

DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE OVER Cu/SiO₂ CATALYSTS: DISPERSION AND CATALYTIC ACTIVITY

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Abstract – Copper catalysts supported on silica (Cu/SiO₂) were prepared by three different methods; incipient wetness, precipitation, and ion exchange. Catalytic properties in the dehydrogenation of cyclohexanol over these catalysts were examined. Copper surface area increased in the order of incipient wetness < precipitation < ion-exchange method for the catalysts with the same loading of copper. Conversion was mainly dependent on the copper surface area regardless of preparation methods, and selectivity to cyclohexanone was very high for all Cu/SiO₂ catalysts.

Key words: Cu/SiO₂ Catalyst, Preparation Method, Copper Surface Area, Cyclohexanol Dehydrogenation, Cyclohexanone

INTRODUCTION

Dehydrogenation of cyclohexanol to cyclohexanone has been of considerable interest, since cyclohexanone is an important intermediate for caprolactam production. Among many dehydrogenation catalysts, copper catalyst has been used in the dehydrogenation process due to its high activity and selectivity [Sivaraj et al., 1988; Chang and Saleque, 1994]. As the equilibrium constant of the dehydrogenation reaction is high at high temperature because of its endothermic character [Cubberley and Mueller, 1947], the dispersion of copper at high temperature is very important for the industrial application. Therefore, copper catalysts are prepared by supporting on inert catalyst support to improve dispersion and thermal stability. Alumina support shows good dispersion and thermal stability of metal, but silica is usually used as support for the dehydrogenation catalyst, because many side reactions occur on acid sites of alumina, reducing the selectivity.

Copper is a well-known active phase for hydrogen participating catalytic reaction, such as dehydrogenation of methanol [Sodesawa et al., 1986] hydrogenolysis of methyl formate [Monti et al., 1985] and steam reforming of methanol [Minochi et al., 1979]. As copper can be the adsorption site of reactant as well as that of hydrogen, the rate determining steps of copper catalyzed reactions are not the same. By the same reason, the structure sensitivity of a catalyst is dependent on the type of reaction.

Several impregnation methods are employed for the preparation of supported copper catalysts such as incipient wetness, precipitation, and ion exchange [Sodesawa, 1984]. Though the dispersion of copper is expected to be relatively good on the catalyst prepared by ion exchange method, the differences in catalytic properties among preparation methods are not clear.

We prepared Cu/SiO₂ catalysts having different copper load-

ing by the three methods mentioned above. In this study the relationship between copper surface area and catalytic activity is discussed in order to elucidate the structure insensitivity of copper catalyst for the dehydrogenation of cyclohexanol.

EXPERIMENTAL

Catalysts were prepared by the incipient wetness (IW), precipitation (PR), and ion exchange (IE) methods. The catalysts were noted as Cu/SiO₂-IW(x), Cu/SiO₂-PR(x), and Cu/SiO₂-IE(x). The number in parenthesis indicated copper loading. The silica support used was Zeosil (Korfran Chem. Co., BET surface area=200 m²·g⁻¹). The copper loadings of the prepared catalysts were 1 and 6 wt% nominally.

Cu/SiO₂-IW catalysts were prepared by wetting with copper nitrate (Shinyo Pure Chem. Co., GR) solution equivalent to the pore volume of silica support followed by drying at 100°C for 12 h in vacuum drying oven. Dried catalysts were calcined under sufficient air flow at 500°C for 5 h.

Cu/SiO₂-PR catalysts were prepared by precipitation of copper from copper nitrate solution with sodium carbonate (Aldrich Co., GR) as described in a previous paper [Jeon and Chung, 1994]. The slurry was washed and then filtered. Dried cake was crushed and sieved under 100 mesh. Drying and calcination procedures were the same with those of Cu/SiO₂-IW catalyst.

Cu/SiO₂-IE catalysts were prepared as the procedure described in literature [Kobayashi et al., 1988]. The proton of silanol group in silica support was exchanged by copper tetraamine complex ion. Drying and calcination procedures of filtrates were the same with those of Cu/SiO₂-IW catalyst.

The copper loading of Cu/SiO₂ catalyst was analyzed by atomic absorption spectroscopy (PC 5100, Perkin-Elmer Co.) and the solid phase of copper was investigated by X-ray diffractometer (D-max-b, Rigaku Co.). Surface area and dispersion of copper were determined by N₂O reactive frontal

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chromatography at 90°C [Chinchen et al., 1987]. Reduction behavior of Cu/SiO₂ catalyst was studied using hydrogen temperature-programmed reduction (TPR). Flow rate of reductant composed of 5% hydrogen and 95% nitrogen is 20 ml·min⁻¹ and ramping rate is 3.4°C·min⁻¹. Hydrogen consumption was detected by a thermal conductivity cell and recorded with a strip chart recorder.

The dehydrogenation of cyclohexanol over Cu/SiO₂ catalyst was carried out in an atmospheric micro fixed-bed flow reactor. The catalyst was reduced with hydrogen gas at 250°C for 4 h before reaction. The flow rate of cyclohexanol feed was 4.9×10^{-2} mol·h⁻¹ and LHSV 15 h⁻¹. A GC (HP 5890 series II) equipped with a capillary Carbowax 20 M column (0.54 mm × 10 m) and FID detector was used to analyze the effluent from the reactor.

RESULTS AND DISCUSSION

Loading amount and dispersion of copper in Cu/SiO₂ catalysts are listed in Table 1. The loading amounts were nicely controlled to nominal values except the Cu/SiO₂-IE(6) catalyst. The loading amount of copper could not reach to 6 wt% by the ion exchange method, since the number of silanol group on silica surface to be able to exchange was limited.

Copper dispersion is dependent on the preparation method and loading amount. The dispersion was high in the order of method: incipient wetness < precipitation < ion exchange. Good dispersion of Cu/SiO₂-IE catalysts was due to homogeneous distribution of copper complex ion on silica surface inhibiting formation of large aggregate during drying and calcination. Dispersions of the Cu/SiO₂-IW catalysts were poor compared to catalysts prepared by other methods. Diffraction peaks of copper oxide were observed only on calcined Cu/SiO₂-IW(1) and Cu/SiO₂-IW(6) catalysts, indicating the formation of large aggregates during drying and calcination. Therefore, poor dispersion of Cu/SiO₂-IW catalysts might be due to incomplete wetting on silica due to high concentration and limited volume of copper nitrate solution.

Copper surface area increased with an increase in loading amount, while dispersion decreased. High concentration of copper precursor on silica surface accelerates the aggregation reducing the dispersion. The dispersion was very high for Cu/SiO₂-IE(1) catalyst, but the dispersion was largely decreased with increase in the loading amount of copper to 6 wt%. These results show that density of copper on silica surface is im-

portant for dispersion. The dispersions of Cu/SiO₂-PR catalysts were not sensitive with increase in the loading amount. As the size of precipitate is determined by the precipitation condition, the particle size of reduced copper is not drastically increased with an increase in loading amount.

Reduction behaviors of Cu/SiO₂ catalysts were also dependent on the preparation method. TPR profiles of Cu/SiO₂ catalysts shown in Fig. 1 can be classified by preparation method regardless of loading amount of copper. Cu/SiO₂-IW catalysts show two peaks while Cu/SiO₂-PR and Cu/SiO₂-IE catalysts show only one peak. The temperature at peak maximum is slightly shifted to higher temperature with an increase in loading amount.

As a small amorphous particle of copper oxide is easily reduced, the reduction peak is observed at a low temperature. On the other hand, reduction of large crystalline particle of copper oxide is more difficult. Diffraction peaks of copper oxide were only observed in the catalysts prepared by the incipient wetness method. Therefore, the reduction peak at a high temperature of Cu/SiO₂-IW catalysts may be related to slow reduction of the crystalline copper oxide particle.

The temperature at peak maximum was slightly shifted toward a high temperature for high loading catalysts. As the average particle size of copper increases with loading amount, reduction of copper oxide becomes harder resulting in a shift to high temperature. The fact that the temperatures at peak maximum are simply related to particle size of copper suggests that there is no significant difference in interaction between copper and silica regardless of preparation methods.

Table 1. Loaded amount and dispersion of copper on Cu/SiO₂ catalysts prepared

| Catalyst | Loaded amount (wt%) | Dispersion (%) | Surface area (m ² ·g ⁻¹) | Average particle size (nm) |
|----------------------------|---------------------|----------------|---|----------------------------|
| Cu/SiO ₂ -IW(1) | 0.99 | 4.7 | 0.30 | 22.2 |
| Cu/SiO ₂ -IW(6) | 6.00 | 2.9 | 1.13 | 35.7 |
| Cu/SiO ₂ -PR(1) | 1.00 | 12.1 | 0.78 | 8.6 |
| Cu/SiO ₂ -PR(6) | 6.00 | 11.3 | 4.38 | 9.2 |
| Cu/SiO ₂ -IE(1) | 1.00 | 57.3 | 3.72 | 1.8 |
| Cu/SiO ₂ -IE(6) | 5.46 | 15.5 | 5.48 | 6.7 |

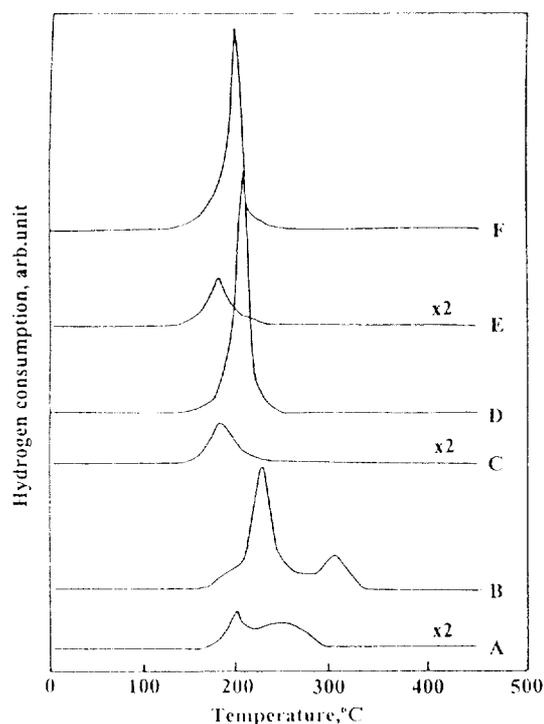


Fig. 1. TPR profiles of Cu/SiO₂ catalyst with respect to preparation method and copper content.

(a) Cu/SiO₂-IW(1), (b) Cu/SiO₂-IW(6), (c) Cu/SiO₂-PR(1), (d) Cu/SiO₂-PR(6), (e) Cu/SiO₂-IE(1), and (f) Cu/SiO₂-IE(6).

Conversion of cyclohexanol and selectivities of products over Cu/SiO₂ catalysts are listed in Table 2. The conversion over silica support is very low, so the effect of support is negligible for this reaction. The conversion of Cu/SiO₂ catalysts is high for the high loading catalyst. The conversion of Cu/SiO₂ catalysts with the same loading increases in the order of incipient wetness<precipitation<ion exchange as the same order of copper surface area indicating that the conversion is mainly dependent on the copper surface area.

Selectivity to cyclohexanone over Cu/SiO₂ catalysts is very high near 99% and selectivity to cyclohexene is negligible. A small amount of phenol was formed over Cu/SiO₂-IE(1), Cu/SiO₂-IE(6), and Cu/SiO₂-PR(6) catalysts showing high conversion, so dehydrogenation of cyclohexane ring may be much slow compared to the dehydrogenation producing cyclohexanone.

Dehydrogenation of cyclohexanol over Cu/Al₂O₃ catalyst was reported as pseudo first order reaction to the pressure of cyclohexanol [Chang and Saleque, 1993]. If catalytic reaction is proceeded on exposed copper metal with the same turnover frequency, the conversion is determined by copper surface area at the reaction condition with the same amount of catalyst and feed rate of cyclohexanol. For the first order reaction proceeding in the integral reactor, the following relation can be derived;

$$-X - 2 \ln(1 - X) = kS$$

Table 2. Conversion and selectivities of Cu/SiO₂ catalysts in the dehydrogenation of cyclohexanol

| Catalyst | Conversion (%) | Selectivities (%) | | |
|----------------------------|----------------|-------------------|-------------|--------|
| | | Cyclohexanone | Cyclohexene | Phenol |
| SiO ₂ | 0.2 | 52.1 | 47.9 | 0 |
| Cu/SiO ₂ -IW(1) | 12.1 | 98.9 | 1.1 | 0 |
| Cu/SiO ₂ -IW(6) | 29.0 | 99.5 | 0.5 | 0 |
| Cu/SiO ₂ -PR(1) | 40.7 | 99.9 | 0.1 | 0 |
| Cu/SiO ₂ -PR(6) | 72.4 | 99.5 | 0.1 | 0.4 |
| Cu/SiO ₂ -IE(1) | 64.5 | 99.1 | 0.6 | 0.2 |
| Cu/SiO ₂ -IE(6) | 80.1 | 98.8 | 0.7 | 0.5 |

Reaction conditions: T=300°C; LWHSV=15 h⁻¹; Flow rate of cyclohexanol feed=4.92 × 10⁻² mol · h⁻¹; Catalyst loading=0.33 g.

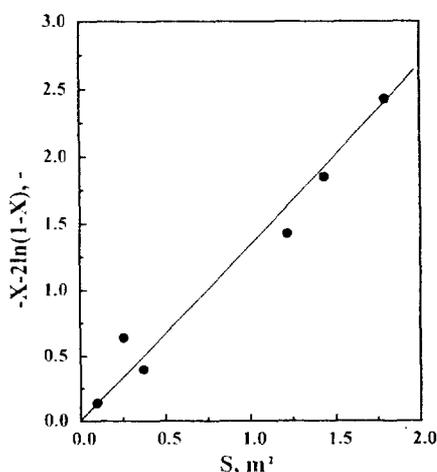


Fig. 2. First order plot for the dehydrogenation of cyclohexanol.

where X is conversion and S copper surface area. k is the complex variable composed of rate constant and flow rate of feed. A nice line shown in Fig. 2 indicates that rate constant is the same for all Cu/SiO₂ catalysts regardless of preparation method and loading amount. The same rate constant shows that copper catalyst is structure-insensitive in the dehydrogenation of cyclohexanol. If the removal step of hydrogen atom from cyclohexanol by copper is the rate-determining step, it is reasonable that catalytic activity of exposed copper atom should be the same.

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