

Study on CO Adsorption on *in-situ* Brass Formed Cu/ZnO

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The isotherms of CO adsorption on the Cu/ZnO sample treated with hydrogen and methanol are investigated. The heats of adsorption of CO on the Cu/ZnO treated with hydrogen at 723 K for 3 h are in the range from 25.7 kJ/mol at $\theta = 0.8$ to 59.8 at $\theta = 0.1$, while those on the Cu/ZnO sample treated with methanol at 523 K for 3 h are in the range 30.3 kJ/mol at $\theta = 0.8$ to 99.8 kJ/mol at $\theta = 0.1$. The Cu/ZnO samples treated with methanol have the higher heats of adsorptions than the Cu/ZnO samples treated with hydrogen do. The heats of adsorption at $q = 0.1$ increase with the methanol treatment time within 30 min and leveled off afterwards.

Key Words : CO adsorption, Heat of adsorption, Brass formation, Cu/ZnO

Introduction

The Cu/ZnO based catalysts have been investigated for methanol synthesis and shift reaction. The synergistic effects of Cu and ZnO have been studied for several decades in the aspects of electronic properties of copper or zinc oxide,¹ mechanisms featuring spillover,²⁻⁶ and specific interaction at the Cu/ZnO interface.⁷ It has been considered that Cu can be alloyed with ZnO reduced in the vicinity of copper,⁸⁻⁹ since ZnO can be reduced in the presence of copper with methanol stream.¹⁰ The structural changes of Cu/ZnO catalysts following the Cu/Zn alloy formation have been studied by the XRD and XPS measurement,¹¹ FT-IR study,¹² and QEXARFS/XRD study.¹³ Recently, it is suggested that the Cu-Zn alloy catalysts for methanol synthesis had the higher reaction rates for methanol synthesis from the structural analysis by XRD.¹⁴ However, it was reported that the Cu-Zn alloy could be formed on the Cu/ZnO treated in the methanol stream and the zinc concentrations in Cu-Zn alloy were quantitatively analyzed.^{10,11} In the present study, CO adsorption behaviors on the Cu-Zn alloy formed *in-situ* at 523 K in a methanol stream are studied.

Experimental Section

The CuO/ZnO catalysts with copper/zinc oxide mol ratio of 1 : 1 were prepared by co-precipitation of metal acetate at pH 7 as previously described.¹¹ A solution containing 1 mol of ammonium carbonate in 400 mL distilled water was added to a solution containing 0.1 mol of copper acetate and 0.1 mol of zinc acetate in 500 mL. The slurry was stirred at room temperature for 2 h and the precipitate was washed, filtered, and dried in a vacuum oven. The dried sample was calcined at 723 K for 16 h.

The CO chemisorption was conducted with ASAP 2000 (Micromeritics, Co). The samples were pretreated to remove water and impurity in a vacuum at 393 K for 12 h. The out-gassed CuO/ZnO samples were treated in 5% H₂/Ar at 573 K for 3 h before the CO adsorption measurement. The Cu/

ZnO samples reduced with hydrogen were further treated at 523 K in a methanol stream and evacuated at 523 K for 12 h. Then, the CO adsorptions for the Cu/ZnO sample treated with methanol were conducted. Methanol was introduced into the sample probe through the thermostated methanol saturator with a He carrier gas. The methanol concentration in He gas was 9.2 mol %.

Results and Discussion

Figure 1 shows the partial pressure and temperature effects on the CO adsorptions at 298 K on the Cu/ZnO reduced at 723 K for 3 h with 5% H₂/Ar. The amounts of CO adsorbed

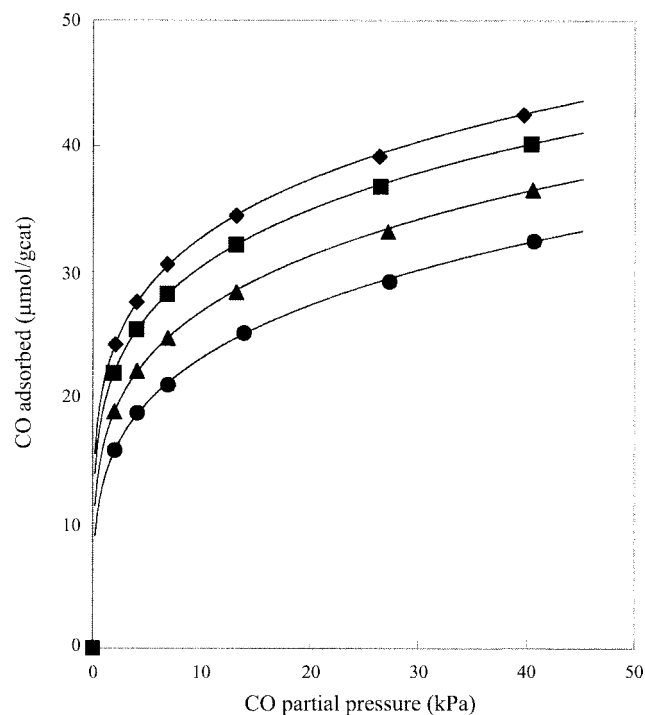


Figure 1. Isotherm of CO chemisorption on the hydrogen reduced Cu/ZnO sample; adsorption temperature: (◆) 298 K, (■) 318 K, (▲) 338 K, (●) 358 K; (symbol) experimental data, (line) Freundlich isotherm.

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decrease with the increased adsorption temperature, indicating the CO adsorption on the Cu/ZnO sample is not activated. It has been reported that CO on ZnO is not adsorbed above the temperature of 250 K.¹⁶ Therefore, the amount of the adsorbed CO is due to the reduced Cu in the Cu/ZnO. The amounts of CO adsorbed increase with the partial pressure of CO. No saturation limit is expected from the isotherms.

Parris and Klier¹⁵ described that CO adsorption isotherms on the Cu/ZnO catalysts were saturated above 13 kPa. However, it should be stressed that the isotherms on the Cu/ZnO with the Cu to Zn ratio of 1/9 and 4/7 in results of Parris and Klier increased with CO partial pressure without the saturation like the results in this study. The adsorption data in this study are well fitted to Freundlich isotherm equation (eq. (1)) as shown in Figure 1, indicating that the surface of the Cu/ZnO is an energetically heterogeneous:

$$\theta = kP^{1/n} \quad (1)$$

Where, k and n are constants at a given temperature. The Freundlich isotherm is expected that θ will increase continually with CO pressure. The theory¹⁶ indicates that

$$n = -\Delta H_m / RT \quad (2)$$

$$-\Delta H_a = +\Delta H_m \ln \theta, \quad (3)$$

Where, $-\Delta H_a$ being the heat of adsorption at coverage θ and H_m a constant.

Therefore, the heat of adsorption at coverage θ can be calculated from the plot of $\ln(P)$ v.s $1/T$. Figure 2 shows the adsorption isosteres for CO on the Cu/ZnO catalyst.

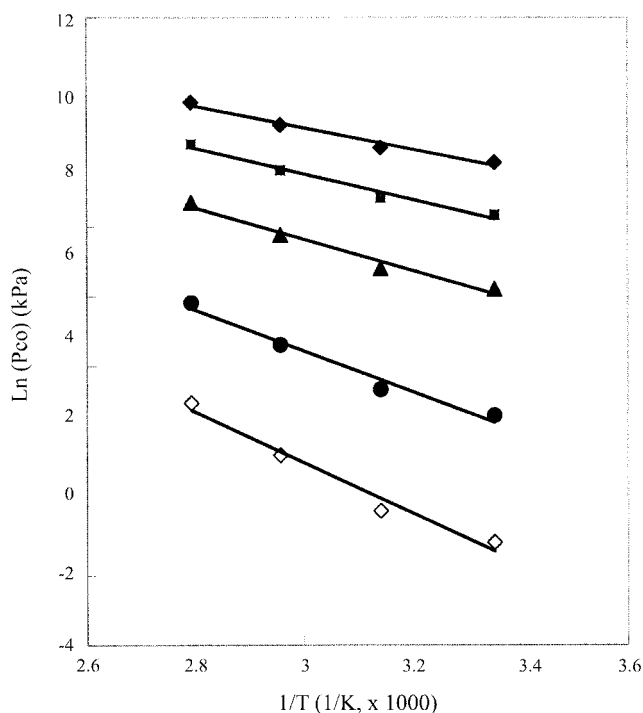


Figure 2. Isotheres for CO adsorption on the hydrogen reduced Cu/ZnO sample; surface coverage; (\diamond) 0.1, (\bullet) 0.2, (\blacktriangle) 0.4, (\blacksquare) 0.6, (\blacklozenge) 0.8.

The coverages are calculated as following:¹⁶

$$\theta = Q/Q_{0,298}$$

Where, Q is the amount of CO adsorbed at constant CO partial pressure and temperature, and $Q_{0,298}$ is the amount of CO adsorbed, interpolated from high CO partial pressure to 0.0 kPa. The heat of adsorption can be calculated from the slope of the adsorption isotheres. Figure 2 indicates that the heats of adsorption decrease with the surface coverage. The decrease of the heats of adsorption with the surface CO coverage is due to a decrease in the extent of d-electron backdonation into the π^* anti-bonding orbital of CO. The heats of adsorption on the hydrogen reduced Cu/ZnO are ranged from 25.7 kJ/mol at $\theta = 0.8$ to 59.8 at $\theta = 0.1$. It has been reported that the heat of adsorption on the copper metal^{17,18} or the supported copper metal^{19,20} are in the range of 20-70 kJ/mol. The wide range of the heats of adsorption can be attributed to the different CO coverages for the measured heats of adsorption as shown in Figure 2.

Figure 3 shows the CO adsorption isotherms for the Cu/ZnO sample treated with methanol. The Cu/ZnO samples treated with hydrogen are further treated in a methanol stream at 523 K for 3 h.

The isotherms of the Cu/ZnO sample treated with methanol are also well fitted to Freundlich isotherm equation, similarly to those of the reduced Cu/ZnO sample. The amounts of CO adsorbed on the Cu/ZnO treated with methanol are smaller than those of the Cu/ZnO sample treated with hydrogen. The isosteres of the Cu/ZnO sample treated with methanol are shown in Figure 4.

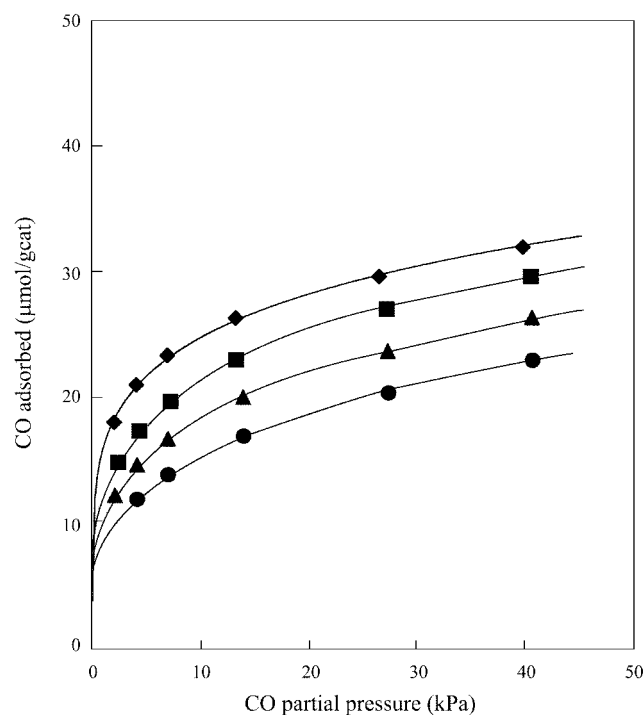


Figure 3. Isotherm of CO chemisorption on the Cu/ZnO sample after treated at 523 K for 1 h with methanol; adsorption temperature: (\blacklozenge) 298 K, (\blacksquare) 318 K, (\blacktriangle) 338 K, (\bullet) 358 K; (symbol) experimental data, (line) Freundlich isotherm.

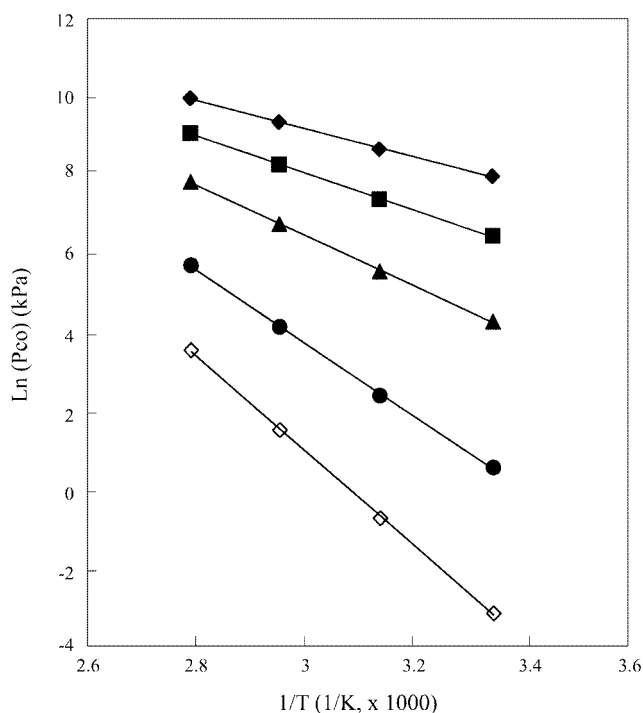


Figure 4. Isotherms for CO adsorption on the Cu/ZnO sample after treated at 523 K for 1 h with methanol; surface coverage; (\diamond) 0.1, (\bullet) 0.2, (\blacktriangle) 0.4, (\blacksquare) 0.6, (\blacklozenge) 0.8.

The heats of adsorption of the Cu/ZnO sample treated with methanol are ranged from 29.2 kJ/mol at $\theta = 0.8$ to 99.8 kJ/mol at $\theta = 0.1$. Although the Cu/ZnO samples treated with methanol have higher heats of adsorption than the Cu/ZnO sample treated with hydrogen do, they have smaller amounts of CO adsorbed. Therefore, the lower amounts of CO adsorbed on the Cu/ZnO sample treated with methanol are attributed to the decrease of the copper surface area. It was reported that the Cu/ZnO treated with methanol at 523 K induced the alloy formation.^{10,11} The Cu/ZnO treated with methanol at 523 K for 3 h showed the 11 mol % zinc concentration in the Cu-Zn alloy by XRD. Therefore, it can be concluded that the high heat of adsorption on the Cu/ZnO treated with methanol can be due to the Cu-Zn alloy formation. Figure 5 shows the heats of adsorption with the Cu/ZnO samples treated with methanol treatment time.

The CuO/ZnO sample was reduced at 573 K for 3 h in 5% H₂/Ar. Then, the reduced Cu/ZnO was treated at 723 K for 15 min, 30 min, 1 h, and 3 h with methanol. The heats of adsorption with methanol treatment time sharply increase within 30 min, then, leveled off afterwards. The core-level binding energy calculation indicates that the binding energy of copper metal shifts to high value in the CuZn alloy,²⁴ indicating that the electron is transferred from Cu to Zn, which was experimentally observed.¹¹ The positive valence of copper should decrease the heat of adsorption of CO from IR spectra analysis of Cu⁺ on Cu/SiO₂ sample.²⁰ In this study, the heats of adsorption on the Cu-Zn alloy. The experimental results indicate that the chemical effect of Cu-Zn alloy should be important for the CO adsorption on the Cu-Zn alloy.

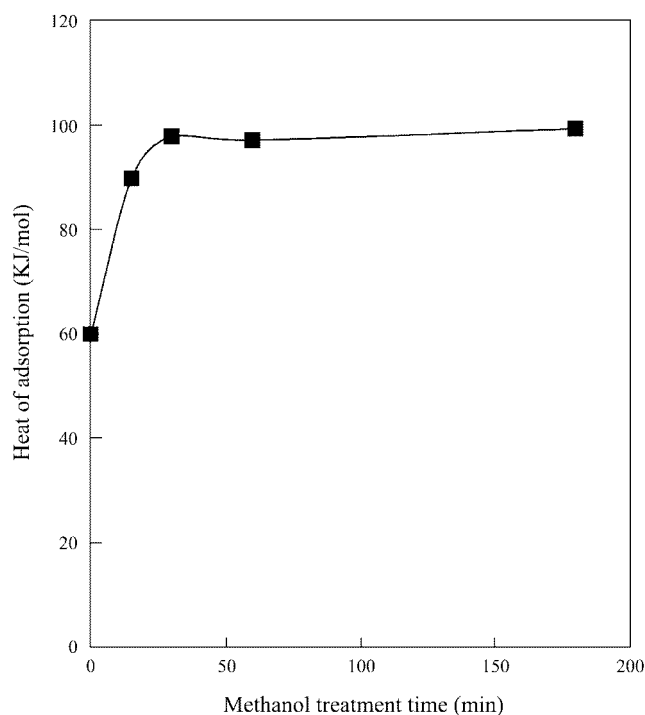


Figure 5. Heats of adsorption of CO at $\theta = 0.1$ on the Cu/ZnO catalysts.

Conclusion

The isotherms of CO adsorption on the Cu/ZnO treated with hydrogen and methanol are investigated. The heats of adsorption of the Cu/ZnO sample treated with hydrogen are in the range from 25.7 kJ/mol at $\theta = 0.8$ to 59.8 kJ/mol at $\theta = 0.1$, while those treated with methanol at 523 K for 1 h are in the range 30.3 kJ/mol at $\theta = 0.8$ to 97.2 kJ/mol at $\theta = 0.1$. The Cu/ZnO samples treated with methanol have the higher heats of adsorption than the Cu/ZnO samples treated with hydrogen do. The heats of adsorption at $\theta = 0.1$ sharply increase with methanol treatment time within 30 min and leveled off afterwards. The Cu-Zn alloy on the Cu/ZnO sample treated with methanol induces the higher CO heats of adsorption.

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