The role of metal oxides in promoting a copper catalyst for methanol synthesis

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The coverage of oxygen formed on the surface of catalysts during methanol synthesis from CO_2 has been measured for copper-based catalysts including various metal oxides using a method called reactive frontal chromatography (RFC). An excellent correlation between the specific activity for methanol synthesis and the oxygen coverage (Θ) was obtained, where the activity increased linearly with oxygen coverage at $\Theta < 0.16$ and then decreased at $\Theta > 0.18$. The results strongly indicate that the support effect or addition of metal oxides revealed in methanol synthesis over copper catalysts is ascribed to the ratio of Cu^+ to Cu^0 on the surface of copper particles.

Keywords: methanol synthesis; copper catalyst; oxygen coverage

1. Introduction

Methanol synthesis from CO_2 and H_2 has recently received much attention as one of the promising processes to convert CO_2 into raw materials for fuels and chemicals. Copper-based catalysts are highly effective for this reaction [1–3], and a number of mechanistic studies have been done concerning the valence state of copper when working as an active center and the effect of supports such as ZnO, Cr_2O_3 and Al_2O_3 [4–6].

Sheffer and King [7,8] have reported that the activity for methanol synthesis from CO over unsupported copper catalysts increases with the concentration of

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Cu^+ sites which are stabilized by alkali compounds. The Cu^+ as well as Cu^0 is possibly an active species for methanol synthesis from CO_2, where carbonate [9], formate, and methoxy species [10] may be intermediates. Szanyi and Goodman [11] have demonstrated that methanol synthesis activity of an oxidized Cu(100) surface was higher than that of an oxygen-free Cu(100) by a factor of two, and concluded that the very low activity of clean Cu(100) was attributed to low concentration of ionic copper. On the other hand, the effect of support, mainly ZnO, on the activity for methanol synthesis has been controversial, despite a large amount of research. Chinchen et al. have reported [2,12,13] that the reaction occurs exclusively on the surface of metallic copper and the activity is directly proportional to copper surface area. They have concluded that ZnO has no special role in the synthesis of methanol. However, several groups have reported [3,14,15] evidence of synergy between Cu and ZnO.

The present paper reports the relationship between the specific methanol activity, i.e., mass–time yield of methanol per copper surface area, and the oxygen coverage for various copper-based catalysts. The essential support effect factor will be explained based on the ratio of Cu^+ to Cu^0 on the surface of copper particles.

2. Experimental

All catalysts were prepared by a coprecipitation method. 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) were added dropwise to distilled water. Subsequently, the precipitate was filtered out, washed with distilled water, dried in air at 393 K overnight, calcined in air at 623 K for 2 h, and finally screened to size between 60 and 80 mesh. 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 the 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 means of gas chromatographs directly connected to the reactor. A routine and reproducible measurement of copper surface area is available by monitoring the reaction of N_2O with copper atoms [16,17,18]. The most convenient form of this method for in situ applications is called reactive frontal chromatography (RFC) [2,19], which is readily employed in the microreactor for assessing copper surface area. After the methanol synthesis reaction, CO_2 and H_2 were depressurized and swept out of 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 RFC technique after rereducing the post-reaction catalysts with H_2 at 523 K. The following equation was used to calculate the oxygen coverage (Θ):

$$\Theta = (\mathrm{Cu_{total}} - \mathrm{Cu_{react}})/(\mathrm{Cu_{total}} \times 2)\,.$$

Here, we assumed that a N_2O molecule reacts with two Cu atoms, which was in agreement with surface science data [20,21], that is, the saturation coverage of O_a on the low index plane of copper was $\Theta \approx 0.5$, where $\Theta = 1$ corresponded to the number of copper surface atoms.

3. Results and discussion

The activities for methanol synthesis and oxygen coverage after the reaction using various catalysts were measured to elucidate the effect of metal oxides contained in copper catalysts and the role of oxygen adsorbed on the copper surface. As shown in table 1, it is clear that the specific activities were different for the various catalysts, indicating an effect of metal oxides contained in the copper catalysts on the methanol synthesis. The order of metal oxides on the specific activity was $Ga_2O_3 > ZnO > Cr_2O_3 > ZrO_2 \approx Al_2O_3 > SiO_2$. In this study, Ga_2O_3 was found to be a more effective material for methanol synthesis than ZnO which is a suitable metal oxide for copper catalysts. The specific activities of Cu/Cr_2O_3, Cu/ZrO_2, and Cu/Al_2O_3 were also promoted by adding ZnO to these three catalysts, where the activities increased with an increase in the ZnO content as seen in table 1.

Fig. 1 shows the relationship between the specific activities and the oxygen coverage which are listed in table 1. An excellent correlation was obtained, where the activity increased linearly with the oxygen coverage at below $\Theta = 0.16$, and then decreased at above $\Theta = 0.18$. The oxygen on the surface of copper may stabilize Cu^+ which is a possible active center that several authors have pointed out [8,10,22]. The results are consistent with data reported by King et al. [8], where the specific activity of the Cu catalyst in methanol synthesis increases with the content of Cu^+ which is formed by the addition of alkali (Li, Na, K, Rb, Cs) to unsupported copper catalysts. However, in our studies, the decrease in activity at $\Theta > 0.18$ was also seen, which suggests that the active component is not only Cu^+ but also Cu^0. Note that the relationship between oxygen coverage (or Cu^+) and specific activity was obtained for various copper catalysts containing different metal oxides. Therefore, the present results provided evidence that the effect of contained metal oxides or the support effect is ascribed to the difference in the amount of Cu^+ stabilized by both surface oxygen and foreign elements.

The increase in specific activity with the oxygen coverage at $\Theta < 0.16$ suggests that the rate determining step during methanol synthesis requires the Cu^+ sites rather than the Cu^0 sites. Waugh et al. have reported [9] that CO_2 is hydrogenated to methanol through carbonate, formate, and methoxy adspecies on the surface of

Table 1
Activities[a], Cu surface area and oxygen coverage of various catalysts

Catalyst	Composition (wt%)	MTY[b] (g-CH_3OH/kg-cat h)	Re-reduced Cu surface area after reaction (m^2/g-cat)	Cu surface area after reaction (m^2/g-cat)	Specific activity (mg-CH_3OH/m^2)	Oxygen coverage of Cu surface
Cu/SiO_2	30/70	116	19.5	16.8	3.5	0.07
Cu/ZnO	50/50	516	36.5	19.6	14.1	0.23
Cu/ZnO/Al_2O_3	50/45/5	721	46.1	25.4	15.6	0.22
Cu/ZnO/Al_2O_3	50/10/40	297	25.0	20.0	11.9	0.10
Cu/Al_2O_3	50/50	216	22.7	18.3	9.5	0.09
Cu/ZnO/Ga_2O_3	50/25/25	738	37.6	23.9	19.6	0.18
Cu/Ga_2O_3	50/50	350	17.9	12.2	19.6	0.16
Cu/ZnO/Cr_2O_3	50/40/10	570	31.6	23.0	18.0	0.14
Cu/ZnO/Cr_2O_3	50/10/40	228	19.8	15.5	11.5	0.11
Cu/Cr_2O_3	50/50	167	13.5	10.5	12.4	0.11
Cu/ZnO/ZrO_2	50/25/25	620	43.7	23.2	14.2	0.23
Cu/ZrO_2	50/50	138	14.4	11.5	9.6	0.10

[a] Reaction conditions: $H_2/CO_2 = 3$, feed gas rate = 300 cm^3/min, total pressure = 5.0 MPa, catalysts weight = 1.0 g.

[b] Mass–time yield per gram of catalyst at 523 K.

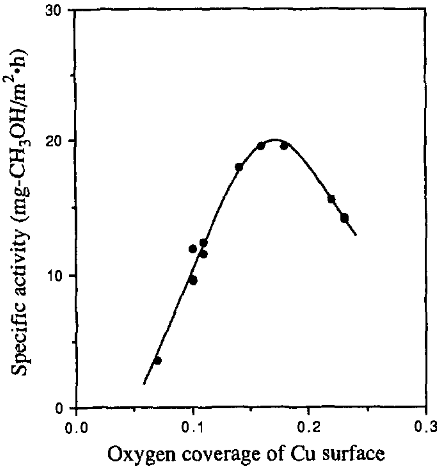

Fig. 1. Specific activity at 523 K as a function of oxygen coverage of Cu surface for various catalysts listed in table 1.

copper. The role of Cu^+ may be due to the stabilization of any oxygenates near the Cu^+ sites.

The oxygen should be formed by the dissociation of CO_2:

$$CO_{2g} \rightarrow O_a + CO_g .$$

On the low index plane of copper, the dissociation of CO_2 is considerably slow [23], and O_a easily reacts with CO and H_2. In contrast, the oxygen, which is measured in this study, may be rather stable and bound to both Cu and other elements such as Zn, Ga, Cr, Al, where the CO_2 dissociation may easily take place. Recently, we observed [24] Zn atoms in copper particles for Cu/ZnO catalysts after reducing with H_2 at temperatures as high as 723 K, indicating that partially reduced ZnO_x migrates on the copper particles. The effect of metal oxides, therefore, can be explained by the role of Cu^+ site formation at the interface between a Cu particle and a metal oxide moiety which is located on the surface of Cu or near the perimeter of the Cu particles.

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References

[1] G.C. Chinchen, M.S. Spencer, K.C. Waugh and D.A. Whan, J. Chem. Soc. Faraday Trans. 83 (1987) 2193.

[2] G.C. Chinchen, K.C. Waugh and D.A. Whan, Appl. Catal. 25 (1986) 101.
[3] R. Burch, S.E. Golunski and M.S. Spencer, J. Chem. Soc. Faraday Trans. 86 (1990) 2683.
[4] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) 263.
[5] E.M. Calverley and K.J. Smith, Ind. Eng. Chem. Res. 31 (1992) 792.
[6] R. Burch and R.J. Chapell, Appl. Catal. 45 (1988) 131.
[7] G.R. Sheffer and T.S. King, J. Catal. 115 (1989) 376.
[8] G.R. Sheffer and T.S. King, J. Catal. 116 (1989) 488.
[9] G.J. Millar, C.H. Rochester and K.C. Waugh, Catal. Lett. 14 (1992) 289.
[10] L.E.Y. Nonneman and V. Ponec, Catal. Lett. 7 (1990) 213.
[11] J. Szanyi and D.W. Goodman, Catal. Lett. 10 (1991) 383.
[12] G.C. Chinchen, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh and D.A. Whan, ACS Symposium on Methanol Synthesis, Philadelphia 1984.
[13] G.C. Chinchen, D.J. Denny, J.R. Jennings, M.S. Spencer and K.C. Waugh, Appl. Catal. 36 (1986) 1.
[14] R. Burch, R.J. Chappell and S.E. Golunski, Catal. Lett. 1 (1988) 439.
[15] R. Burch, S.E. Golunski and M.S. Spencer, Catal. Lett. 5 (1990) 55.
[16] M.R. Dell, S.F. Stone and F.P. Tiley, Trans Faraday Soc. 49 (1953) 195.
[17] B. Dvorak and J. Pasek, J. Catal. 18 (1970) 108.
[18] W.J. Evans, S.M. Wainwright, J.A. Bridgewater and J.D. Young, Appl. Catal. 7 (1983) 75.
[19] G.C. Chinchen and K.C. Waugh, J. Catal. 97 (1986) 280.
[20] F.H.P.M. Habraken, E. Kieffer and G.A. Bootsma, Surf. Sci. 83 (1980) 45.
[21] F.H.P.M. Habraken, C.M.A.M. Masters and G.A. Bootsma, Surf. Sci. 97 (1980) 264.
[22] K. Klier, V. Chatikavaij, R.G. Hevman and G.W. Simmons, J. Catal. 74 (1982) 343.
[23] J. Nakamura, J.A. Rodriguez and C.T. Campbell, J. Phys. Condens. Matter 1 (1989) SB149.
[24] Y. Kanai, T. Watanabe and M. Saito, CO_2 Chemical Workshop, Hemavan 1993.