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EFFECT OF IRON ON Cu/SiO_2 CATALYSTS FOR THE DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE

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Abstract – At the temperature range of 250-390°C, the addition of iron to Cu/SiO_2 catalyst increased the conversion and the selectivity of cyclohexanone. The iron incorporation into Cu/SiO_2 catalyst enhanced the reduction temperature of copper oxide, increased the dispersion of copper metal and decreased the selectivity of cyclohexene. Copper was enriched on the surface of the used metal catalyst compared to that in freshly calcined or reduced catalyst. Unlike Cu dispersed on bulk iron oxide, the Cu-Fe dispersed on silica showed negligible amount of phenol formation, thus keeping the selectivity of cyclohexanone very high even at high reaction temperatures. The Fe^{3+} ion in the reduced $Cu/Fe/SiO_2$ catalyst resulted in a significant resistance of the Cu particle to sintering and a decrease in the selectivity of phenol arisen from the magnetite.

Key words: Cyclohexanol Dehydrogenation, Cu/SiO_2, Fe Additive, Mössbauer Spectroscopy, XPS, XRD/XLB

INTRODUCTION

Copper catalysts were widely used in industrial processes. Supported copper catalysts have been used to promote methanol steam reforming [Minochi et al., 1979; Kobayashi et al., 1981], dehydrogenation [Sodesawa et al., 1986; Sodesawa, 1984], methyl formate hydrogenolysis [Monti et al., 1985] and ester hydrogenolysis [Kohler et al., 1987]. Cyclohexanone is an important intermediate for the manufacture of caprolactam. It is generally produced by catalytic dehydrogenation of cyclohexanol. Although the selectivity of cyclohexanone is very high (i. e., more than 95 %), the reversible feature of the reaction limits its conversion to a low value [Cubberley and Mueller, 1947]. To overcome the limitation in the conversion, the oxidative dehydrogenation route has recently been attempted using Cu/ZnO as catalyst [Lin et al., 1988]. However, the selectivity of cyclohexanone in the oxidation route is not high enough to compete with that in the dehydrogenation route.

The catalyst reported to be good for the dehydrogenation reaction includes various form of copper such as Cu-MgO [Komarov et al., 1974], Cu-ZnO [Emelyanov et al., 1972], Cu-Cr-O [Fridman et al., 1988], Cu-ZnO-Al_2O_3 [Wang and Lin, 1990], and Cu-Fe-O catalyst [Chen et al., 1992]. Carbon-supported nickel [Uemichi et al., 1989] or tin oxide [Hino and Arata, 1990] were also reported in the literature. The active site for the dehydrogenation reaction has been studied very recently by Sivaraj et al. [1988] and Jeon and Chung [1994]. Sivaraj et al. [1988] have shown that the main reaction is well correlated with the reversible CO uptakes, a measure of metallic copper species [Cu(0)] [Klier, 1982]. It is also well known that cyclohexene is obtained as a by-product via dehydration route on the acidic sites of the catalyst [Chen et al., 1992; Sivaraj et al., 1990]. From these results, it may be deduced that any metallic copper dispersed on a support would be a good candidate catalyst for the reaction. The main issue is how to make copper particles which are well dispersed on the support and have a good resistance to sintering. Among the catalyst supports, silica shows the highest copper dispersion [Rachel et al., 1993] and the best dehydrogenation activity [Jeon and Chung, 1994, 1995] for the dehydrogenation of cyclohexanol.

For further improvement of Cu/SiO_2 catalyst, iron was added to as a promoter. The effect of iron addition on catalytic activity and the behavior and state of iron in Cu/SiO_2 catalyst were studied using various tools of characterization methods in comparison with Cu-Fe catalyst.

EXPERIMENTAL

1. Preparation of Catalyst

The catalysts were prepared by an incipient-wetness method. The support was silica (Oriental Chemical Co., surface area: 250 m^2/g). The copper precursor was copper nitrate [$Cu(NO_3)_2$ $5H_2O$, Sinyo Pure Chemical Co.] and the iron precursor was iron nitrate [$Fe(NO_3)_3$ $9H_2O$, Junsei Chemical Co.]. In order to investigate the effect the addition of iron to Cu/SiO_2 catalyst on the activity, two groups of catalysts were prepared. One was the catalysts in which the Fe loading was varied at constant copper content (6 wt%). The other was the catalyst in which the Cu loading was varied at constant Fe loading (5.28 wt%). The catalyst was prepared as follows: First, silica support was dried in vacuum oven for 10 hr at 100°C in order to remove the residual water in the pores of silica support. An aqueous solution of iron nitrate equivalent to the pore volume of silica was impregnated very slowly on dried silica support. The iron catalyst supported on silica was dried in vacuum oven for 10 hr at 110°C and was calcined at fixed-bed flow reactor in air

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flow of 100 cc/min for 12 hr at 300 °C. Then, the solution of copper nitrate was impregnated on Fe/SiO_2 catalyst. The copper supported on the Fe/SiO_2 catalyst was dried, and calcined at the same condition as the Fe/SiO_2 catalyst preparation. Cu/SiO_2, Fe/SiO_2 and Cu-Fe catalysts were also prepared for comparison.

2. Reaction Test

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reactor was made of Pyrex tube with an I.D. of 1.0 cm. About 0.1-0.5 g of catalyst was charged in the reactor. LWHSV was kept at 10-30 hr^{-1}. No carrier gas was used. Liquid cyclohexanol (Aldrich, 99 %) fed with a syringe pump (Sage Instruments, model 341B) was vaporized in an evaporator which was filled with glass beads at 180 °C. The feed lines located after the evaporator was heated to 180 °C in order to prevent the condensation of cyclohexanol vapor. Before conducting the reaction, the catalyst was reduced in-situ by the following steps. First, after introducing 5 % H_2 diluted with N_2 at a flow rate of 50 cc/min, the reactor was heated to 250 °C and kept at the same temperature for 1 hr. The flowing gas was then switched to pure H_2 and the catalyst was reduced further for 4 hr. The reducing gases were purified with MnO/silica trap and molecular sieve 3A trap to remove oxygen and water, respectively. For the start of reaction, the hydrogen gas was switched to cyclohexanol vapor. A steady state was obtained in about 2 hr after the start of reaction. A gas chromatograph (Hewlett Packard 5890 series II) equipped with a capillary column (Carbowax 20 M, 0.54 mm × 10 m) equipped with the flame ionization detector was used to analyze effluent from the reactor. The conversion of cyclohexanol was obtained by determining the ratio of moles of cyclohexanol consumed to moles of cyclohexanol fed into the reactor. The selectivity to a given product was defined as the ratio of moles of the product to the total moles of all the converted reactants.

3. Measurement of Total Surface Area

The BET surface area was measured using a BET measuring apparatus (Accusorb 2100E, Micrometrics Co.). Before N_2 adsorption, catalyst sample was evacuated for 2 hr at 150 °C. The dead volume of sample port was measured with He gas.

4. N_2O Reactive Frontal Chromatographic Method

The principle of N_2O reactive frontal chromatographic method was to react two molecules of copper metal on the catalyst surface with one molecule of N_2O and then to generate one molecule of N_2 [Chinchen et al., 1987].

$$N_2O\ (g) + 2\ Cu\ (s) \rightarrow N_2\ (g) + Cu_2O\ (s)$$

where g denotes gas phase and s denotes surface phase of catalyst. The surface area of copper metal of Cu/SiO_2 catalysts was calculated from the amount of generated N_2.

$$\text{Volume of } N_2 \text{ produced (cc)} = F.\ C.\ S/R$$

where F : the flow rate of N_2O gas (cc/min)
C : the volume fraction of N_2O in diluted N_2O gas (-)
S : chart distance during generated N_2 (cc)
R : chart speed (cc/min)

In order to reduce the dead volume between reactor and TCD cell, all experiments of N_2O titration were performed in gas chromatograph (Shimadzu, GC-14A). The plotter (Shimadzu, C-R6A) was used to measure the amount of generated N_2. The surface area of copper metal could be calculated from the fact that surface density of copper metal was equivalent to 1.41×10^{19} atoms of copper/m^2 of copper surface [Parris and Klier, 1986]. The N_2O gas diluted to 6 vol% N_2O diluted with He gas was used. The N_2O titration was following. The catalyst was reduced with the same procedure of activity test. After being reduced, the catalyst was cooled to 60 °C at the flow of 40 cc/min He. After the response of TCD cell in gas chromatograph becomes stable, the base line of the strip chart recorder was adjusted, and then the 6 % N_2O gas was injected to the reduced catalyst bed at 60 °C and at the flow of 20 cc/min.

5. Temperature Programmed Reduction

Temperature Programmed Reduction (TPR) was carried out using a TCD type detector cell. A gas flows through the sample and reference compartment of the cell which were connected in series. About 25 mg of a preoxidized catalyst sample was charged in a U-shaped reactor made of 1/4" quartz tube. The catalyst reduced with the same procedure in the reaction test was dried at 150 °C for 1 hr in a flow of He which was purified through a trap charged with MnO/silica and molecular sieve 3A. After cooling to room temperature, the reactor was switched to a flow of a reducing gas, 5 % hydrogen in N_2. The gas was also purified by the same method as He. Temperature of the reactor was swept to 800 °C at a rate of 3.4 °C/min using a temperature controller.

The extent of reduction of a catalyst which was reduced according to the same procedure as the reaction measurement was calculated by measuring the amount of consumed hydrogen during TPR.

6. Powder X-ray Diffraction and X-ray Photoelectron Spectroscopy

X-ray diffraction (XRD) analysis was conducted using a Rigaku diffractometer (model D Max-B) with CuKα radiation to identify the copper phase and to calculate the size of copper particle. The scan rate was 3°/min and the range of scan (2θ) was 3-70°. The average copper particle size of catalyst sample was calculated from the XLB (X-ray line broadening) analysis using the Scherrer equation assuming spherical shape [Anderson, 1975].

In order to carry out XPS measurement, the $Cu/Fe/SiO_2$ catalysts were pretreated into three kinds of states; (i) calcined state in the same condition of the catalyst manufacturing, (ii) reduced state in the same reduction condition of the activity test, and (iii) used state after the activity test at 390 °C.

XP spectra were recorded using a PHI 5400 ESCA spectrometer employing MgKα source (hν=1253.6 eV). The X-ray gun was operated with a stabilized electron current of 20 mA at an acceleration voltage of 15 KV. The spectrometer was operated in the fixed analyzer transmission mode with a pass energy of 71.52 eV. The binding energy of Si_{2p} as 103.4 eV was regarded as reference [Wagner et al., 1979].

7. Ammonia Temperature Programmed Desorption

Catalyst sample was treated at the same procedure as the activity test. After reduction, the catalyst sample was flushed in a He flow (30 cc/min) at 250 °C for 1 hr, cooled to 100 °C, and then maintain for 30 min in the same flow. The catalyst sample

was adsorbed with ammonia (30 cc/min) for 30 min at 100°C, and then flushed with a He flow for 1 hr at 100°C. Adsorbed ammonia was desorbed while increasing the temperature from 100°C to 900°C at a ramping rate of 10°C/min in a He flow of 30 cc/min.

8. Atomic Absorption Spectroscopy and Mössbauer Spectroscopy

In order to determine the copper loading of catalysts, atomic absorption spectroscopic measurement (model: Perkin-Elmer PC 5100) was carried out. The copper loading was measured after metal digestion in the calcined catalyst in a 3:1 HCl:HNO_3 acid mixture at 60°C for 6 hr.

Mössbauer spectra of the $Cu/Fe/SiO_2$ and Cu/Fe catalysts were collected using an Austin Science Associates model S-600 Mössbauer spectrometer, connected to a Seiko EG&G model MCA 7800 multichannel analyzer. The spectometer was operated in the constant acceleration mode, with a 10 mCi single line γ-rays was achieved with a Kr-CO_2 proportional counter. Isomer shifts were reported with respect to iron foil at room temperature. Mössbauer spectra were computer fitted to Lorentzian lineshapes by a least-square nonlinear fitting program. Linear constraints were applied when close overlaps of lines led to nonphysical fitted parameters from unconstrained fits. In some cases, the relative positions of the peaks were fixed at expected values. A glass cell with beryllium windows was utilized for the collection of all Mössbauer spectra. For the Mössbauer experiments catalyst samples weighing about 120 mg were pressed into self-supporting wafers of 13 mm in diameter, which were subsequently loaded into the cell for each run. The samples were reduced in a flow of hydrogen at 250°C for 5 hr, then cooled down to room temperature. All spectra were taken at room temperature.

RESULTS AND DISCUSSION

1. Activity Test

Silica support and Fe/SiO_2 catalyst hardly showed the dehydrogenation activity of cyclohexanol at the temperature region of 250-390°C. At high temperature of 390°C, both catalysts showed considerable dehydration activities of cyclohexanol to cyclohexene. It has been known that the dehydration of cyclohexanol to cyclohexene occurs on acidic sites of catalyst. Uemich et al. [1989] reported that alumina itself showed exclusively the dehydration of cyclohexanol to cyclohexene. Sivaraj et al. correlated the activity of dehydration of cyclohexanol to the amount of ammonia uptake over $Cu/Zn/Al_2O_3$ catalysts [Sivaraj et al., 1990]. Chen et al. [1992] observed that the active site for the formation of cyclohexene for Cu-Fe catalyst was related to the acidity of catalyst.

For 6 wt% Cu/SiO_2 catalyst, the effect of the space velocity on the conversion of cyclohexanol and on the selectivity of cyclohexanone was demonstrated at 300°C as shown in Fig. 1.

Table 1 shows the effect of the iron addition to Cu/SiO_2 catalyst on the activity of dehydrogenation of cyclohexanol at 250°C. Chen et al. [1992] observed that unsupported Cu-Fe catalyst produced magnetite site on the catalyst was responsible for the formation of phenol. In our studies, however, phenol was detected in a trace amount. The reactor effluents were cyclohexanol, cyclohexene and unreacted cyclohexanol.

When iron was added to Cu/SiO_2 catalyst, the conversion increased with iron loading up to 2 wt%, then it decreased with further increase in the iron addition. The increase is more prominent at lower reaction temperature of 250°C than at 390°C (Table 2). More than 3 times increase of the conversion with a small amount of iron addition (1.32 wt%) was observed at 250°C. A sharp increase in the selectivity of cyclohexanone with concomitant decrease in the selectivity of cyclohexene was observed when a small amount (1.32 wt%) of iron was added. When the iron addition exceeded 1.32 wt%, the selectivities did not change any more at 250°C or a slight decrease in the cyclohexanone selectivity was observed at 390°C. The decreases in the cyclohexanone selectivity at high temperature

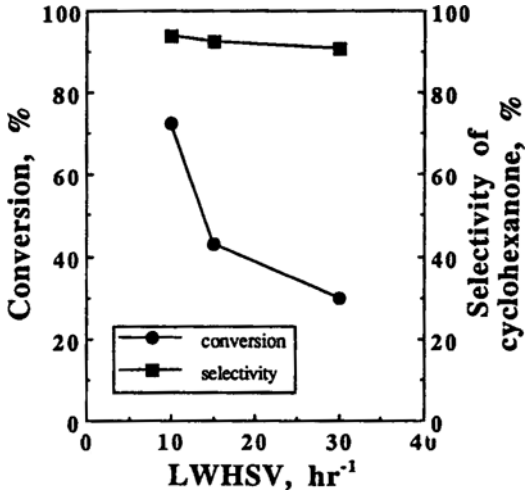

Fig. 1. Effect of space velocity on the conversion of cyclohexanol and the selectivity of cyclohexanone for Fe-free, 6 wt% Cu/SiO_2 catalyst at 300°C.

Table 1. The comparison of productivity of Cu-Fe catalyst with that of $Cu/Fe/SiO_2$ for the dehydrogenation of cyclohexanol at 250°C with feed rate=0.049 mol/hr and space velocity=6724 cc/g/hr

Catalyst $Cu/Fe/SiO_2$ (wt%)	Conversion (%)	Selectivity (%)			Productivity	
		Cyclohexanone	Cyclohexene	Phenol	(mol/hr/g_{cat}) $\times 10^2$	(mol/hr/m^2_{Cu}) $\times 10^3$
24/76/0	29.64	99.23	0.50	0.27	8.9	9.9
6/0/94	10.21	94.75	2.49	0	3.1	12.7
6/1.32/92.68	33.13	99.81	0.19	0	10.9	33.2
6/2.64/91.36	45.31	99.84	0.16	0	13.6	41.6
6/5.28/88.72	36.65	99.75	0.25	0	9.8	33.3
6/10.56/83.44	36.24	99.71	0.29	0	10.9	27.0

Table 2. The comparison of productivity of Cu-Fe catalyst with that of $Cu/Fe/SiO_2$ for the dehydrogenation of cyclohexanol at 390°C with feed rate=0.049 mol/hr and space velocity=6724 cc/g/hr

Catalyst $Cu/Fe/SiO_2$ (wt%)	Conversion (%)	Selectivity (%)			Productivity	
		Cyclohexanone	Cyclohexene	Phenol	(mol/hr/g_{cat}) $\times 10^2$	(mol/hr/m^2_{Cu}) $\times 10^3$
24/76/0[1)]	99.10	73.05	13.93	10.09		
24/76/0[2)]	74.21	83.08	9.94	6.98	22.3	24.9
6/0/94	84.07	51.84	48.16	0	25.2	104.2
6/1.32/92.68	88.84	97.72	2.28	0	26.6	81.5
6/2.64/91.36	90.62	96.19	3.81	0	27.2	83.1
6/5.28/88.72	91.16	93.31	6.69	0	27.6	94.3
6/10.56/83.44	94.49	91.63	8.37	0	28.3	70.3

[1)] Result of Chen et al. [1992]. Reaction condition : space velocity=1272 cc/g/hr (7.0 % dilution with N_2). Catalyst was prepared by mixing proportionate copper nitrate solution and iron nitrate solution.

[2)] Catalyst was prepared by coprecipitating copper nitrate solution and iron nitrate solution using sodium carbonate solution at pH 7.

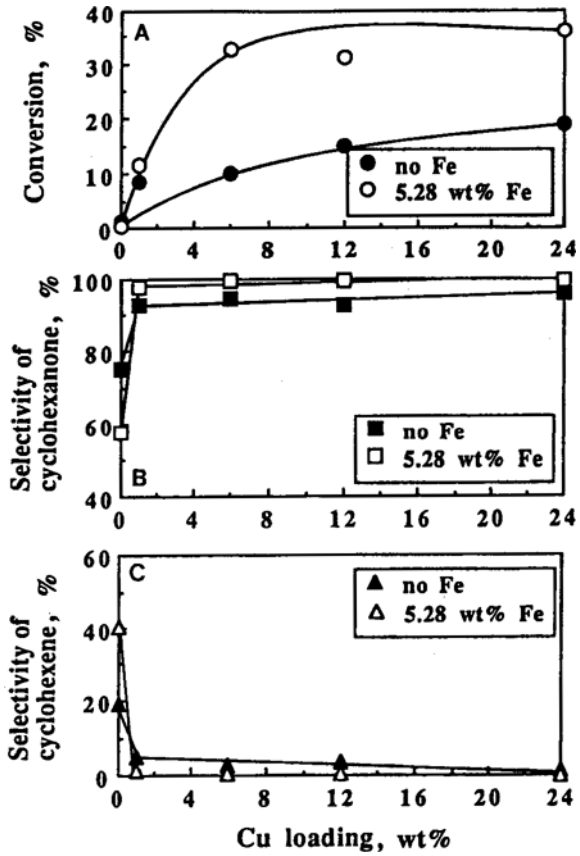

Fig. 2. Effect of Cu loading of $Cu/Fe/SiO_2$ catalysts (Fe loading= 5.28 wt%) on the catalytic activities (a) and the selectivities of cyclohexanone (b) and cyclohexene (c). Temp.= 250°C; LWHSV=30 hr^{-1}; cyclohexanol flow rate=4.9× 10^{-2} mol/hr.

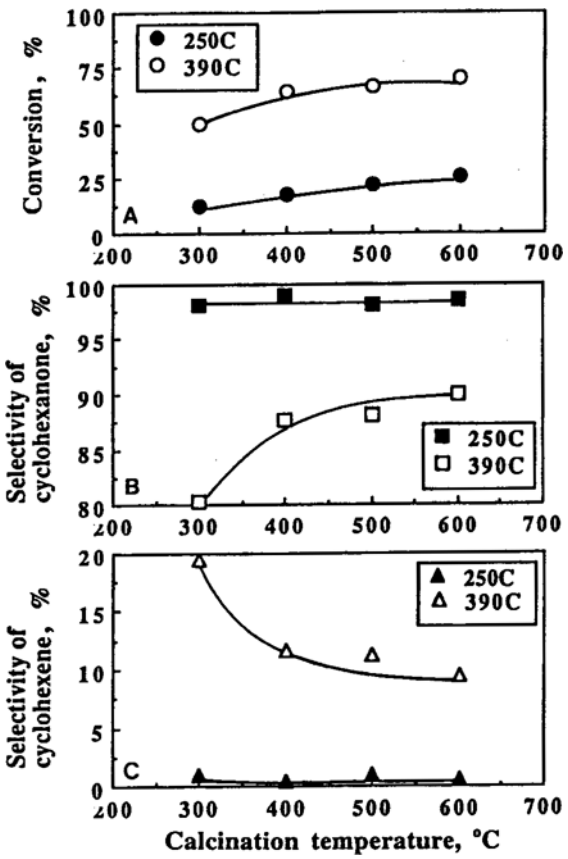

Fig. 3. Effect of the calcination temperature of 6 wt% Cu-5.28 wt% Fe/SiO_2 catalysts on the catalytic activity (a) and the selectivities of cyclohexanone (b) and cyclohexene (c). Temp.=250, 390°C; LWHSV=30 hr^{-1}; cyclohexanol flow rate=4.9× 10^{-2} mol/hr.

of 390°C were also observed for unsupported Cu-Fe catalysts [Chen et al., 1992]. It was believed that tetrahedral copper oxide itself exhibited dehydration activity at high temperatures.

The promotional effect of iron in Cu/SiO_2 catalysts was also shown in Fig. 2. At a constant loading of iron (5.28 wt%), the increase of copper loading enhanced the conversion of cyclohexanol and the selectivity of cyclohexanone but decreased the selectivity of cyclohexene compared to the results of the Fe-free Cu/SiO_2 catalysts.

The effect of the calcination temperature was studied for 6 wt% Cu-5.8 wt% Fe/SiO_2 catalyst (Fig. 3). Generally, the conversion and the selectivity of cyclohexanone increased but the selectivity of cyclohexene decreased as the calcination temperature increased.

The Fe^{3+} ion in reduced $Cu/Fe/SiO_2$ catalyst resulted in the better resistance of Cu particle sintering and the lower selec-

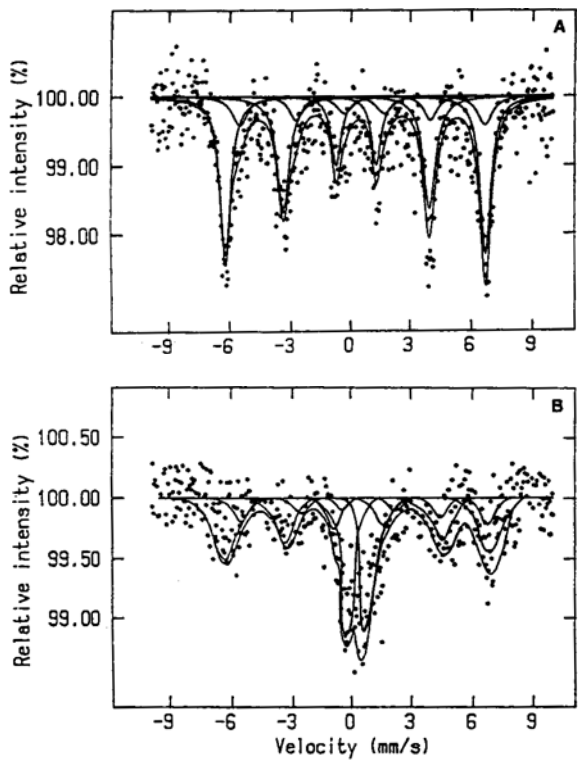

Fig. 4. Mossbauer spectra of reduced catalyst. (a) Cu/Fe (24/76); (b) $Cu/Fe/SiO_2$ (6/10.56/83.44).

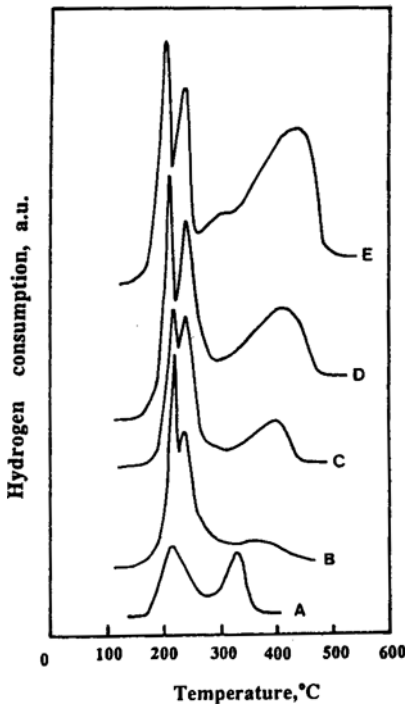

Fig. 5. TPR profiles of $Cu/Fe/SiO_2$ catalysts (Cu loading=6 wt%) with respect to the Fe loading; (a) Fe-free, (b) 1.32 wt% Fe, (c) 2.64 wt% Fe, (d) 5.28 wt% Fe, (e) 10.56 wt% Fe.

tivity of phenol arisen from the magnetite in Cu-FeO catalyst (Fig. 4).

2. Hydrogen TPR Test

The reduction behavior of $Cu/Fe/SiO_2$ catalyst was studied using hydrogen TPR analysis. The Fe-free 6 wt% Cu/SiO_2 catalyst showed two kinds of reduction peaks at 235 °C and at 354 °C, respectively (Fig. 5). The peak at 235 °C was assigned to the reduction of bulk CuO whereas the other at 354 °C to that of strong interaction between silica support and copper oxide [Jeon and Chung, 1996]. Upon the addition of iron, three kinds of reduction peaks appeared. For 6 wt% Cu/1.32 wt% Fe/SiO_2 catalyst, three reduction peaks appeared at 220 °C, 239 °C and 394 °C, respectively. The peak at 220 °C (α) was attributed to the reduction of highly-dispersed CuO on silica support, the one (β) at 239 °C to the reduction of bulk CuO, and the one (γ) at 394 °C to the reduction of Fe_2O_3. With increasing the loading of iron to Cu/SiO_2 catalyst, the α peak shifted to lower temperature (for example, 199 °C for the 10.56 wt% Fe), the β peak did not shift (239 °C for 10.56 wt% Fe) and the γ peak shifted to higher temperature (433 °C for 10.56 wt% Fe). The shift of the α peak seemed to be correlated to the particle size of copper metal (i.e. the less the particle size of copper oxide, the lower the temperature of reduction of copper oxide). This may be explained as follows [Charcosset et al., 1971]. The addition of iron to Cu/SiO_2 catalyst led to generate small particle of copper oxide. The some surface point of copper oxide was firstly reduced. Therefore, copper metal nuclei was generated. And then copper metal nuclei grew until the coalition occurs to produce copper metal shell of the core of unreduced copper nuclei. Finally, reduction proceeds at the copper metal/copper oxide interface until all the copper oxide in the cores is reduced. Iron in Cu/SiO_2 catalyst enhanced the reduction temperature of copper oxide for Cu/SiO_2 catalyst. As shown in Table 3, the more iron loading in Cu/SiO_2, the more the extent of reduction of copper oxide.

The effect of the calcination temperature on the reduction behavior of the catalyst was also investigated using TPR analysis. As shown in Fig. 6, the catalyst calcined at 300 °C showed two peaks at 201 °C and 303 °C, respectively. With increasing the temperature of calcination, these peaks shifted to higher temperature. This may be arisen from the variation from the particle size of $CuFe_2O_4$. With increasing calcination temperature, the particle size of $CuFe_2O_4$ became large. In conjunction with XRD results, the first peak was assigned to the reduction of CuO originated from the decomposition of $CuFe_2O_4$ and the second peak to that of Fe_2O_3 originated from $CuFe_2O_4$.

Gentry et al. [1981] reported that for cupric oxide containing 2 mol % Fe additive, a single reduction process occurred about 30 °C lower temperature than that observed for pure CuO. Promoting influence of iron additive on reduction was interpreted as the production of extra copper nucleation sites by non-specific distortion of CuO lattice. Promoting role of the metal additive on reduction of bulk oxide has been explained by two mechanisms. One is that the metal additive forms the sites of hydrogen adsorption. Therefore, hydrogen is enriched on the surface of the substrate through spillover phenomena [Semon and Bond, 1974]. The other is that the metal additive produces the sites of nucleation through lattice or surface deformation [Charcosset et al., 1971]. A possible explanation on the enhancement in the temperature of reduction upon loading of iron of Cu/SiO_2 catalyst is that iron interacts well with hydrogen.

Table 3. Copper content determined by atomic absorption spectroscopy, hydrogen consumption and degree of reduction measured by hydrogen TPR (catalyst weight: 25 mg), copper surface area by N_2O titration and BET surface area for Cu-Fe and $Cu/Fe/SiO_2$ catalysts

Catalyst	AA	TPR		N_2O titration		BET
$Cu/Fe/SiO_2$ (wt%)	Copper content (wt%)	Hydrogen consumption (μmol)	Degree of reduction (%)	Copper surface area (m^2/g_{cat})	(m^2/g_{Cu})	Total surface area (m^2/g_{cat})
24/76/0	23.98	86.23	97.0	12.63	52.68	71.5
6/0/94	5.24	10.71	52.6	2.42	46.18	154.0
6/1.32/92.68	5.28	12.44	60.7	3.27	61.93	115.5
6/2.64/91.36	5.40	13.61	64.9	3.27	60.56	127.8
6/5.28/88.72	5.51	16.76	78.4	2.93	57.45	116.5
6/10.56/83.44	5.44	17.20	81.5	4.03	74.08	114.2

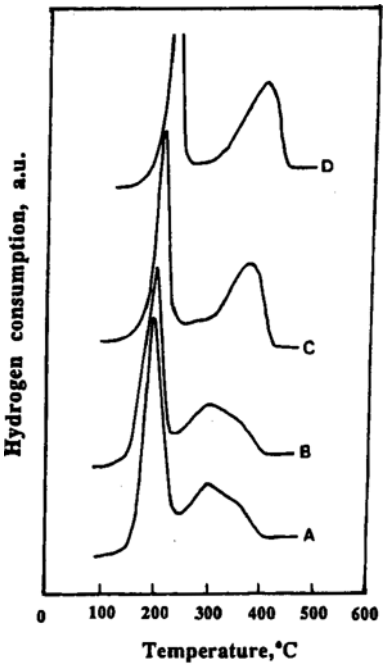

Fig. 6. TPR profiles of 6 wt% Cu-5.28 wt% Fe/SiO_2 catalysts with respect to the calcination temperature; (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.

Dowden [1965] reported that for H_2-D_2 exchange reaction, Fe_2O_3, CuO and MnO showed poor activity whereas Cr_2O_3 and Co_3O_4 did the opposite. In our studies, TPR analyses for $Cu/Fe/SiO_2$ catalyst showed that the reduction temperature of copper oxide shifted to higher temperature about 20°C compared to that of Cu/SiO_2 catalyst. From the above results, enhancement of copper reduction temperature for $Cu/Fe/SiO_2$ catalyst was not indicated to the interaction between iron ion and hydrogen.

3. XRD Test

Phases of freshly-calcined $Cu/Fe/SiO_2$ catalyst are Fe_2O_3 and CuO. In the freshly-calcined $Cu/Fe/SiO_2$ catalyst, the intensity of CuO peak decreased with increasing the loading of iron (Fig. 7). The Fe_2O_3 existed in the form of amorphous below 2.64 wt% iron loading in Cu/SiO_2 catalyst. Upon reducing the $Cu/Fe/SiO_2$ catalysts, CuO reduced to Cu and Fe_2O_3 to Fe_3O_4. Similar to that of the freshly-calcined $Cu/Fe/SiO_2$ catalyst, the intensity of the Cu peak decreased with increasing the loading of iron. In the used $Cu/Fe/SiO_2$ catalysts, the diffractograms are similar to those of the reduced $Cu/Fe/SiO_2$ catalysts. Compared to those of the reduced catalysts, the peak intensity of Cu decreased in the used catalysts.

The effect of calcination temperature was studied (Fig. 8). In the freshly-calcined catalyst, only $CuFe_2O_4$ phase was found above the calcination temperature of 400°C. In the reduced catalyst, the phases of Cu, Fe_3O_4, and $FeFe_2O_4$ appeared in $Cu-Fe/SiO_2$ catalyst (i.e. $CuFe_2O_4$ under H_2 atmosphere seems to be disintegrated to CuO and Fe_2O_3 and then reduced to Cu and Fe_3O_4). Compared to the reduced catalyst, the intensity of Cu increased for the used catalyst. Amorphous Fe_3O_4 particles for the reduced catalyst grew during the activity test. Therefore, the peak of Fe_3O_4 appeared in used catalyst.

4. N_2O Titration Test

In order to measure the surface area of copper metal, N_2O titration analysis was carried out for $Cu/Fe/SiO_2$ catalyst. Unfortunately, N_2O molecule reacted with not only copper metal but also iron oxide. Therefore, we corrected the copper surface area of $Cu/Fe/SiO_2$ catalyst after subtracting the amount of N_2 produced on Cu-free Fe/SiO_2 catalyst. As shown in Table 3, the particle size of copper metal of $Cu/Fe/SiO_2$ catalyst decreased with respect to the loading of iron. i.e. the addition of iron to Cu/SiO_2 catalyst caused the increase of dispersion of copper metal on silica support. The result of copper particle size from X-ray line broadening was summarized in Table 4. The particle size measured from XLB was larger than that from N_2O titration. Trend of particle size of copper with respect to the loading of iron was similar to that in N_2O titration. The difference of the size of copper particle between two methods seemed to be caused by several reasons. First, if the shape of copper particle was not spherical, the result of XLB calculated from Scherre equation was not reasonable. Secondly, if the interaction between copper and iron oxide increased the amount of N_2 produced, the result of N_2O titration was not also reasonable. In this correction, only the amount of N_2 produced on Fe/SiO_2 catalyst was subtracted from that of $Cu/Fe/SiO_2$ catalyst.

With increasing the calcination temperature, the size of copper metal increased until the calcination temperature was 500°C. Above 500°C, the particle size of copper metal sharply decreased. In conjunction with the result of XRD, the surface of copper metal arises from the decomposition of $CuFe_2O_4$.

5. Ammonia TPD Test

The type of acid sites and acidic strength for $Cu/Fe/SiO_2$ cat-

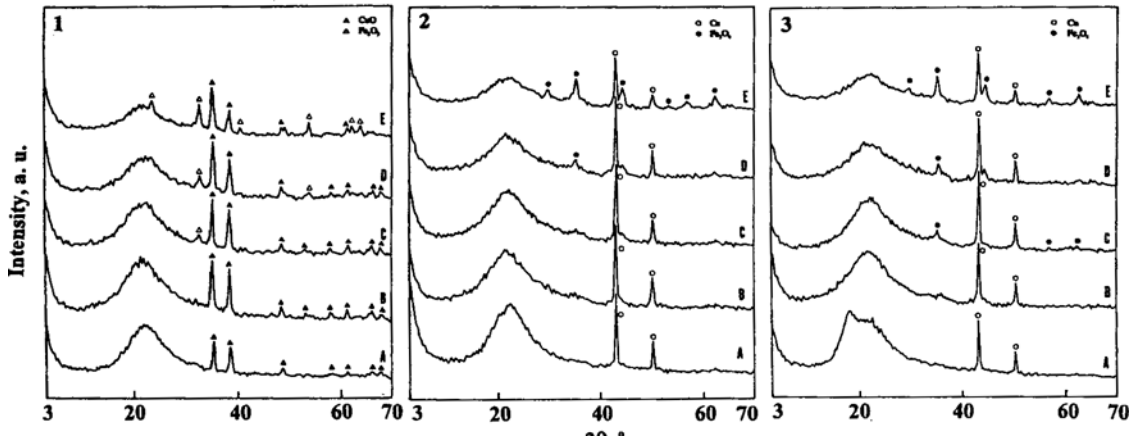

Fig. 7. Powder XRD diffractograms of $Cu/Fe/SiO_2$ catalysts (Cu loading=6 wt%) with respect to the Fe loading and pretreatment conditions (1; after calcination, 2; after reduction, 3; after use); (a) Fe-free, (b) 1.32 wt% Fe, (c) 2.64 wt% Fe, (d) 5.28 wt% Fe, (e) 10.56 wt% Fe.

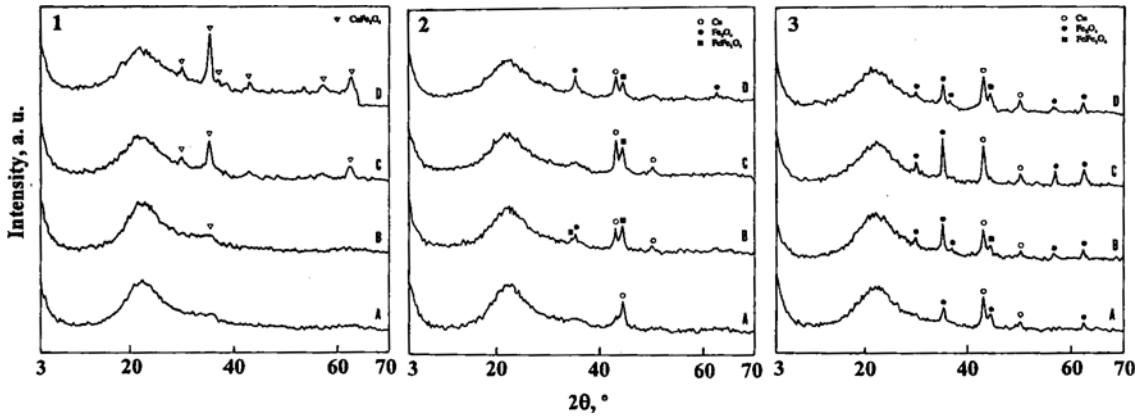

Fig. 8. Powder XRD diffractograms of 6 wt% Cu-5.28 wt% Fe/SiO_2 catalysts with respect to the calcination temperature and pretreatment coditions (1; after calcination, 2; after reduction, 3; after use); (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C.

Table 4. Effect of iron loading of $Cu/Fe/SiO_2$ catalysts on copper particle sizes of catalysts. The copper particle sizes of catalysts after reduction were determined by N_2O titration and X-ray line broadening method; those after calcination and reaction were determined by X-ray line broadening method

$Cu/Fe/SiO_2$ (wt%)	Particle size of copper (A)					
	N_2O titration			XLB		
	N_2 produced ($\mu mol/g_{cat}$)	N_2 subtracted for Fe/SiO_2 ($mmol/g_{cat}$)	After reduced	After calcined[1)]	After reduced[2)]	After used[3)]
24/76/0	272.90	157.70	128.0 (71.7)	125.0	110.0	124.0
6/0/94	29.36	0	166.6	197.7	149.4	238.3
6/1.32/92.68	45.93	6.22	123.3 (106.5)	172.7	210.7	195.7
6/2.64/91.36	52.22	12.53	123.3 (93.7)	164.4	195.7	195.7
6/5.28/88.72	52.57	17.08	137.8 (93.1)	167.4	210.7	189.0
6/10.56/83.44	98.93	50.03	100.1 (49.5)	145.2	177.0	182.8

[1)]calcined for 12 hr at 300 °C.
[2)]reduced for 5 hr at 250 °C.
[3)]reacted for 5 hr at 390 °C.
( ): results of N_2O titration before subtraction of N_2 resulted from iron oxide.

alysts were measured with TPD of ammonia. As shown in Fig. 9, two kinds of acid sites appeared for $Cu/Fe/SiO_2$ catalyst. A weak acid-site appeared near at 170 °C for the all catalysts tested. The amount and strength of the weak acid site were almost constant with respect to the iron loading. An intermediate acid site appeared near at 420 °C. The amount decreased with increasing the loading of iron. In conjunction with the results of activity tests, the dehydration of cyclohexanol to cyclohexene proceeded on intermediate acid site. As the iron loading increased, the selectivity of cyclohexene decreased due to the de-

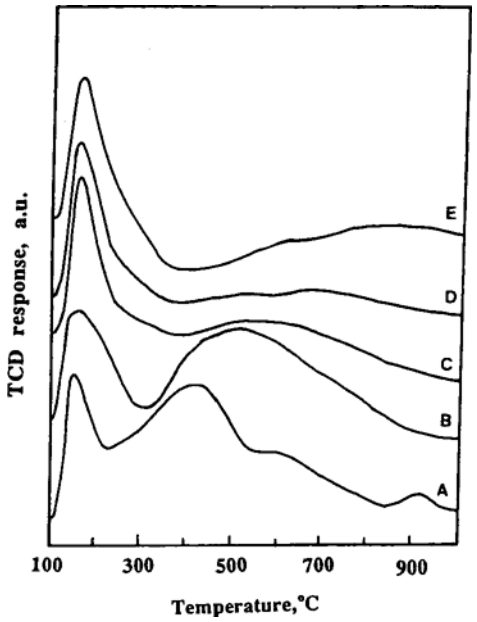

Fig. 9. Ammonia TPD profiles of $Cu/Fe/SiO_2$ catalysts (Cu loading=6 wt%) with respect to the Fe loading; (a) SiO_2 support, (b) Fe-free, (c) 1.32 wt% Fe, (d) 5.28 wt% Fe, and (e) 10.56 wt% Fe.

creased amount of strong acid site. Strong acid site at 900°C was observed with silica becomes negligible when either Cu or Cu/Fe is doped on silica.

6. XPS Test

The surface oxidation state of catalyst sample was analyzed using XPS. In general, Cu(II) is distinguished from the other copper phases [Cu(I) and Cu(0)]. Many researchers reported that Cu(II) spectra have shake up satellites arisen from the electron transfer between metal-ligand whereas Cu(I) and Cu(0) have no satellite [Boyce et al., 1991; Schon, 1973; Haber et al., 1978]. Also, the width of the main peak of Cu $2p_{3/2}$ is larger than that of Cu(I) and Cu(0) due to multiple splitting [Yin et al., 1974]. As summarized in Table 5, the oxidation state of copper for freshly-calcined $Cu/Fe/SiO_2$ catalyst was exclusively Cu(II). This identification was supported by the fact that the binding energy of the Cu $2P_{3/2}$ main peak is 933.6 eV and it has shake up satellites of Cu $2P_{3/2}$ and Cu $2P_{1/2}$. This result is consistent with XRD data. However, for both reduced and used catalyst, binding energy of Cu did not show constant pattern due to probably the contact with oxygen after the reduction and the activity test.

In order to know the surface composition of $Cu/Fe/SiO_2$ catalyst, XPS analysis was employed. As summarized in Table 6, the ratio of Cu/Fe at surface for $Cu/Fe/SiO_2$ catalyst varied with respect to the state of catalyst (freshly-calcined, reduced, used state). The ratio of Cu/Si of freshly-calcined catalyst was kept to the reduction treatment. That is, the sintering of copper particle hardly occurred during reduction process. After reaction, the ratio of Cu/Si increased compared to that of freshly-calcined or reduced catalyst. Because XPS confined the region of surface, ratio of Cu/Si mention here was regarded as the dispersion of copper on silica. The ratio of Cu/Si of reduced catalyst showed the same trend of copper dispersion determined by

Table 5. The binding energies of Cu 2p, Fe 2p, C 1s and O 1s for $Cu/Fe/SiO_2$ catalysts calcined at 300°C for 12 hr under air flow

$Cu/Fe/SiO_2$ (wt%)	Binding energies of each atom (eV)				
	Cu $2p_{3/2}$	Cu $2p_{1/2}$	Fe $2p_{3/2}$	O1s	C 1s
6/0/94	933.6	953.5	-	532.7	284.9
6/2.64/91.36	932.9	952.5	711.7	532.5	280.0
6/5.28/88.72	933.0	953.8	711.1	532.4	280.7
6/10.56/83.44	933.6	953.3	711.1	532.5	280.6

Table 6. The atomic surface ratios of Cu/Si, Fe/Si, and Cu/Fe for $Cu/Fe/SiO_2$ catalysts determined by XPS analyses

$Cu/Fe/SiO_2$ (wt%)	$[Cu]/[Si]\times10^2$			$[Fe]/[Si]\times10^2$			[Cu]/[Fe]		
	fc	red	used	fc	red	used	fc[1]	red[2]	used[3]
6/0/94	2.10	2.22	0.81						
6/2.64/91.36	4.66	4.76	4.22	2.78	1.46	1.36	1.68	3.27	3.10
6/5.28/88.72	4.09	3.84	9.17	6.81	2.16	3.54	0.60	1.77	2.59
6/10.56/83.44	3.28	4.01	7.83	2.62	5.06	2.49	1.26	0.79	3.14

[1] calcined for 12 hr at 300°C.
[2] reduced for 5 hr at 250°C.
[3] reacted for 5 hr at 390°C.

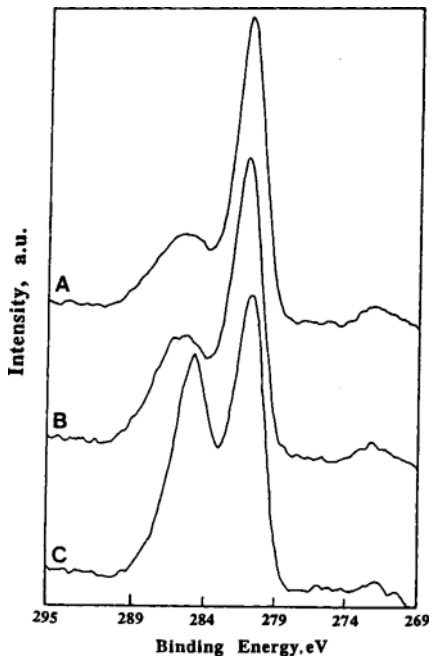

Fig. 10. C1s XP-spectra of 6 wt% Cu/2.64 wt% Fe/SiO_2 catalyst with respect to the pretreatment conditions: (a) after calcination, (b) after reduction, and (c) after use.

N_2O titration. The ratio of Fe/Si did not show any trend. The ratio of Cu/Fe of used catalyst is three times as large as that of freshly-calcined catalyst. Surface enrichment of copper was especially observed for used catalyst. The high activity of catalyst seems to arise from the surface enrichment of copper of $Cu/Fe/SiO_2$ catalyst. In the case of Fe-free Cu/SiO_2 catalyst, the copper composition for used catalyst is as much as approximately a half of that for freshly-calcined catalyst. This may be caused by copper sintering or copper sublimation during reaction. The enrichment of copper over iron for used $Cu/Fe/SiO_2$ catalyst may be explained by the difference of surface energy

Table 7. Computer-fitted parameters of Mössbauer spectra of reduced catalysts

Catalyst composition $Cu/Fe/SiO_2$ (wt%)	Iron phase		I. S. (mm/s)	Q.S. (mm/s)	Area (%)
24/76/0	Fe_3O_4	A[1)]	0.29	−0.09	21.0
		B[2)]	0.61	−0.09	79.0
6/10.56/83.44	Fe_3O_4	A	0.29	−0.06	17.1
		B	0.60	−0.07	47.4
	Fe^{3+}		0.37	0.59	35.5

[1)]A : tetrahedral
[2)]B : octahedral

of two metals and the high sintering resistance of copper particle due to the presence of iron. Carbonaceous overlay seems to be deposited on the catalyst surface during reaction. Also, the reduction treatment of catalyst sample hardly removes the carbonaceous material of freshly-calcined catalyst (Fig. 10). The results of Mössbauer experiment of $Cu/Fe/SiO_2$ and Cu-Fe catalyst were summarized in Table 7.

CONCLUSION

Addition of iron to Cu/SiO_2 enhances the temperature of reduction of copper oxide, increases the dispersion of copper metal, and decreases the selectivity to cyclohexene. However, excessive iron loading more than 1.32 wt% iron loading in $Cu/Fe/SiO_2$ catalyst does not affect the dispersion of copper metal. Dehydration of cyclohexanol to cyclohexene occurs in the intermediate, acidic sites of catalyst. As the temperature range of 250-390 °C, addition of iron of Cu/SiO_2 catalyst increases the conversion of cyclohexanol and selectivity of dehydrogenation to cyclohexanone. The atomic ratio of Cu/Fe at the surface is larger for the used catalyst than for the freshly-calcined or reduced catalyst. The surface enrichment of copper over iron may play an important role in increasing the activity. For copper iron oxide ($CuFe_2O_4$) supported on silica, copper iron oxide decomposes into copper metal and iron oxide (Fe_3O_4, $FeFe_2O_4$) under hydrogen reduction at 250 °C. Therefore, high activity can be obtained from the fine particle of copper metal.

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