

EFFECT OF COPPER LOADING ON PRODUCT SELECTIVITIES IN THE DEHYDROGENATION OF CYCLOHEXANOL OVER Cu/SiO₂ CATALYST

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Abstract – Silica-supported copper catalysts were prepared by the ion-exchange method. Copper was loaded on silica as copper tetramine ion-exchanged to proton of silanol group and copper hydroxide entrapped in the fine pores of silica. Copper dispersion decreased with copper loading. The selectivity to cyclohexanone increased with copper loading, accompanying by decrease in the selectivity to cyclohexene. The selectivity to phenol increased sharply with high loading of copper. The decrease in the selectivity to cyclohexene with copper loading was interpreted by the masking of weak acid site, while the increase in the selectivity to phenol by existence of large particles to enhance multiple dehydrogenation of cyclohexane ring.

Key words: Cu/SiO₂, Cyclohexanol Dehydrogenation, Ion-exchange Method, TEM, N₂O Titration

INTRODUCTION

Cyclohexanone is an important intermediate for the manufacture of caprolactam, so the dehydrogenation of cyclohexanol to cyclohexanone has been studied extensively over copper catalysts [Komarov et al., 1974; Emelyanov et al., 1972; Fridman et al., 1988; Wang and Lin, 1990; Sivaraj et al., 1988; Chen et al., 1992]. Though copper species shows high selectivity to cyclohexanone, the enhancement of the selectivity to cyclohexanone and the suppression of deactivation due to sintering are required for a better performance of the catalyst. Therefore, various copper catalysts such as CuMgO [Komarov et al., 1974], CuZnO [Emelyanov et al., 1972], Cu-Cr-O [Fridman et al., 1988], Cu/ZnO/Al₂O₃ [Wang and Lin, 1990; Sivaraj et al., 1988] and Cu-Fe-O [Chen et al., 1992] catalyst have been studied to improve the performance of copper catalyst.

It has been already suggested that metallic copper provides the active sites on Cu/SiO₂ catalyst for the dehydrogenation of cyclohexanol to cyclohexanone [Jeon and Chung, 1994; Jeon, 1995; Jeon et al., 1996b]. This suggestion is based on the linear relationship between the yield of cyclohexanone and the surface area of metallic copper, determined by reversible CO uptake [Klier, 1982]. But the dehydrogenation of cyclohexanol over copper catalyst does not produce cyclohexanone only. Though the dehydrogenation of the substituted hydroxyl group produces cyclohexanone, the multiple dehydrogenation of cyclohexane ring produces phenol [Jeon and Chung, 1994; Jeon, 1995]. Also cyclohexene can be produced through the dehydrogenation of cyclohexanol over acid site [Sivaraj et al., 1990; Jeon and Chung, 1994; Jeon, 1995]. The increase in the selectivity to cyclohexanone in the dehydrogenation of cyclohexanol can be achieved by the suppression of the formation to phenol

and cyclohexene.

Copper catalyst supported on alkali-doped silica shows a high selectivity to cyclohexanone and a small deposit of coke compared to Cu/ZnO and Cu/MgO catalysts [Jeon and Chung, 1994, 1995; Jeon et al., 1996a]. Neutral silica support is better than basic support in the aspect of dimerization leading to coke deposit [Jeon et al., 1996a]. Alkali doping neutralizes weak acid sites responsible for producing cyclohexene.

Copper loading is also an important factor to affect the selectivity to cyclohexanone, because the dispersion of copper strongly depends on copper loading. Large particle of copper provides multiple adsorption site promoting multiple dehydrogenation of cyclohexane ring [Jeon and Chung, 1994; Jeon, 1995] and masks the weak acid site of silanol group to catalyze the dehydration reaction. In this paper, we report the effects of copper loading and copper dispersion on the selectivity to cyclohexanone in the dehydrogenation of cyclohexanol over Cu/SiO₂ catalyst.

EXPERIMENTAL

1. Preparation of Catalyst

Copper catalysts supported on silica were prepared following the ion-exchange method by using copper ammonium nitrate solution as described by Kobayashi et al. [1980]. pH of the copper solution was controlled to 11 by the addition of an ammonia solution. The silica support used was Cab-O-Sil-M5. The mixture of 15 g of dry silica and 500 ml of copper solution was stirred at room temperature till no further copper uptake occurred. The mixture was kept at the desired pH by the periodic addition of ammonia solution. The suspension was filtered through Buchner filter, then resuspended in 300 ml of distilled water and stirred for 20 min. This procedure was repeated four times until pH of the washing solution became neutral. The cat-

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alyst cake obtained after the last filtration was dried overnight in a vacuum oven at 110°C. Then it was crushed, sieved, and calcined under sufficient air flow at 500°C for 5 h. The catalyst obtained was named as Cu() catalyst. The number in the parenthesis denoted copper loading as wt%.

2. Characterization of Catalyst

Copper of Cu/SiO₂ catalyst was dissolved by digestion of the calcined catalyst with 3:1 HCl:HNO₃ acid mixture at 60°C for 6 h. The copper loading was calculated from the measured concentration of the digested solution by atomic absorption spectroscope (Perkin-Elmer PC 5100). The BET surface area was measured using a Micrometrics Co. apparatus (Chemisorb 102).

The copper particle sizes on the catalyst were examined with a transmission electron microscope (ZEOL JAM 400FX) accelerated to 400 kV. After 5 h of reduction at 250°C with H₂ flow, the catalyst was passivated with 6% N₂O/He (20 ml/min) for 1 h at 90°C, and dispersed ultrasonically in ethanol. Droplets of the suspension were placed on a perforated carbon film supported on a copper grid.

The surface area of metallic copper was determined by N₂O reactive frontal chromatography [Chinchen et al., 1987]. N₂O titration was performed with a gas chromatograph (Shimadzu Co., GC-14A) and a plotter (Shimadzu Co., C-R6A). The reduced catalyst was cooled to 90°C under a flow of 40 ml/min of He, and then 6% of N₂O gas diluted with He was continuously fed to the reduced catalyst at the rate of 20 ml/min. The surface area of metallic copper was calculated from the generated amount of N₂.

3. Reaction Tests

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was made of a Pyrex tube with an I.D. of 10 mm. About 0.1-0.5 g of catalyst was charged in the reactor and LHSV (Liquid weight hourly space velocity) was kept at 10-30 h⁻¹. No carrier gas was used. Liquid cyclohexanol (Aldrich Co.) was fed into the reactor with a syringe pump (Sage Instruments 341B) and vaporized in an evaporator which was filled with glass beads and kept at 180°C. The lines drawing out of the evaporator to GC were heated to 180°C in order to prevent condensation of cyclohexanol and products. Before conducting the reaction, the catalyst was reduced in-situ by the following steps. The reducing gases were purified with a MnO/SiO₂ trap and a molecular 3A trap to remove oxygen and water, respectively. First, 5% H₂ gas diluted with N₂ was introduced to reactor at a flow rate of 50 ml/min. Then the reactor was heated to 250°C and kept at the same temperature for 1 h. The flowing gas was then switched to pure H₂ gas and the catalyst was reduced further for 4 h. To start the reaction, H₂ gas was switched to cyclohexanol vapor. A steady state was obtained about 2 h afterwards. A gas chromatograph (Hewlett Packard 5890 series II) equipped with a capillary column (Carbowax 20 M, 0.54 mm × 10 m) and a flame ionization detector was used to analyze the effluent from the reactor.

RESULTS AND DISCUSSION

1. Catalyst Preparation

Proton of silanol group can be exchanged with Cu²⁺ ion under low pH condition. But the possibility of Cu²⁺ ion-exchange

under high pH condition is very low. As the isoelectric pH of silica is 2.0±0.2 [Parks, 1965] and precipitation pH of Cu(OH)₂ is 5.4 [Richardson, 1989], most of copper is precipitated as Cu(OH)₂ under high pH condition. On the contrary, the solubility of copper tetramine complex ion Cu(NH₃)₄²⁺ is high under high pH condition. Therefore, it is possible to load copper on silica by the ion-exchange method under high pH condition, even though some copper is precipitated as Cu(OH)₂ simultaneously.

Removing the precipitated copper hydroxide by washing with neutral water is not easy, because the solubility of Cu(OH)₂ is low and some of the precipitated particles are entrapped in the fine pores of silica. Even after overnight filtration, a portion of copper hydroxide remains in the fine pores of silica as soluble interstitial liquid [Lee et al., 1988]. However, Cu(OH)₂ reacts with ammonia forming soluble Cu(NH₃)₄(OH)₂, the precipitated copper hydroxide can be removed by washing with a high concentrated solution of ammonia.

Fig. 1 shows the variation of the copper loading on Cu/SiO₂ catalyst with the concentration of copper tetramine solution used to prepare the catalyst. Full squares denote the copper loadings which remained after four times washing with neural water (pH =7), while full circles those remaining after washing with a pH 11 ammonia solution. In the washing with neural water, copper loading increased linearly with increase in copper concentration of the solution used. The ammonia solution washed catalyst also exhibited increase in the copper loading corresponding to the copper concentration of the preparatory solution, but only at lower levels of concentration. On the catalyst washed with ammonia solution, copper loading reached a limit, beyond which increased concentrations of copper did not result in increased loading.

Since the amount of precipitated Cu(OH)₂ increases with copper concentration of the preparatory solution, it is reasonable that copper loading on Cu/SiO₂ catalyst which is washed with neutral water increases with the concentration of copper solution. It also makes sense that copper loading on the ammonia

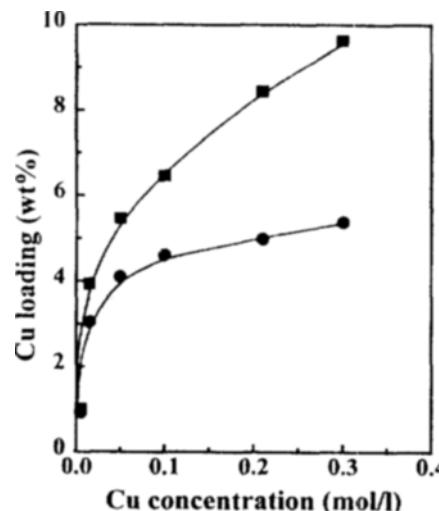


Fig. 1. Variation of copper loading with the concentration of preparation solution.

■: washed with neutral water and ●: washed with ammonia solution (pH=11).

solution-washed catalyst remains at a certain value regardless of the copper concentrations of the preparatory solution, because the ion-exchange capacity is limited and precipitated Cu(OH)₂ is easily removed with ammonia solution. BET surface area of Cu/SiO₂ catalysts showed similar values, ranging from 185 to 200 m²/g, while copper loading varied from 1 to 18%. This means that the pore blockage of copper is not significant.

2. Dispersion of Copper

The copper species loaded on silica is converted to copper oxide by calcination under air flow, and then to metallic copper by reduction in H₂ flow, whether the loaded state is ion-exchanged or precipitated. But the dispersion of copper, an important factor in determining catalytic properties, is varied with the loaded state and loading amount of copper. The following results are for the catalysts prepared by washing with neutral water.

Copper particles can not be observed in TEM photos of the Cu(1.0) catalyst, while a small number of copper particles are observed on the Cu(3.9) catalyst as shown in Fig. 2. The par-

ticle shapes are heterogeneous. Some are flat disc and others are hemispherical. The diameter of copper particle range from 2 to 4 nm. The sizes of copper particles are larger on the Cu(9.6) catalyst than on the Cu(3.9) catalyst. As shown in Fig. 2(d), the agglomeration of copper particle in Cu(18.2) catalyst can be easily observed. The observed frequency of copper particles per unit area is also high on Cu/SiO₂ catalyst with high loading. The fact that the particle size increases with copper loading, shows that the dispersion of copper decreases as copper loading increases. The failure to observe copper particles on the Cu(1.0) catalyst may be due to the high dispersion of copper, though the deficiency of copper on surface may also contribute.

TEM examination gives only a qualitative comparison of the particle sizes of copper. The quantitative dispersion of copper particles can be deduced from the copper surface area measured by N₂O reactive frontal chromatography [Chinchen et al., 1987]. The total surface area of copper per gram of catalyst (m²/g_{cat}) increases with copper loading, but its surface area per gram of copper (m²/g_{Cu}) decreases as shown in Table 1. This shows the

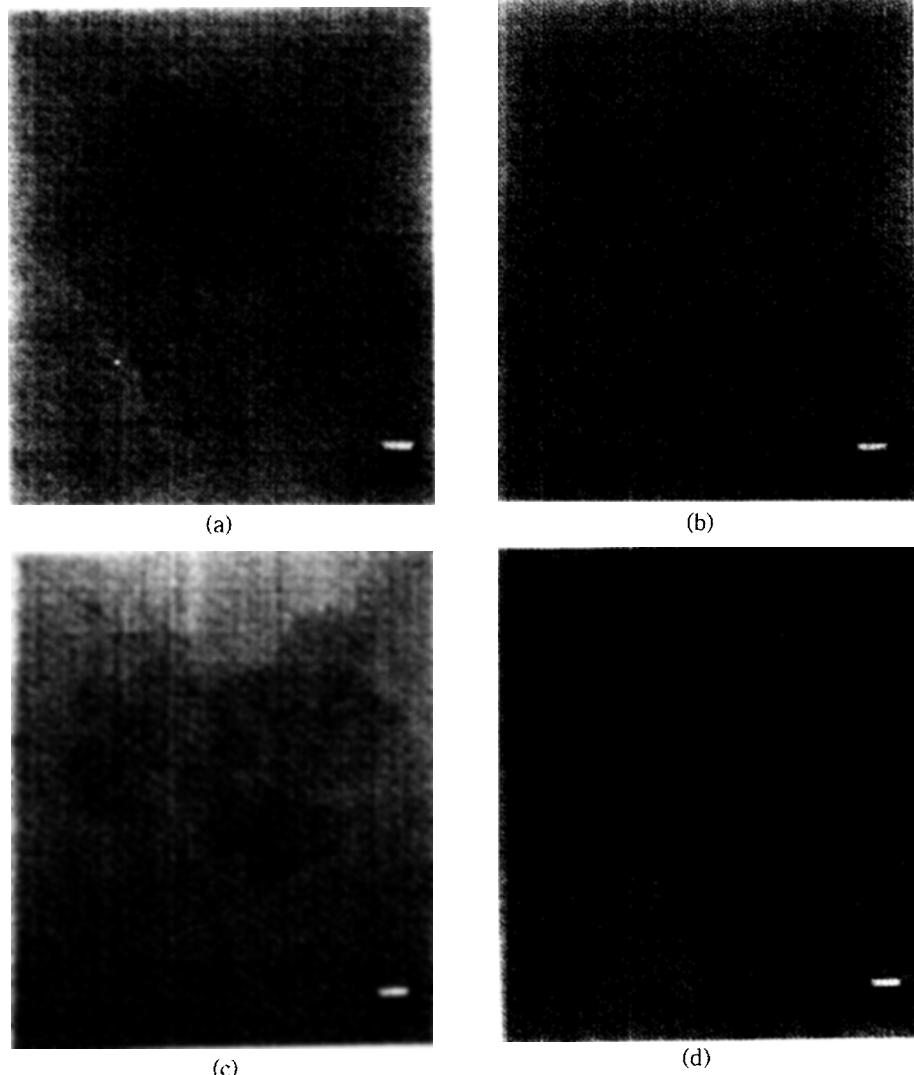


Fig. 2. TEM photos of reduced Cu/SiO₂ catalysts.

(a) Cu(1.0), (b) Cu(3.9), (c) Cu(9.6), and (d) Cu(18.2) catalysts.

Table 1. Cu surface area, dispersion, and average particle size of copper in Cu/SiO₂ catalyst by N₂O titration

Catalyst	Cu surface area (m ² /g _{cat})	Dispersion (%)	Average particle size (nm)
Cu(1.0)	3.7	372	57.3
Cu(3.9)	4.6	116	17.9
Cu(5.5)	5.5	100	15.5
Cu(9.6)	8.1	84	13.0
Cu(18.2)	12.4	68	10.5
Cu(3.0)*	4.3	141	21.7
Cu(4.1)*	4.6	112	17.3
Cu(5.4)*	5.1	94	14.5

*denotes the catalyst washed with ammonia solution (pH=11).

particle size of copper increases with copper loading.

Though the maximum surface area of copper varies with copper loading, there is a limit at which a copper monolayer is formed on the support. To calculate the surface area of copper required to form a copper monolayer, physical data listed below are used;

- (1) The surface area of silica support, 200 m²/g.
- (2) Surface density of copper is assumed to be 1.41×10^{19} atoms/m² [Parris and Klier, 1986].

The calculated limit of copper surface area required for monolayer formation is 153 m²/g_{cat} and the necessary copper loading is 23.6 wt%.

The dispersion of copper on the Cu(1.0) catalyst is high as 57.3%, while the dispersion is low as 18% on the Cu(3.9) catalyst. The dispersion decreases with copper loading, and the dispersion on the Cu(18.2) catalyst is very low, about 10%. The copper dispersion of the catalysts washed with ammonia solution (pH=11) is slightly higher than those washed with neutral water. But the difference in the dispersion is not large. So the copper dispersion of the Cu/SiO₂ catalyst with low loading mainly depend on copper loading and does not significantly depend on the pH of the washing solution.

3. Catalytic Property in the Dehydrogenation of Cyclohexanol

The conversion and the selectivities of the Cu/SiO₂ catalyst in the cyclohexanol dehydrogenation reaction vary with copper loading. The increase in the conversion with copper loading is not large, but the changes in the selectivities to cyclohexanone, cyclohexene, and phenol are remarkable as shown in Fig. 3 and 4. Though the effect of copper loading on the product selectivities is negligible at 250°C, the product selectivities of Cu(1.0) and Cu(18.2) catalyst are quite different at 390°C. The selectivity to cyclohexanone and cyclohexene are high on Cu(1.0) catalyst, but low on Cu(18.2) catalyst. On the contrary, the selectivity to phenol is very low on Cu(1.0) catalyst, but relatively high on Cu(18.2) catalyst.

As the active site of cyclohexene formation is known to be acid site [Sivaraj et al., 1990; Jeon and Chung, 1994; Jeon, 1995], the decrease in the selectivity to cyclohexene with copper loading can be explained by the masking effect of copper on weak acid sites of silica surface.

Phenol is formed from cyclohexanol through the multiple dehy-

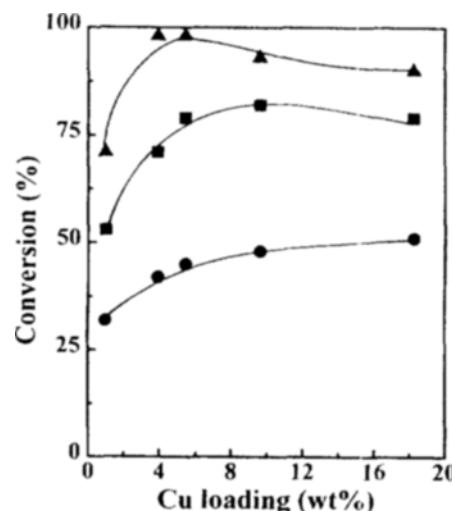


Fig. 3. Conversion of cyclohexanol over Cu/SiO₂ catalyst.

LWHSV: 15 h⁻¹, cyclohexanol, flow rate: 4.9×10^{-2} mol/h.
●: 250°C, ■: 300°C, ▲: 390°C

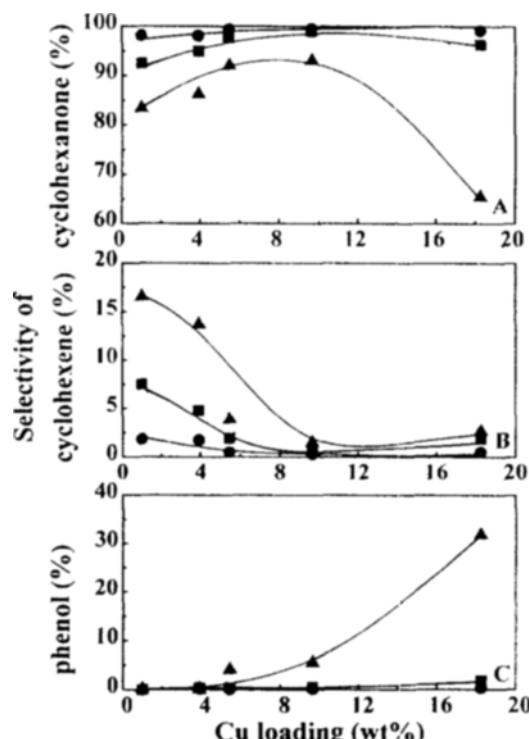


Fig. 4. Selectivities of cyclohexanone (a), cyclohexene (b) and phenol (c) over Cu/SiO₂ catalyst.

LWHSV: 15 h⁻¹, cyclohexanol, flow rate: 4.9×10^{-2} mol/h.
●: 250°C, ■: 300°C, ▲: 390°C

drogenation of cyclohexene ring [Jeon and Chung, 1994; Jeon, 1995]. A copper catalyst with large particles may act as a better catalyst for the multiple dehydrogenation of cyclohexane ring than one with small particles in the sense of a preference for multiple adsorption. The dispersion of Cu(18.2) catalyst is the lowest among the catalyst used in this study. Therefore, the high selectivity to phenol on Cu(18.2) catalyst is due to the low dispersion of copper, indicating the presence of large par-

ticles.

CONCLUSIONS

On Cu/SiO₂ catalyst prepared by ion-exchange method at high pH condition, copper can be loaded on silica support as ion-exchanged and precipitated before calcination treatment. The dispersion of copper on reduced Cu/SiO₂ catalyst deduced from N₂O reactive frontal chromatography decreases with increase in copper loading, showing the easy agglomeration of copper at high levels of loading. On heavily loaded Cu/SiO₂ catalyst the selectivity to cyclohexanone is low due to the preferred formation of phenol on large particle of copper, and the selectivity to cyclohexene is also low due to the masking of acid sites by copper.

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