds to the number of copper surface atoms.

The characterization of the powder catalysts were performed by XRD (X-ray diffraction) and TEM coupled with energy-dispersive X-ray spectroscopy (EDX).

We also attempted to carry out surface science studies in which methanol synthesis over a Zn-deposited Cu(111) surface was examined using XPS and Auger electron spectroscopy (AES). The apparatus is basically composed of three chambers: an analysis chamber equipped with XPS and AES, a preparation chamber for changing the sample and for the deposition of Zn on the Cu(111) surface by resistibly heating a Zn wire, and a high pressure flow reactor which allows us to carry out the hydrogenation of CO_2 at 18 atm. The sample can be trans-

ferred between the chambers using a transfer rod and a manipulator without exposure to the atmosphere. The heater and thermocouple for controlling the sample temperature are attached to the rear side of the sample holder, which are located outside the reactor. The products and reactants were analyzed using an on-line gas chromatograph.

3. Results and discussion

3.1. Catalytic activity vs. oxygen coverage

The activity for methanol synthesis and the oxygen coverage after the reaction using various powder catalysts were measured to elucidate the effect of metal oxides contained in Cu catalysts as well as the role of oxygen adsorbed on the Cu surface. Fig. 1 shows the relationship between the specific activity and the oxygen coverage for the Cu catalysts containing metal ox-

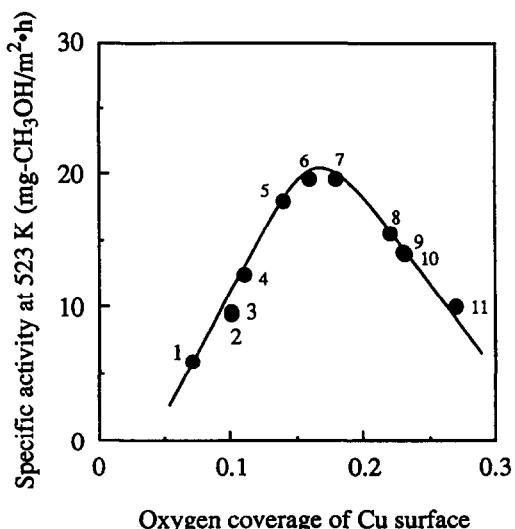


Fig. 1. Specific activity at 523 K as a function of oxygen coverage of the Cu surface for various Cu-based supported catalysts. The compositions (wt.%) are shown in parentheses. 1; Cu/SiO_2 , 2; $\text{Cu}/\text{Al}_2\text{O}_3(50/50)$, 3; Cu/ZrO_2 (50/50), 4; $\text{Cu}/\text{Cr}_2\text{O}_3$ (50/50), 5; $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ (50/40/10), 6; $\text{Cu}/\text{ZnO}/\text{Ga}_2\text{O}_3$ (50/25/25), 7; $\text{Cu}/\text{Ga}_2\text{O}_3$ (50/50), 8; $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ (50/45/5), 9; Cu/ZnO (50/50), 10; $\text{Cu}/\text{ZnO}/\text{ZrO}_2$ (50/25/25), 11; $\text{Cu}/\text{ZnO}/\text{La}_2\text{O}_3$ (50/45/5).

ides such as Ga_2O_3 , ZnO , Cr_2O_3 , ZrO_2 , Al_2O_3 , and SiO_2 . An excellent correlation was obtained, where the activity increased linearly with the oxygen coverage at below $\Theta_O = 0.16$, and then decreased at above $\Theta_O = 0.18$. The oxygen on the surface of Cu may stabilize Cu^+ as an active species. This is consistent with the data reported by King et al. [3], where the specific activity of Cu catalysts in the methanol synthesis increased with the content of Cu^+ formed by addition of alkalis (Li, Na, K, Rb, Cs) to the unsupported Cu catalysts. The decrease of activity at $\Theta_O > 0.18$ in this study also suggests that the active component is not only Cu^+ but also Cu^0 . Note that the relationship between the oxygen coverage (or Cu^+) and the specific activity was obtained for the Cu catalysts containing different metal oxides. These results thus provides evidence that the effect of metal oxide or the support effect may be ascribed to the difference in the amount of Cu^+ stabilized by both surface oxygen and foreign metals.

3.2. Physical mixture of Cu/SiO_2 and ZnO/SiO_2

To clarify the role of ZnO in the creation of active sites such as Cu^+ species, a physical mixture of Cu/SiO_2 and ZnO/SiO_2 was used as a catalyst after reduction with H_2 at different temperatures. Fig. 2 shows the methanol synthesis activity of the physical mixtures with the various volume ratios as well as Cu/SiO_2 as a function of the reduction temperature. Clearly, the specific activity significantly increased with increasing reduction temperature in the range 573 to 723 K. The increase in the activities was more remarkable at the higher contents of ZnO/SiO_2 in the physical mixtures. These showed 7-fold more activity than that of Cu/SiO_2 . This results show that the increase in the reduction temperature enhanced the synergy between Cu and ZnO .

The oxygen coverage on the Cu surface during the methanol synthesis was estimated by the adsorption of N_2O to characterize the Cu sur-

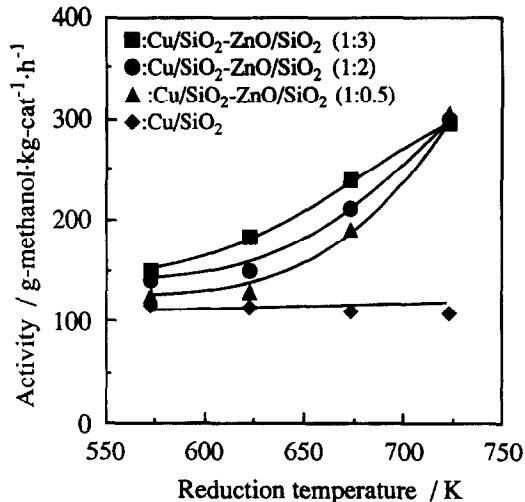


Fig. 2. Activity of Cu/SiO_2 and the physical mixtures of $\text{Cu}/\text{SiO}_2 + \text{ZnO}/\text{SiO}_2$ for methanol formation as a function of reduction temperature.

face in $\text{Cu}/\text{SiO}_2 + \text{ZnO}/\text{SiO}_2$ mixture. Fig. 3 shows the oxygen coverage as a function of reduction temperature for Cu/SiO_2 and a physical mixture (Cu/SiO_2 : $\text{ZnO}/\text{SiO}_2 = 1:0.5$). It is clear that the oxygen coverage for the physical mixture increases from $\Theta_O = 0.08$ to 0.15 with increasing reduction temperature, while no change in the oxygen coverage is observed upon the reduction for Cu/SiO_2 and the value of the

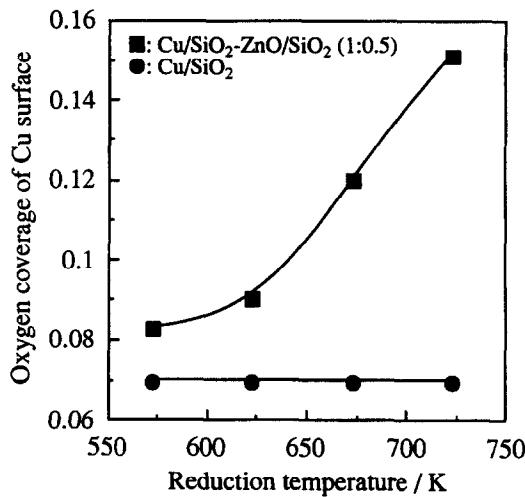


Fig. 3. Oxygen coverage on the Cu surface for Cu/SiO_2 and the physical mixtures of $\text{Cu}/\text{SiO}_2 + \text{ZnO}/\text{SiO}_2$ as a function of reduction temperature.

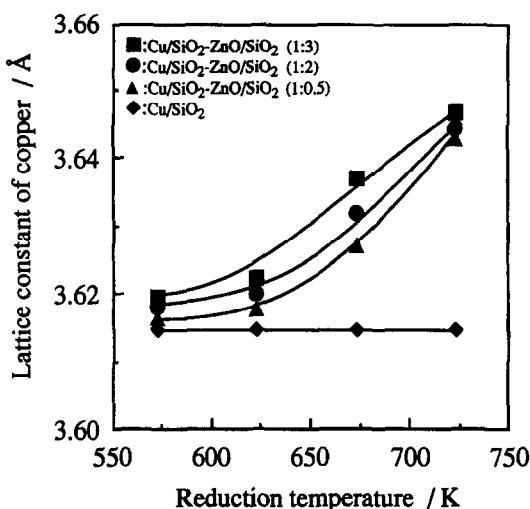


Fig. 4. Lattice constant of metallic copper in Cu/SiO_2 and the physical mixtures of $\text{Cu}/\text{SiO}_2 + \text{ZnO}/\text{SiO}_2$ as a function of reduction temperature.

$\Theta_O = 0.07$ is lower than those for the physical mixture. The increase in the oxygen coverage upon reduction was also observed for the physical mixtures with the different ratio of $\text{Cu}/\text{SiO}_2:\text{ZnO}/\text{SiO}_2$. The increase of oxygen coverage on the Cu surface suggests that the ZnO_x species migrate from the ZnO particles onto the Cu particles upon reduction at high temperatures. To probe this, XRD and TEM-EDX were used to characterize the Cu particles in the physical mixtures reduced at different temperatures. Fig. 4 shows the lattice constant of copper in Cu/SiO_2 and the physical mixtures measured by XRD as a function of the reduction temperature. The lattice constant of Cu was determined from the peak position of the (111) line using the Bragg equation. It was found that the lattice constant for the physical mixtures increased from 3.62 to 3.64 Å with reduction temperature, while no such a change in the lattice constant of Cu was observed for Cu/SiO_2 . The increase in the lattice constant was more remarkable for higher contents of ZnO/SiO_2 , indicating that the ZnO_x species migrated onto the Cu surfaces and dissolved into the Cu particles to form a Cu–Zn alloy. It is known that there is a linear relationship be-

tween the lattice constant of Cu and the content of Zn in Cu–Zn alloys in the range of Zn content less than 20 atomic % [14]. From the literature value [14], the average content of Zn in the Cu particles was estimated to be 13–15 atomic % for the physical mixtures reduced at 723 K with different ZnO/SiO_2 content. The lattice constant of Cu for Cu/SiO_2 was exactly the same as the literature value of 3.615 Å for pure copper.

The XRD results described above strongly suggest that the ZnO_x species migrate to the Cu particles in the physical mixtures. Thus, elemental analyses to confirm the presence of Zn atoms in the Cu particles were performed using TEM coupled with EDX, which can analyze a local site with a resolution of 50 Å. Fig. 5 shows the photo obtained by the TEM measurement for the physical mixture ($\text{Cu}/\text{SiO}_2:\text{ZnO}/\text{SiO}_2 = 1:0.5$) reduced at 573 K. The results of the elemental analysis on the spots A–C by EDX are also shown in Fig. 5. The copper, zinc, silicon, and oxygen atoms were detected with the presence of carbon and molybdenum which are due to the materials of a microgrid and a collodion film. For the spot C, no copper was detected, but zinc was detected, indicating that the spot C corresponds to a ZnO/SiO_2 particle, where small black spots were assigned to ZnO particles. It is also indicative of no migration of Cu atoms into ZnO particles. On the other hand, coexistence of Zn with Cu was observed in spots A and B. These particles involving the spots A and B correspond to Cu/SiO_2 , where black and white phases are Cu and SiO_2 , respectively. The atomic contents of Zn or $\text{Zn}/(\text{Cu} + \text{Zn})$ for the spots A and B were estimated to be 22.3 and 27.3%, respectively, based on the elemental sensitivity for the yield of X-ray fluorescence. The coexistence of Zn with Cu was also observed for the physical mixture reduced at 723 K, and the Zn contents were estimated to be 30–40%, indicating that the Zn content in the Cu particles increased with the reduction temperature. This is consistent with the results of XRD on the migration of

ZnO_x to Cu particles to form Cu–Zn alloy, which is more remarkable at higher temperatures. However, the content of Zn in the bulk of a Cu particle is possibly overestimated because the size of a spot (ca. 50 Å) analyzed by TEM is larger than that of a Cu particle.

From the results of XRD, TEM, and EDX, the synergy between Cu and ZnO in the physical mixture catalyst can be explained by the model that the ZnO_x moieties formed by the reduction of ZnO/SiO_2 at 573–723 K migrate onto the surface of Cu particles, and the ZnO_x partly dissolve into the bulk of copper to form Cu–Zn alloy, and partly cover the surface of Cu creating the $\text{Cu}^+–\text{O}–\text{Zn}$ sites. Accordingly, the role of ZnO is ascribed to the stabilization of

Cu^+ species which are the pivotal catalytic species for methanol synthesis.

3.3. Zn-deposited Cu(111) model catalyst

To prove the proposed ZnO_x promotional model, we attempted to carry out UHV studies in which methanol synthesis over the Zn-deposited Cu(111) was examined using surface science techniques. We successfully detected methanol in the hydrogenation of CO_2 on the Zn-deposited Cu(111) because of the high pressure of the reactants (18 atm). Fig. 6 shows the turnover frequencies (TOF) for the methanol synthesis at 523 K as a function of the Zn coverage on Cu measured by XPS after the

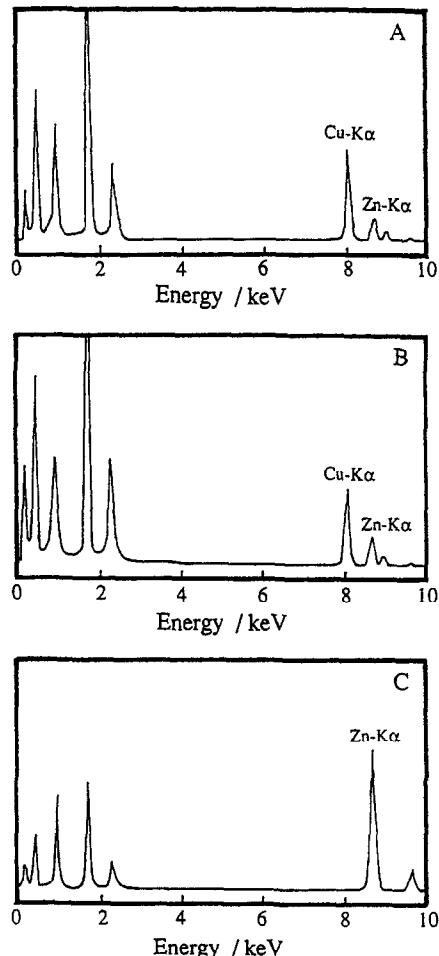
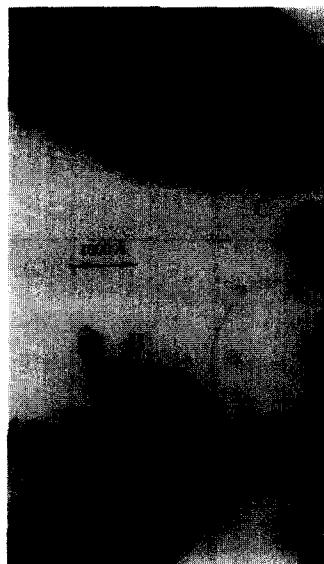


Fig. 5. TEM photograph and EDX analysis of the physical mixture of $\text{Cu}/\text{SiO}_2 + \text{ZnO}/\text{SiO}_2$ reduced at 523 K.

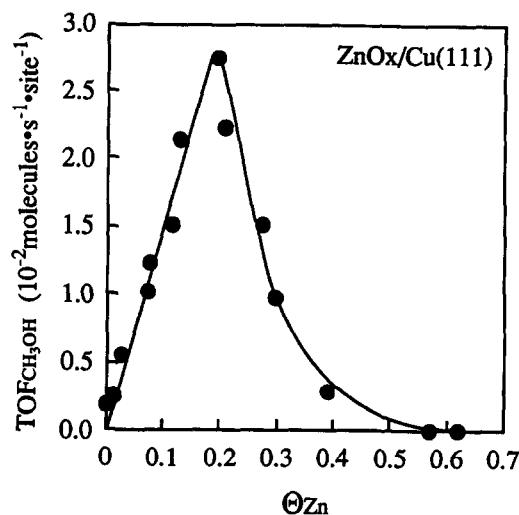


Fig. 6. Turnover frequency (TOF) for methanol formation at 523 K as a function of the Zn coverage on the $\text{ZnO}_x/\text{Cu}(111)$ model catalyst.

reaction, where the reactant gas was evacuated after cooling the sample to ca. 373 K. Here, Zn is oxidized to ZnO_x by the reaction mixture as described later. The coverage $\Theta = 1$ corresponds to the number of Cu surface atoms (1.77×10^{15} atoms/cm²). The yield of methanol was of the order of $3 \times 10^{-4}\%$ at a TOF of 2×10^{-2} molecules/sites s, which was much less than the equilibrium conversion of 6.2%, implying that the reaction occurring is far from equilibrium. It is shown that the TOF increases with Θ_{Zn} below $\Theta_{\text{Zn}} = 0.19$, and then decreases above $\Theta_{\text{Zn}} = 0.19$. These results definitely contradict a model of Cu^0 single active sites because the activity increased with Θ_{Zn} in spite of the decrease in the surface area of metallic Cu. That is, new active sites are created on the Zn-deposited Cu(111).

Fig. 7 shows the Arrhenius plots for methanol formation over clean Cu(111), Zn-deposited Cu(111) ($\Theta_{\text{Zn}} = 0.19$), and a Cu/ZnO powder catalyst, where the activation energy was estimated as 73.6, 83.7, and 69.3 kJ mol⁻¹, respectively. No significant difference was seen for the activation energies over the model and powder Cu/ZnO catalysts. Further, the TOF for Zn-deposited Cu(111) and the Cu/ZnO catalyst

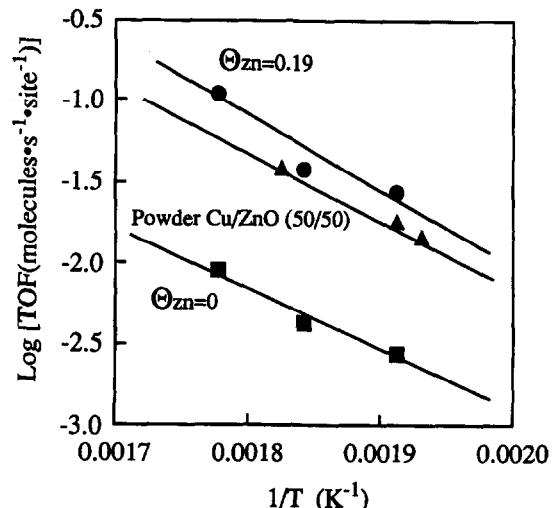


Fig. 7. Arrhenius plot of TOF for methanol formation for a Cu/ZnO powder catalyst and $\text{ZnO}_x/\text{Cu}(111)$ model catalysts.

was very close. Thus, it is safe to conclude that the Zn-deposited Cu(111) is a model of the Cu/ZnO catalyst.

The reverse water-gas shift (RWGS) reaction, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$, also occurred on the Zn-deposited and Zn-free Cu(111) surfaces, as recognized by the formation of CO. Fig. 8 shows the TOF for CO formation as a function of Θ_{Zn} at the reaction condition of Fig. 1 (523 K, 18 atm), where the amount of CO, depending

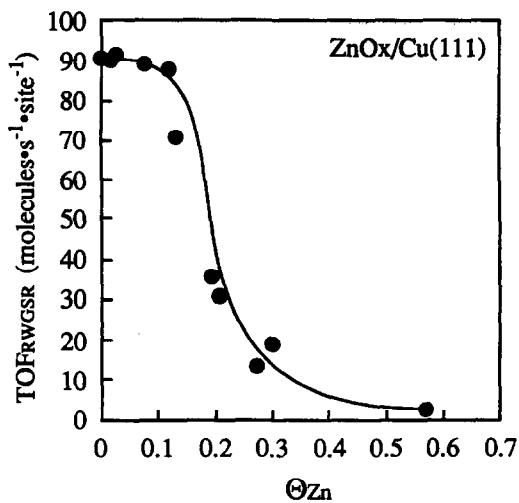


Fig. 8. Turnover frequency (TOF) for the water-gas shift reaction at 523 K as a function of the Zn coverage on the $\text{ZnO}_x/\text{Cu}(111)$ model catalyst.

on Θ_{Zn} , was 3–4 orders of magnitude larger than that of methanol. In contrast with methanol, the TOF of CO decreased with increasing Θ_{Zn} , indicating no promotional effect of Zn deposited on Cu(111) upon catalytic activity of the RWGS reaction. Thus, we consider that Cu^0 is active sites for the RWGS reaction. It seems, however, that the decrease in TOF of CO in Fig. 8 corresponds to the decrease in TOF of methanol above $\Theta_{Zn} = 0.19$, suggesting that Cu^0 is also necessary for hydrogenation step in the methanol synthesis.

In the post-reaction surface analysis by XPS, the C 1s and O 1s peaks attributable to formate species on the Zn-deposited Cu(111) were observed at 288.8 and 531.8 eV, respectively [15]. The Zn 2p 3/2 peak at 1021.1 eV for the Zn-deposited Cu(111) before reaction, which value was slightly less than that of metallic Zn (1021.4 eV) [16], shifted to higher energies by ca. 0.7 eV, accompanied by the O1s peaks due to oxygen in ZnO species at 530.4 eV. This indicates the oxidation of Zn to ZnO_x . The zinc tends to be oxidized to ZnO_x ($x = 0.5–1.0$) at high Zn coverage $\Theta_{Zn} > 0.15$, while below $\Theta_{Zn} = 0.15$ the Zn was not readily oxidized to ZnO_x . At the low Zn coverage $\Theta_{Zn} < 0.15$, the formate coverage increased with Zn coverage, suggesting that the role of the active sites is to stabilize the formate species. Currently, we infer that the active species is $Cu^{+}–O–Zn^{n+}$ or $Cu^{\delta+}–Zn^{\delta-}$.

4. Conclusions

(1) An excellent correlation was obtained between the specific activities for methanol formation and the oxygen coverages for the Cu catalysts containing metal oxides such as Ga_2O_3 , ZnO , Cr_2O_3 , ZrO_2 , Al_2O_3 , and SiO_2 . The activity increased linearly with the oxygen coverage below $\Theta_O = 0.16$, and then decreased above $\Theta_O = 0.18$. The results suggest that the active component is not only Cu^+ but also Cu^0 , and the ratio of Cu^+/Cu^0 control the specific activity.

(2) The specific activity as well as the oxygen coverage on Cu of the physical mixtures of Cu/SiO_2 and ZnO/SiO_2 increased with increasing reduction temperature in the range 573 to 723 K. High-temperature reduction resulted in an increase of the lattice constant of Cu, suggesting the formation of a Cu–Zn alloy. This was then proved by TEM-EDX results that the ZnO_x moieties formed by the reduction of ZnO/SiO_2 migrate onto the surface of the Cu particles; the ZnO_x partly dissolves into the bulk of the copper to form a Cu–Zn alloy, and partly covers the surface of Cu creating a $Cu^{+}–O–Zn$ site. Accordingly, the role of ZnO is ascribed to the stabilization of Cu^+ species, the pivotal catalytic species for the methanol synthesis.

(3) To prove the ZnO_x promotional model proposed in the studies of powder catalysts, methanol synthesis was performed over the Zn-deposited Cu(111) using surface science techniques. The TOF of methanol formation increased with Θ_{Zn} below $\Theta_{Zn} = 0.19$, and then decreased above $\Theta_{Zn} = 0.19$. These results definitely contradict a model of Cu^0 single active sites because the activity increased with decreasing surface area of metallic Cu. No significant difference was seen for the activation energy and the TOF for the Zn-deposited Cu(111) and the powder Cu/ZnO catalyst, indicating that the Zn-deposited Cu(111) is a good model of Cu/ZnO catalyst. The RWGS reaction also occurred on the Zn-deposited and Zn-free Cu(111) surfaces. The TOF of CO, however, decreased with increasing Θ_{Zn} , indicating that there was no promotional effect of Zn upon the catalytic activity.

Acknowledgements

This work was partly supported by New Energy and Industrial Technology Development Organization.

References

- [1] J.C.J. Bart and R.P.A. Sneeden, *Catal. Today*, 2 (1987) 1.
- [2] J. Szanyi and D.W. Goodman, *Catal. Lett.*, 10 (1991) 383.
- [3] G.R. Sheffer and T.S. King, *J. Catal.*, 115 (1989) 376; *ibid.*, 116 (1989) 488.
- [4] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, *J. Chem. Soc., Faraday Trans.*, 83 (1987) 2193.
- [5] G.C. Chinchen, K.C. Waugh and D.A. Whan, *Appl. Catal.*, 25 (1986) 101.
- [6] W.X. Pan, R. Cao, D.L. Roberts and G.L. Griffin, *J. Catal.*, 114 (1988) 440.
- [7] P.B. Rasmussen, P.M. Holmblad, C.V. Askgaard, C.V. Ovesen, P. Stoltze, J.K. Norskov and I. Chorkendorff, *Catal. Lett.*, 26 (1994) 373.
- [8] R. Burch, R.J. Chappel and S.E. Golunski, *J. Chem. Soc., Faraday Trans. 1*, 85 (1989) 3569.
- [9] R. Burch, S.E. Golunski and M.S. Spencer, *J. Chem. Soc., Faraday Trans.*, 86 (1990) 2683.
- [10] J.C. Frost, *Nature*, 334 (1988) 577.
- [11] T. Fujitani, M. Saito, Y. Kanai, T. Kakumoto, T. Watanabe, J. Nakamura and T. Uchijima, *Catal. Lett.*, 25 (1994) 271.
- [12] Y. Kanai, T. Watanabe, T. Fujitani, M. Saito, J. Nakamura and T. Uchijima, *Catal. Lett.*, 27 (1994) 67.
- [13] J. Nakamura, I. Nakamura, T. Uchijima, Y. Kanai, T. Watanabe, M. Saito and T. Fujitani, *Catal. Lett.*, 31 (1995) 325.
- [14] N. Suzuki, *Kinzoku Data Book*, Maruzen Press, Tokyo, 1993.
- [15] M. Bowker and R.J. Madix, *Surf. Sci.*, 102 (1981) 542.
- [16] G.E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN, 1979.