

Support Effects of Copper Containing Catalysts on Methanol Dehydrogenation

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Received May 20, 2002

CuO/ZnO, CuO/SiO₂, and CuO/ZrO₂ catalysts were prepared for investigating the support effects on methanol dehydrogenation. It was found that the conversion of methanol was proportional to the copper surface area on Cu/ZnO catalysts and was independent on that on Cu/ZrO₂ and Cu/SiO₂. The highest copper surface area was obtained with the Cu/ZrO₂ (9/1). The unusual deactivation of the Cu/ZnO, which showed the highest selectivity among the catalysts tested, was observed. Pulse reaction with methanol indicated that the lattice oxygen in ZnO could be removed by forming CO₂ in the catalytic reaction, supporting that the ZnO reduction was responsible for the severe deactivation of the Cu/ZnO.

Key words : Methanol dehydrogenation, Deactivation, Pulse reaction, ZnO reduction

Introduction

Methanol has been considered as a building block in the synthesis of various chemicals from synthesis gas.¹ The synthesis of methanol from synthesis gas is an efficient and established technology.^{2,3} Recently, the importance of methanol is stressed as one candidate for the storage and transportation of hydrogen.^{4,5} On the other hand, methyl formate has been suggested as another candidate for storage and transportation of carbon monoxide and hydrogen.⁶ Methyl formate can be prepared by methanol dehydrogenation to produce H₂.^{7,8} Then, methyl formate can be selectively decomposed into CO and methanol on the base catalysts. Therefore, if methanol can be selectively converted into methyl formate and H₂, it can be good way to obtain H₂ and CO from methanol. It has been known that methyl formate can be produced by methanol dehydrogenation on copper catalysts since the 1920s.⁹ Combinations of copper oxide with various metal oxides such as Cu/SiO₂,¹⁰ Cu/ZrO₂,¹¹ Cu/ZnO/Al₂O₃,¹² and Cu/Cr₂O₃¹³ have been studied for methanol dehydrogenation and the support effects on copper catalyst cannot be overstressed. Therefore, this study deals with the support effects on copper-containing catalysts for methanol dehydrogenation to form methyl formate.

Experimental Section

CuO/ZnO, CuO/SiO₂, and CuO/ZrO₂ catalysts were prepared by co-precipitation at pH 7. For example of CuO/ZnO preparation with the mol ratio of 1/1, 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. Zirconium oxychloride and sodium metal-silicate were used as precursors for preparation of Cu/ZrO₂ and CuO/SiO₂ catalysts. The mol ratios of Cu to

metal component of supporting oxides in the prepared catalysts were 1/9, 3/7, 5/5, 7/3, and 9/1. The prepared catalysts are designated as Cu/M_sO_y (the mol ratio of Cu to metal component of support oxide).

BET surface areas were measured with a ASAP 2000 (Micromeritics, Co.) and copper surface areas were measured by a N₂O titration method.¹⁹

Methanol dehydrogenation was conducted with a fixed bed reactor at atmospheric pressure. The catalyst was pre-reduced at 573 K for 3 h by 5% H₂/Ar (60 mL/min) before the reaction. The methanol was introduced by passing helium gas through a thermostated methanol saturator. Methanol concentration in He gas was 9.2 mol %. The flow rate of methanol was adjusted by controlling helium flow rate passed through the methanol saturator. Concentrations of products were analyzed by an on-line G.C. (T.C.D. detector, Porapak Q column, 1/8" × 10 ft).

Pulse reactor was used to estimate the activity comparison at initial stage of methanol dehydrogenation on the physically mixed CuO/support oxide samples. The physically mixed samples were prepared by grinding CuO and support oxides on the mortar. CuO, ZnO, SiO₂ and ZrO₂ were prepared by the co-precipitation method described above. Zirconyl chloride and sodium meta-silicate were used as precursors for the preparation of ZrO₂ and SiO₂, respectively. The methanol in He gas (9.2 mol %), flowing through 1 mL sample loop attached to a six-port valve, was pulse-injected into the reactor. The exit port of the reactor was directly connected to the G.C. for analysis of the products.

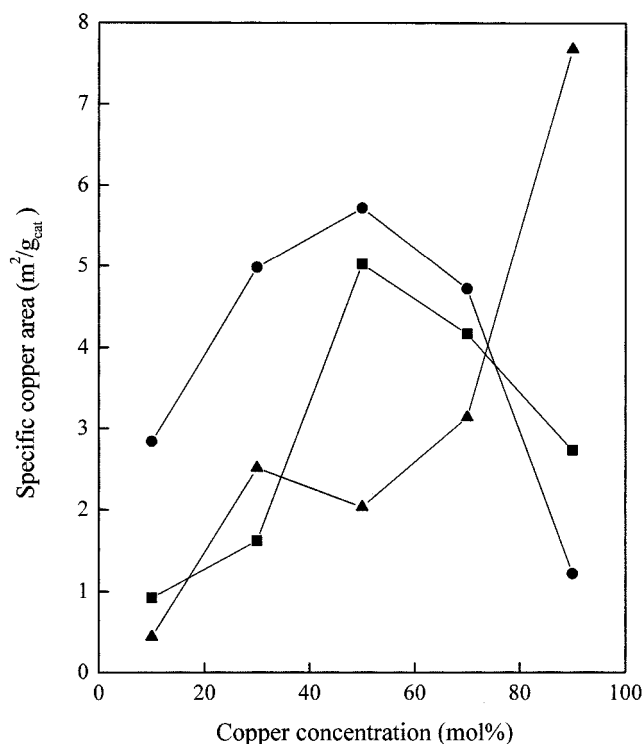
Results and Discussion

Table 1 shows the BET surface areas, copper surface areas of catalysts with various Cu/metal oxide ratios. The last two columns in Table 1 show the conversion of methanol and the selectivity of methanol to methyl formate on catalysts with various Cu/metal oxide ratios at the reaction time of 15 min, the temperature of 493 K and GHSV of 3000 mL/g_{cat}·h. The

Table 1. The surface areas of copper containing catalysts and the catalytic performance in methanol dehydrogenation (temperature: 493 K, GHSV = 3000 mL/g_{cat})

Catalysts	BET surface area (m ² /g _{cat})	Copper surface area (m ² /g _{cat})	Conversion of methanol	Selectivity to methyl formate
Cu/ZnO (1/9)		0.9	19.3	82.3
Cu/ZnO (3/7)	21.0	1.6	32.3	85.2
Cu/ZnO (5/5)	26.9	5.0	42.5	85.1
Cu/ZnO (7/9)	22.2	4.2	51.7	85.3
Cu/ZnO (9/1)	16.3	2.7	41.1	87.3
Cu/SiO ₂ (1/9)	175.8	2.8	19.6	78.2
Cu/SiO ₂ (3/7)	398.0	5.0	43.2	64.4
Cu/SiO ₂ (5/5)	167.3	5.7	50.7	62.2
Cu/SiO ₂ (7/3)	88.3	4.7	50.9	55.2
Cu/SiO ₂ (9/1)	78.6	1.2	43.4	82.2
Cu/ZrO ₂ (1/9)	74.0	0.4	25.4	53.2
Cu/ZrO ₂ (3/7)	52.9	2.5	27.9	75.1
Cu/ZrO ₂ (5/5)	23.9	2.0	43.2	75.4
Cu/ZrO ₂ (7/3)	54.4	3.1	41.1	75.4
Cu/ZrO ₂ (9/1)	64.6	7.7	26.5	85.3

BET surface area of Cu/ZnO catalysts is not so much changed with the mol ratio of copper to metal oxide and that of Cu/SiO₂ catalysts decreased with the copper concentration. The BET surface area of Cu/ZrO₂ catalysts shows U shape with respect to copper concentration. The selectivity of methanol to methyl formate is the high on Cu/ZnO catalysts.

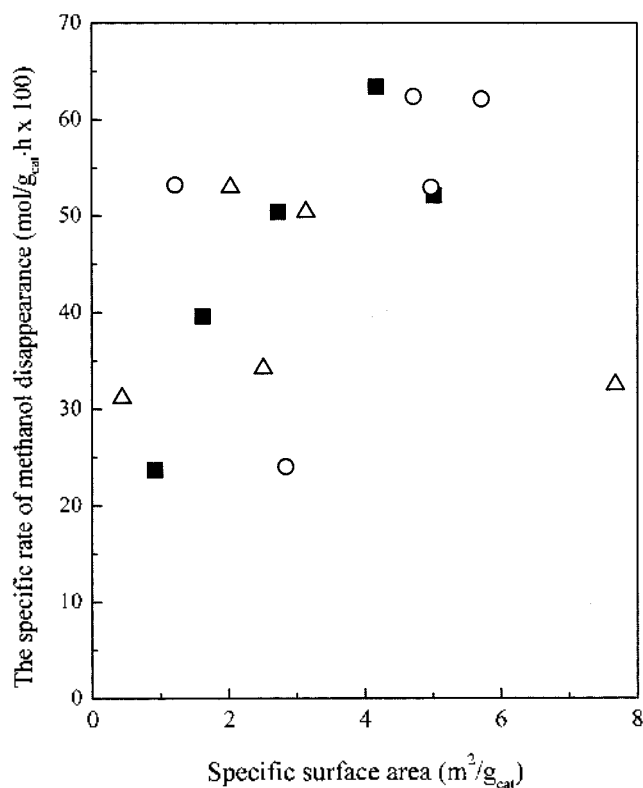
**Figure 1.** Relation of the specific rate of methanol dehydrogenation at 493 K and the copper surface areas on Cu/ZnO (■), Cu/ZrO₂ (●), and Cu/SiO₂ (▲) catalysts.

which is not so much changed with the conversion.

Figure 1 shows the copper surface area with respect to copper concentration. The Cu/ZrO₂ (9/1) catalyst has the highest specific copper surface area, while Cu/ZrO₂ (1/9) catalyst has the lowest one among the tested catalysts. It is interesting to observe that the specific copper surface areas of Cu/ZrO₂ increase with the copper content in the catalysts. On the other hand, the specific copper surface areas of the Cu/ZnO and Cu/SiO₂ are maximized in the Cu/metal oxide ratio of 3/7-7/3.

Figure 2 shows the specific rate of methanol disappearance to the specific copper surface area. The catalytic activities increase with the specific copper surface area on Cu/ZnO catalysts, but are not dependent on the Cu/SiO₂ and Cu/ZrO₂ catalysts. Specially, the Cu/ZrO₂ catalysts show a large deviation for the relation of the activity with respect to copper surface. The Cu/ZrO₂ (9/1) with the highest copper surface area shows the very low activity. However, the conversion of methanol is maximized on the catalysts with the Cu/metal oxide ratio of 5/5-7/3.

The methanol dehydrogenation was conducted at 493 K and GHSV = 3000 mL/g_{cat}·h with the catalysts with the 5/5 mol ratio of copper to metal oxide for examining the stability of the catalysts. Figure 3 shows the conversion of methanol and the selectivity of methanol to methyl formate with the reaction time. The Cu/SiO₂ (5/5) catalyst shows the highest conversion of methanol and the lowest selectivity of methanol to methyl formate among the three catalysts tested.

**Figure 2.** Area ratio of copper/metal oxide in the surface to copper concentration in bulk on Cu/ZnO (■), Cu/ZrO₂ (●), and Cu/SiO₂ (▲) catalysts.

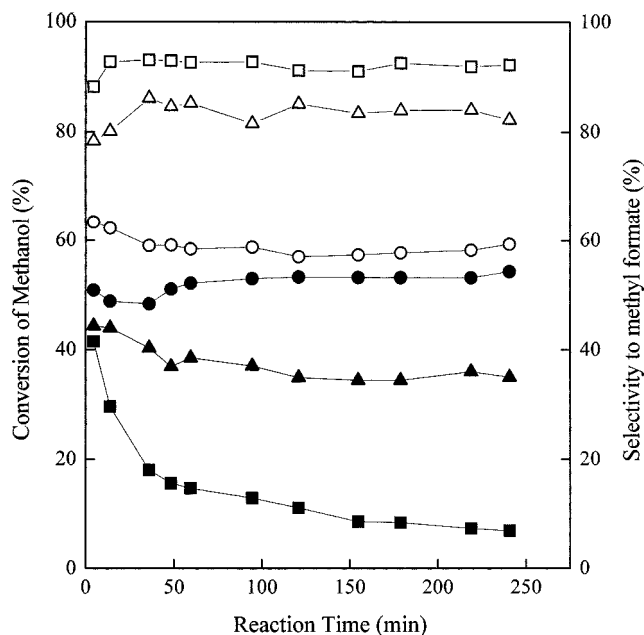


Figure 3. Support effects on methanol dehydrogenation at 493 K on Cu/ZnO (1/1) (rectangle), Cu/ZrO₂ (1/1) (circle), Cu/SiO₂ (1/1) (triangle) catalysts; conversion of methanol: filled symbol; selectivity of methanol to methyl formate: open symbol.

The conversion of methanol on the Cu/SiO₂ catalyst increases with the reaction time. The Cu/ZnO (5/5) catalyst shows the highest selectivity, but severely deactivated with the reaction time. It has been proved that the cause of the deactivation of the Cu/ZnO catalyst can be due to the reduction of ZnO in the Cu/ZnO catalyst,^{1,11,15} but the kinetic behavior of the reduction of ZnO should be scrutinized.

To clarify the support effects in methanol dehydrogenation, the activity on unsupported copper metal was compared with that of the physically mixed Cu/SiO₂, Cu/ZrO₂ and Cu/ZnO samples by the pulse reaction as shown in Table 2.

The pulse reaction was conducted at 493 K on the reduced copper oxide, physically mixed Cu/SiO₂, Cu/ZrO₂ and Cu/ZnO samples (the copper oxide: 30 mg, the support such as SiO₂, ZrO₂ and ZnO: 30 mg). The amount of the injected methanol was 4.1 μmol/pulse. The conversion of methanol in the pulse reaction is not changed with the number of methanol pulse injection until 30 times except that on the ZnO. The conversion on ZnO decreases from 5% at the first pulse reaction to 3% at the fifth pulse reaction and is not changed afterwards. The conversion of methanol and the selectivity of methanol to methyl formate on the physically mixed Cu/SiO₂ and Cu/ZrO₂ samples are similar to those of the metallic copper. Since the conversion of methanol on the SiO₂ and ZrO₂ is below 2%, the copper metal and support interaction of the physically mixed Cu/SiO₂ and Cu/ZrO₂ catalysts seems to be negligible. The most distinctive feature in the Table 2 is that the selectivity of methanol to methyl formate is low on the physically mixed Cu/ZnO sample. The carbon oxides are produced upto 20% on the Cu/ZnO sample. The low activity of ZnO only can exclude the possi-

Table 2. Product distribution in pulse reaction with methanol at 493 K

Catalysts	Conversion of methanol (%)	Yield of methyl formate (%)	Yield of CO (%)	Yield of CO ₂ (%)
Reduced copper	66.9	53.7	12.8	1.4
ZnO only	4.8	–	0.7	4.1
SiO ₂ only	1.1	–	1.1	–
ZrO ₂ only	1.2	–	1.2	–
Physically mixed Cu/ZnO	68.1	2.6	41.2	24.3
Physically mixed Cu/SiO ₂	66.8	53.3	11.1	2.4
Physically mixed Cu/ZrO ₂	65.4	51.3	11.2	2.9

bility of the secondary reaction by ZnO in the physically mixed Cu/ZnO.

The product distribution in methanol pulse reaction on the ZnO sample is different from that on other supports. The major product is carbon monoxide on the SiO₂ and ZrO₂ sample while carbon dioxide on the ZnO sample. It indicates that ZnO can be reduced with methanol and carbon dioxide may result from the interaction of lattice oxygen of ZnO and methanol. A few percentages of CO₂ on copper based samples come from oxygen in He gas. It was not possible to remove oxygen in He perfectly, although He gas of high purity (99.999%) was treated with a Oxytrap (Alltech, Co). Taharashi and Hansen¹⁶ and Ueno *et al.*¹⁷ suggested that carbon dioxide from methanol decomposition on ZnO could be due to the decomposition of formate species formed via methoxy on ZnO. Ahkter *et al.*¹⁸ demonstrated that carbon monoxide from methanol decomposition on ZnO came from lattice oxygen of ZnO and methanol by TPD experiments using CH₃O¹⁸H. It indicates that the lattice oxygen of ZnO can be removed during methanol dehydrogenation on ZnO. The removal of lattice oxygen of ZnO can occur by decomposition of zinc-formate formed by methanol on ZnO as described by several authors.¹⁶⁻¹⁸ It is interesting to note that the physically mixed Cu/ZnO catalyst produce CO₂ upto 24% in the methanol pulse reaction. The high yield of CO₂ means that copper plays an important role in removing the lattice oxygen in ZnO significantly. This severe reduction of ZnO in the presence of copper can be a cause of deactivation of the Cu/ZnO catalyst in methanol dehydrogenation.

From experimental results, it is observed that the conversion of methanol is proportional to copper surface area except Cu/ZrO₂ (9/1) catalysts. The Cu/ZnO catalysts show the selectivity of methanol to methyl formate. The unusual deactivation of the Cu/ZnO catalysts is observed. It can be concluded that the severe deactivation of Cu/ZnO catalyst can be due to the removal of lattice oxygen in ZnO with methanol from the pulse reaction.

Acknowledgment. This research was performed for the clean energy technology development, funded by R&D Management Center for Energy and Resources of Korea Energy Management Corporation.

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