Korean J. of Chem. Eng., **14**(2), 79-87 (1997)

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

Gyung Soo Jeon† and Jong Shik Chung*

Kumho Tire Technical R&D Center, Kwangju 506-040, South Korea
*Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH),
Pohang 790-784, South Korea
(Received 8 July 1996 • accepted 7 March 1997)

Abstract – The effect of the addition of manganese to Cu/SiO_2 catalysts for cyclohexanol dehydrogenation reaction was investigated. At reaction temperature of 250 °C, the conversion and the selectivity to cyclohexanone were both increased with the addition of manganese to Cu/SiO_2 catalyst. However, as the reaction temperature was further increased, higher loading of manganese in Cu/SiO_2 catalyst led to a decrease in the conversion of cyclohexanol. Manganese in Cu/SiO_2 catalyst decreased the reduction temperature of copper oxide, increased the dispersion of copper metal, and decreased the selectivity to cyclohexene. It was found that the dehydration of cyclohexanol to cyclohexene occurred on the intermediate acid sites of catalyst. At high Mn loading, catalyst surface was more enriched with manganese in used catalyst compared to that in freshly calcined or reduced catalyst, which may account for the sharp decrease of the conversion at high temperature of 390 °C. Upon reduction, copper manganate on silica was decomposed into fine particles of copper metal and manganese oxide (Mn_3O_4).

Key words : $Cu/Mn/SiO_2$, Cyclohexanol Dehydrogenation, Hydrogen TPR, XRD, N_2O Titration, Ammonia TPD, XPS

INTRODUCTION

Cyclohexanone is an important intermediate for the manufacture of caprolactam. It is generally produced by catalytic dehydrogenation of cyclohexanol. Although the selectivity to cyclohexanone is very high (i.e., more than 95 %), the reversible and endothermic feature of the reaction limit 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 to cyclohexanone in the oxidation route is not high enough to compete with that in the dehydrogenation route.

The catalysts reported to be good for the dehydrogenation reaction include various forms of copper such as CuMgO [Komarov et al., 1974], CuZnO [Emelyanov et al., 1972], Cu-Cr-O [Fridman et al., 1988], $CuZnO/Al_2O_3$ [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 was studied very recently by Sivaraj et al. [1988] and Jeon and Chung [1994, 1996b]. They have shown that the extent of 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 formed via dehydration on the acidic sites of 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 as catalyst for the reaction if the support is not acidic [Jeon and Chung, 1994, 1995]. The main issue is how to make copper particles well dispersed well on the support and having a good resistance against sintering.

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

In the screening test of promoter of Cu/SiO_2 catalyst for the dehydrogenation of cyclohexanol, manganese showed a high activity among various metal additives [Jeon, 1995].

In this work, manganese was chosen as a promoter for the further improvement of Cu/SiO_2 catalyst. The effect of manganese addition to Cu/SiO_2 catalyst on catalytic activity and catalyst characteristics was studied using various tools of characterization.

EXPERIMENTAL

1. Preparation of Catalyst

The catalysts were prepared by incipient-wetness method using the silica support (Oriental Chemical Co., surface area : 250 m^2/g). The precursors were copper nitrate pentahydrate [$Cu(NO_3)_2 \cdot 5H_2O$, Sinyo Pure Chemical Co.] and manganese nitrate hexahydrate [$Mn(NO_3)_2 \cdot 6H_2O$, Junsei Chemical Co.]. In order to evaluate the effect of the addition of manganese to Cu/SiO_2 on the activity, two groups of catalysts were made. One sets of the catalysts were prepared with varied amount of Mn loading at constant copper contents (6 wt%), while the others were prepared in

---

†To whom all correspondence should be addressed.

which the loading amount of Cu was changed at constant Mn loading (7.6 wt%). Catalyst preparation of the Cu/SiO_2 and Mn/SiO_2 catalyst preparation steps were as follows: First, silica support was dried in oven under vacuum for 10 hr at 100 °C in order to remove the residual water from the pores of silica support. Appropriate amount of copper or manganese solution equivalent to the pore volume of silica was then impregnated very slowly on the dried silica support. The manganese or copper 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 flow of 100 cc/min for 12 hr at 300 °C. The $Cu/Mn/SiO_2$ catalyst preparation steps were as follows: First, silica support was dried in oven under vacuum for 10 hr at 100 °C in order to remove the residual water from the pores of silica support. Appropriate amount of manganese precursor solution equivalent to the pore volume of silica was impregnated to silica support, dried and calcined by the same method of Cu/SiO_2 catalyst preparation mentioned above. And then, copper precursor solution equivalent to copper loading amount was impregnated to Mn/SiO_2 catalyst, dried and calcined by the same method mentioned above.

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 gram of catalyst was charged in the reactor and LWHSV (Liquid Weight Hourly Space Velocity) 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 and was kept at 180 °C. The feed lines located after the evaporator was heated to 180 °C in order to avoid the condensation of cyclohexanol vapor. The reducing gases were purified with MnO/silica trap and molecular sieve 3A trap to remove oxygen and water, respectively. Before initiating the reaction, 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. For the start of reaction, the hydrogen gas was switched to cyclohexanol vapor. A steady state was obtained in about 2 hr after reaction starts. 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.

3. Measurement of Total Surface Area

The total surface area was measured using a BET measuring apparatus (Chemisorb 102, Micrometrics Co.). Before N_2 adsorption, catalyst sample was evacuated for 2 hr at 150 °C. The dead volume of sample port was measured by static measurement using He.

4. N_2O Reactive Frontal Chromatographic Method

The surface area of copper metal of Cu/SiO_2 catalysts was calculated from the amount of generated N_2 in the following reaction [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.

Volume of N_2 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 formed between reactor and TCD cell, all experiments of N_2O titration were performed in a 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 used N_2O gas was 6 % N_2O diluted with He gas. The N_2O titration procedure was carried out as follows: The catalyst was reduced with the same procedure of reaction 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 50 cc/min of He which was purified with MnO/silica and molecular sieve 3A trap. After cooling to room temperature, the reactor was switched to a flow of a reducing gas, 5 % hydrogen in nitrogen. The gas was also purified by the same method as He treatment. Temperature of the reactor was linearly increased 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 in the reaction measurement can be calculated by measuring the amount of injected hydrogen pulses at 400 °C The degree of reductions of the reference copper oxide and cuprous oxide samples were found to be 80.5 % and 54.2 %, respectively.

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 copper phase and to calculate the size of copper particle. The scan rate was 3^{o}/min and the range of scan (2θ) 3^{o}-70^{o}. The average copper particle size of catalyst sample was calculated from the XLB (X-ray line broadening) analysis using the Scherrer equation after assuming spherical shape [Anderson, 1975].

In order to carry out XPS measurement, $Cu/Mn/SiO_2$ catalysts were pretreated into three kinds of states; (1) calcined state to the same condition of catalyst preparation, (2) reduced state to the same reduction condition of activity test, and (3) used state after activity test at 390 °C.

XPS 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

A catalyst sample was treated at the same procedure as the activity test. After reduction of the sample, it was flushed in a He flow (30 cc/min) at 250°C for 1hr, cooled to 100°C, and then maintained for 30 min in the same flow. 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 from 100°C to 900°C at a ramping rate of 10°C/min in a He flow of 30 cc/min.

RESULTS AND DISCUSSION

1. Activity Test

Silica support itself and manganese supported on silica (Mn/SiO$_2$) were not active for the dehydrogenation of cyclohexanol to cyclohexanone at temperatures below 300°C as shown in Fig. 1. At higher temperatures, exponential increase of the total conversion of cyclohexanol was mostly caused by increased production of cyclohexene. It has been known that cyclohexene is formed by the dehydration of cyclohexanol on acidic sites of catalyst [Chen et al., 1992; Sivaraj et al., 1990]. Acidic alumina also produced cyclohexene as a main product [Uemichi et al., 1989]. The introduction of Mn on silica did not increase the conversion [Fig. 1(a)] but improved the selectivity of cyclohexanone in a small amount [Fig. 1(b)]. It is believed that the manganese itself has little activity for cyclohexanol conversion.

Fig. 2 shows the effect of the Mn doping on the conversion and selectivity for a Cu/SiO$_2$ catalysts. It was observed that up to 2% Mn loading, the conversion increases sharply. An increase in the dispersion of copper for Cu/Mn/SiO$_2$ catalyst is likely to the increase the activity (conversion) as shown in Table 1. However, with further increases in the Mn loading, the conversion decreases after showing a maximum value at about 2 wt% of Mn. This decreasing tendency of the conversion with increased Mn loading after the maximum point is more pronounced at higher reaction temperature.

On the other hand, the selectivity of cyclohexanone remained nearly constant at Mn loadings above 2 wt% Mn. The increase in the selectivity of cyclohexanone with the addition of manganese is produced by removal of acid sites on silica support by the manganese doping, and it is believed that 2 wt% loading of Mn is sufficient to dope of acid sites of silica support. However above 2 wt% Mn loading, the excess manganese does not contribute to the removal of acid sites on silica

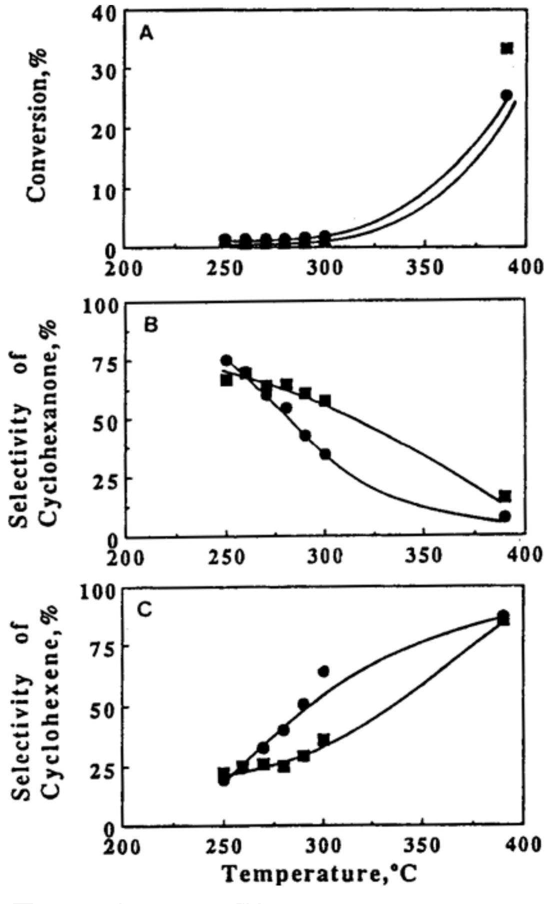

Fig. 1. The activities of pure SiO$_2$ and 7.6 wt% Mn/SiO$_2$ catalysts for cyclohexanol dehydrogenation with LWHSV 30 hr^{-1} (a) conversion (●, SiO$_2$; ■, 7.6 Mn/SiO$_2$), (b) selectivity of cyclohexanone (●, SiO$_2$; ■, 7.6 Mn/SiO$_2$), (c) selectivity of cyclohexeme (●, SiO$_2$; ■, 7.6 Mn/SiO$_2$).

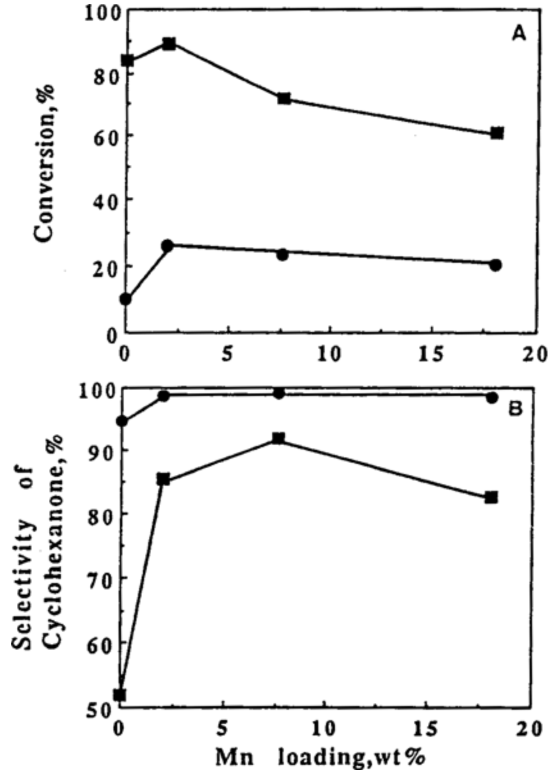

Fig. 2. Effect of the manganese loading for Cu/Mn/SiO$_2$ catalysts (Cu loading: 6 wt%) on the conversion (a) and the selectivity (b) of cyclohexanone with LWHSV 30 hr^{-1} (a) conversion (●, 250°C; ■, 390°C), (b) selectivity of cyclohexanone (●, 250°C; ■, 390°C).

Table 1. Effect of manganese loading of Cu/Mn/SiO_2 catalysts on the BET surface area, copper surface area and the copper particle sizes

Cu/Mn/SiO_2 (wt%)	BET surface area (m^2/g)	Cu surface area (m^2/g)	d_{Cu} (Å)			
			N_2O titration	X-ray line broadening (XLB)		
			After reduced[2]	After calcined[1]	After reduced	After used[3]
6/0/94	154.0	2.42	166.6(6.0)	197.7	182.8	238.3(4.2)
6/2/92	127.8	3.89	103.6(9.7)	184.4	149.4	195.7(5.1)
6/7.6/86.4	116.5	3.93	102.6(9.8)	149.1	137.8	161.6(6.2)
6/18/76	114.2	3.98	101.3(9.8)	167.4	125.6	161.6(6.2)

[1] after calcination for 12 hr at 300 °C. [2] after reduction for 5 hr at 250 °C. [3] after reaction for 5 hr at 390 °C. The value in parenthesis is Cu dispersion (%).

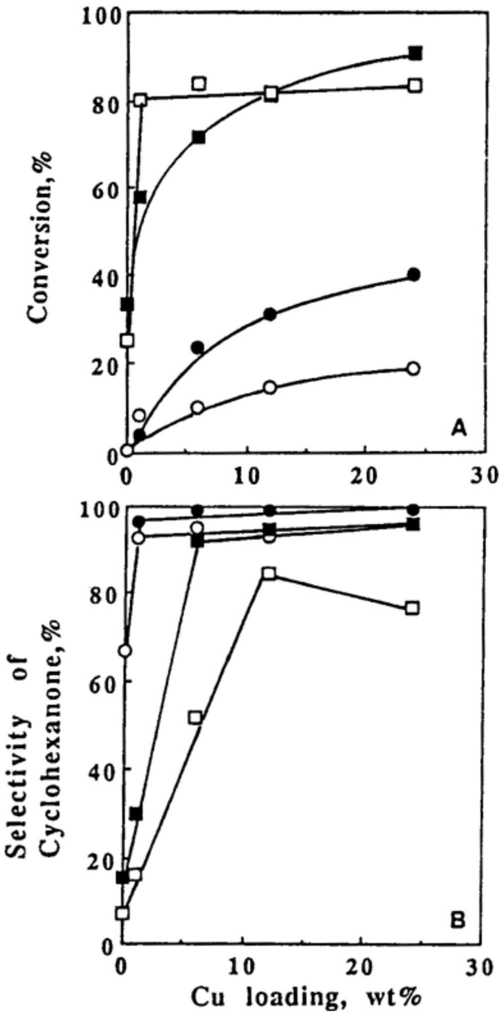

Fig. 3. Effect of the copper loading of Mn-free Cu/SiO_2 and Cu/Mn/SiO_2 catalysts on the conversion (a) and the selectivity of cyclohexanone (b) with LWHSV 30 hr^{-1} at 250 °C (○, Mn-free; □, 7.6 Mn) and at 390 °C (●, Mn-free; ■, 7.6 Mn).

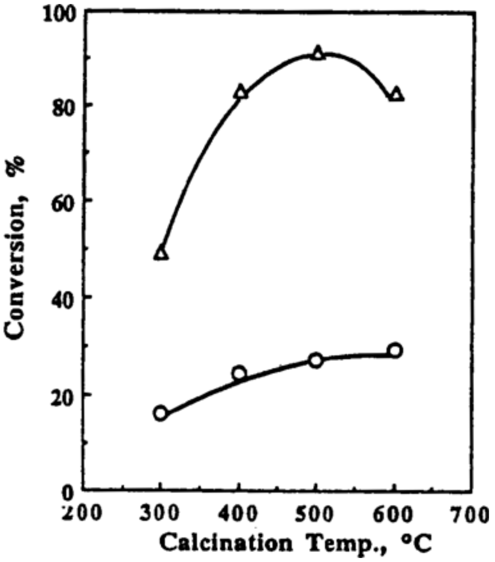

Fig. 4. Effect of the calcination temperature of Cu/Mn/SiO_2 catalysts on the conversion with LWHSV 30 hr^{-1} at 250 °C (○) and 390 °C (△).

support. According to Sivaraj et al. [1990], the dehydrogenation activity of cyclohexanol to cyclohexanone increased with increased copper dispersion in Cu/Al_2O_3 catalyst.

Fig. 3 shows the effect of copper loading on the activity (a) and selectivity (b) of cyclohexanone for Mn-free Cu/SiO_2 and Cu/Mn/SiO_2 catalysts while keeping the Mn loading constant (7.6 wt%). With increased copper loading, both the conversion and the selectivity of cyclohexanone increase sharply. The results clearly show that copper is more effective than manganese in neutralizing acid sites of silica support. Busca [1987] reported that CuO displayed a basic character in FT-IR study. The increased selectivity of cyclohexanone with increased copper loading was also in accord with the reported [Chen et al., 1992; Sivaraj et al., 1988, 1990].

In order to study the structural properties of Cu-Mn/SiO_2 catalyst, a series of Cu-Mn/SiO_2 catalysts were prepared by a simultaneous impregnation of Cu and Mn on silica support. Activity increases with higher temperature of calcination (Fig. 4). At low temperature of reaction (250 °C), the activity increases slowly but monotonically, whereas, at high reaction temperature (390 °C), the activity stays as a maximum even if calcination temperature increases. The selectivity of cyclohexanone was nearly constant regardless the calcination temperature.

2. Powder X-ray Diffraction

In the oxidized state of Mn-free Cu/SiO_2 catalyst, CuO phase appeared exclusively, and no Cu_2O or copper-silicate was detected. X-ray measurements for reduced catalysts were done after the catalysts were passivated with N_2O at 60°C for 30 min before exposed to air. The reduced Cu/SiO_2 catalyst showed the peaks of Cu(111) and Cu(200) only. Cu$_2$O phase did not appear. Therefore, CuO on silica seems to be reduced into Cu(0) directly, not through Cu$_2$O. After reaction at 390°C, the profile of XRD for Cu/SiO$_2$ catalyst remained virtually the same as that for reduced Cu/SiO$_2$ catalyst, except a slight decrease in the peak intensity. Generally, the catalysts with high copper loadings were known to be reduced to Cu(0). But the catalysts with low copper loadings were reported to be reduced to Cu(0) through Cu (I) [Takezawa et al., 1982]. Fierro et al. reported that CuO was reduced directly to Cu(0), not through Cu$_2$O during the CuO TPR [Guczi et al., 1992].

Cu/Mn/SiO$_2$ catalyst in an oxidized state showed that the dominant phases of copper are CuO($\bar{1}$11) and CuO(111), as was the case of Mn-free Cu/SiO$_2$ catalyst [Fig. 5(x)-a]. With increased Mn loading while copper loading being kept constant (6 wt%), CuO peak intensity becomes weak and broad [Fig. 5(x)-c, d], and led to the conclusion that the particle size of copper becomes small upon addition of manganese in Cu/SiO$_2$ catalyst. Also, β-MnO$_2$ phase appears at Mn loading higher than 7.6 wt%. CuO seems to be reduced to Cu(0) whereas β-MnO$_2$ is reduced to MnO upon reduction [Fig. 5(y)-c, d]. For thermodynamic reasons, manganese oxide is reported to be reduced to Mn(II)O rather than Mn(0) [Leith and Howden, 1988]. After reaction at 390°C, the intensity of Cu peak was more denounced, especially the catalysts having high Mn loadings, and MnO peak became sharper.

The effect of calcination for 6 wt% Cu-7.6 wt% Mn/SiO$_2$ catalyst was further investigated (Fig. 6). Using XRD, the oxidized Cu-Mn/SiO$_2$ catalyst calcined at 300°C did not show the peak of any phase, while copper manganate, CuMn$_2$O$_4$, is formed above 400°C [Fig. 6(x)]. With increased in calcination temperature the peak intensity of CuMn$_2$O$_4$ phase increases.

The stoichiometry for the synthesis of copper manganate is as follows [Sinha et al., 1958] and its mechanism can be explained with the charge exchange [Cocke and Veprek, 1986; Schwab and Kanungo, 1977; Sinha et al., 1958; Vanderberghe, 1978].

$$CuO+Mn_2O_3 \rightarrow CuMn_2O_4$$

$$Cu(II)+Mn(III) \rightarrow Cu\ (I)+Mn(IV)$$

Upon reduction of Cu-Mn oxide (copper manganate)/SiO$_2$ catalyst at 250°C, CuMn$_2$O$_4$ on silica is decomposed into Cu(0) and MnO [Fig. 6(y)]. The stoichiometry of decomposition for CuMn$_2$O$_4$ with hydrogen reduction may be expressed as follows:

$$CuMn_2O_4+2H_2 \rightarrow Cu+2MnO+2H_2O$$

The decomposed Cu and MnO were considerably amorphous. After activity test at 390°C, a considerable amount of Cu and MnO forms crystal confirmed by XRD result.

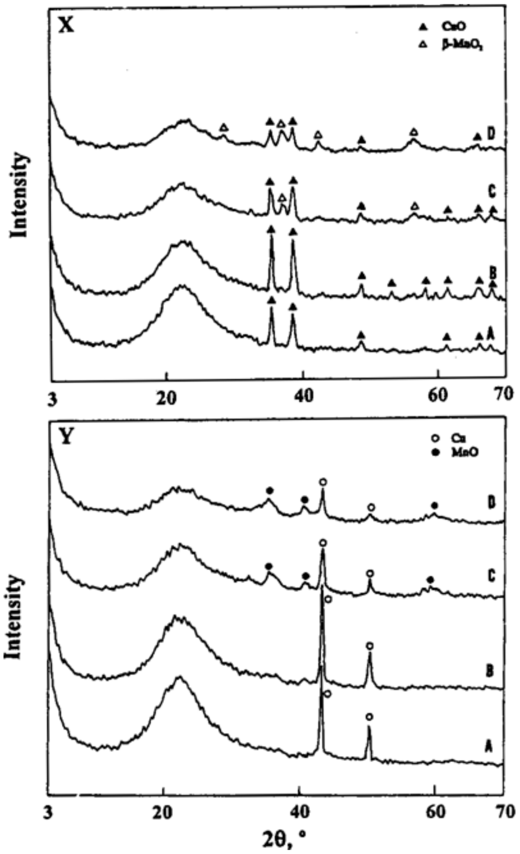

Fig. 5. Powder X-ray diffractograms of Cu/Mn/SiO$_2$ catalysts with respect to the manganese loading after calcination (x) and after reduction (y) (a) 6 Cu/SiO$_2$, (b) 6 Cu/2 Mn/SiO$_2$, (c) 6 Cu/7.6 Mn/SiO$_2$, (d) 6 Cu/18 Mn/SiO$_2$.

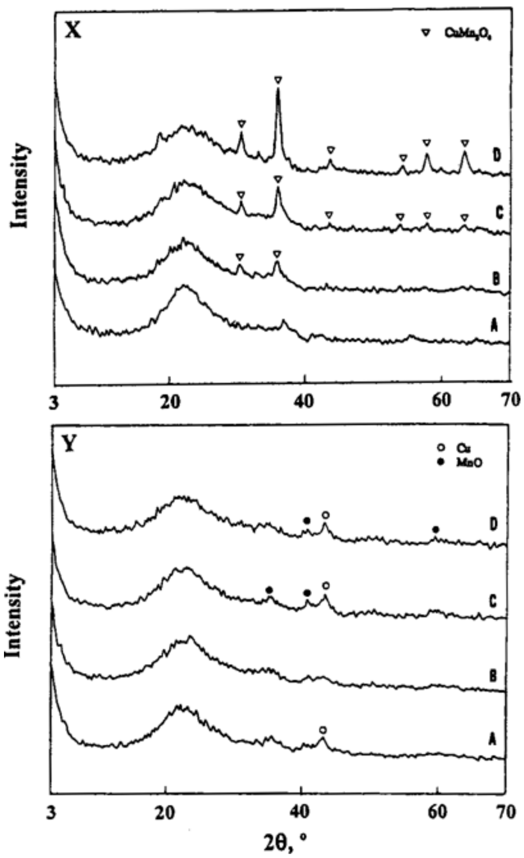

Fig. 6. Powder X-ray diffractograms of Cu-Mn (6-7.6)/SiO$_2$ catalysts with respect to the calcination temperature after calcination (x) and after reduction (y) (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C.

Table 2. Effect of copper loading of Cu/Mn/SiO$_2$ catalysts on the BET surface area, copper surface area and the copper particle sizes

Cu/Mn/SiO$_2$ (wt%)	BET surface area (m^2/g)	Cu surface area (m^2/g)	d_{Cu} (Å)			
			N$_2$O titration	X-ray line broadening (XLB)		
			After reduced[2]	After calcined[1]	After reduced	After used[3]
1/7.6/91.4	141.8	2.61	25.8(38.8)	N.D.	N.D.	N.D.
6/7.6/86.4	116.5	3.93	102.6(9.8)	149.1	137.8	161.6(6.2)
12/7.6/80.4	105.2	4.48	180.3(5.6)	176.9	167.4	182.8(5.5)
24/7.6/76	98.3	5.07	318.7(3.1)	202.9	184.5	228.3(4.4)

[1]after calcination for 12 hr at 300°C. [2]after reduction for 5 hr at 250°C. [3]after reaction for 5 hr at 390°C. The value in parenthesis is Cu dispersion (%). N.D.: not detected.

3. Measurement of Copper Particle Size

The particle size of copper metal in Cu/SiO$_2$ and Cu/Mn/SiO$_2$ catalyst was measured with N$_2$O reactive frontal chromatography method [Bartley et al., 1988; Chinchen et al., 1987]. The influence of Mn loading for 6 wt% Cu/Mn/SiO$_2$ catalyst on the particle size of copper metal was summarized in Table 1. The particle size of copper metal by N$_2$O titration of 6 wt% Cu/SiO$_2$ catalyst was 167 Å whereas those of Cu/Mn/SiO$_2$ catalysts from N$_2$O titration was approximately 100 Å irrespective of Mn loading. Also, the influence of Cu loading for 7.6 wt% Mn/SiO$_2$ catalyst on the particle size of copper metal was summarized in Table 2. It was evident that the role of manganese in Cu/Mn/SiO$_2$ catalyst was to increase dispersion of copper metal. The role of structural promoter of Mn to disperse copper particle was more pronounced as the copper loading becomes higher as shown in Fig. 7.

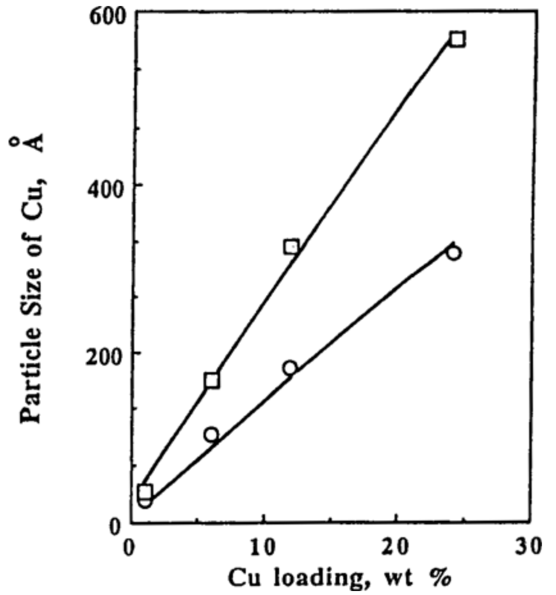

Fig. 7. Effect of copper loading on the particle size of copper for Mn-free Cu/SiO$_2$ and Cu/Mn/SiO$_2$ catalysts (○, Mn-free; □, 7.6 Mn).

4. Hydrogen TPR

Fig. 8 shows TPR results of Cu/Mn/SiO$_2$ catalysts together with TPR measurements for single component, Cu/SiO$_2$ and Mn/SiO$_2$ catalyst. Mn/SiO$_2$ catalyst showed a sharp peak at 282°C and three broad peaks at higher temperature. The peak at 282°C is assigned to the reduction of β-MnO$_2$ to MnO. The catalyst with 6 wt% Cu/SiO$_2$ has two peaks of TPR at 235°C and 354°C. The peak at 235°C is considered as the reduction peak of highly-dispersed copper supported on silica, and the other at 354°C is considered as the reduction peak of the interaction between copper and silica support. With increasing copper loading, the peak at 354°C disappears, indicating that the interaction between copper and silica support is negligible. The peak at 235°C for 6 wt% Cu/SiO$_2$ catalyst shifts to 220°C at copper loading above 6 wt%. For 24 wt% Cu/SiO$_2$ catalyst, a new peak at 248°C appears [Jeon, 1995]. Perhaps, the peak at 248°C is attributed to the reduction of bulky copper. The TPR peak for a physical mixture of copper metal powder with silica appears at 276°C [Jeon and Chung, 1994]. The TPR profile seems to relate the particle size of copper. The shift to lower temperature of TPR peak for Cu/SiO$_2$ catalyst compared to that of bulk CuO was reported by Robertson et al. [1975]. Silica support was considered as the dispersing agent of copper oxide and is seemed to play a role to increase the reduction activity of copper oxide for Cu/SiO$_2$ catalyst. Therefore, the reduction temperature of Cu/SiO$_2$ catalyst is lower than that of bulk CuO.

Reducibility of copper oxide is higher than that of manganese oxide, since the negative free energy of formation for copper oxide is less than that of manganese oxide. Therefore, the TPR peak of copper oxide seems to appear at lower temperature than that of manganese oxide [Lockwood and Frazer, 1934].

For a series of Cu/Mn/SiO$_2$ catalysts, two strong peaks are noticeable. One is located at 220°C and the other is at 265-255°C (Fig. 8). The peak at 220°C corresponds to the reduction of highly-dispersed copper and that at 265-255°C does to the reduction of β-MnO$_2$ phase. It is interesting to observe that the peak intensity of highly-dispersed copper remains almost the same with increased Mn loading, although the peak is shifted to lower temperature (220°C) when compared to that of Mn-free Cu/SiO$_2$ (235°C). Therefore, it can be suggested that only a small amount of Mn less than 2 wt% contributes in promoting dispersion of 6 wt% Cu on silica. Excess Mn does not play any role at least concerning the dispersion of copper particles. The results coincide with the activity results in Fig. 2(a) in which the conversion stays almost constant at Mn loadings higher than 2 wt%, and also agree with the results in Table 1 in which the size of copper particle remains almost the same (100 Å) at Mn loadings higher than 2 wt%. Compared with Cu-free Mn/SiO$_2$ catalyst, the reduction peak of β-MnO$_2$ is not only shifted to lower temperature (from 282°C to 265-255°C) but the peak intensity is much stronger than that of Cu-free Mn/SiO$_2$. Therefore, it is established that Cu facilitates the reduction of

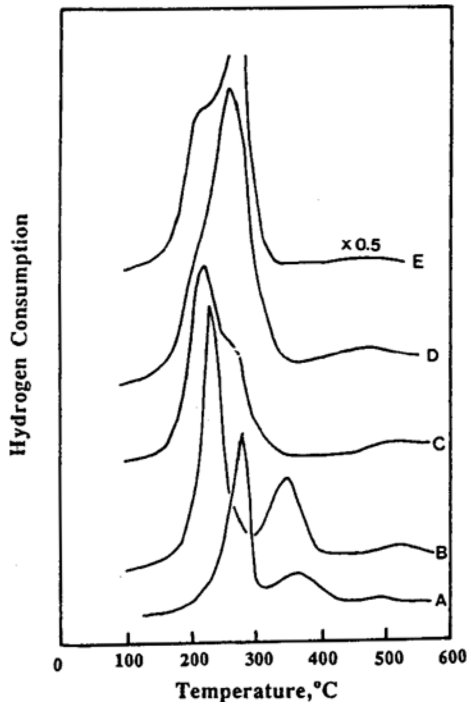

Fig. 8. TPR profiles of freshly-calcined Cu/Mn/SiO$_2$ catalysts (Cu loading: 6 wt%) with respect to the manganese loading (a) 7.6 Mn/SiO$_2$, (b) 6 Cu/SiO$_2$, (c) Cu/2 Mn/SiO$_2$, (d) 6 Cu/7.6 Mn/SiO$_2$, (e) 6 Cu/18 Mn/SiO$_2$.

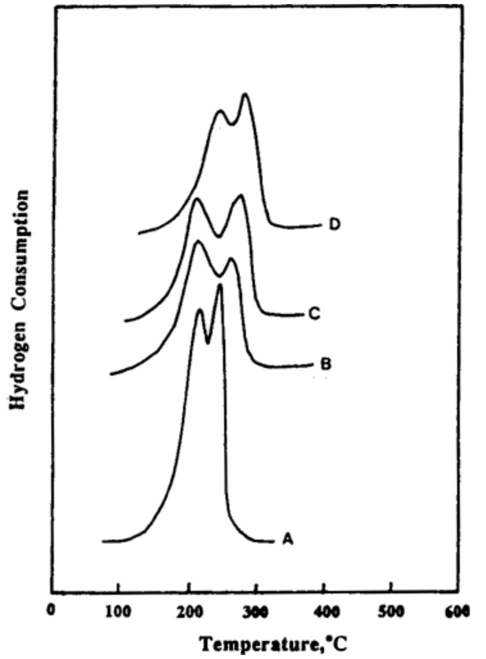

Fig. 9. TPR profiles of freshly-calcined Cu-Mn/SiO$_2$ catalysts (Cu loading: 6 wt%, Mn loading: 7.6 wt%) with respect to calcination temperature (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C.

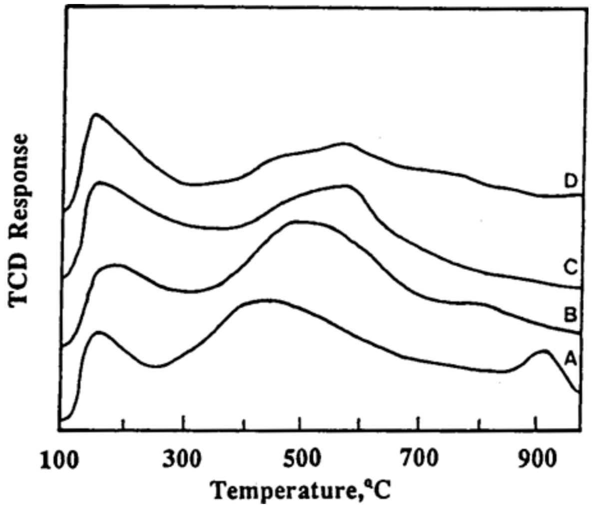

Fig. 10. Ammonia-TPD profiles for a series of reduced Cu/Mn/SiO$_2$ catalysts (Cu loading: 6 wt%) (a) silica support, (b) 6 Cu/SiO$_2$, (c) 6 Cu/2 Mn/SiO$_2$, (d) 6 Cu/7.6 Mn/SiO$_2$.

β-MnO$_2$. Similar results were also reported by Sermon and Bond [1974]; Copper enhanced the reducibility of manganese oxide due to hydrogen spillover.

The influence of the calcination temperature is studied with TPR test. CuMn$_2$O$_4$ identified from XRD result is disintegrated into Cu and MnO with reductive pretreatment at 250°C (Fig. 9). The catalyst with calcined at 300°C has two-characteristic peaks of TPR at 219°C and 248°C. Up to 500°C of temperature of calcination, the peak at 219°C appears indicating the disintegration of CuMn$_2$O$_4$ into highly dispersed Cu. The other peak at 248°C for catalyst with calcined at 300°C shifts to higher temperature with increased the temperature (265°C for calcination at 400°C, 278°C for 500°C). Perhaps, this peak seems to the reduction peak of disintegrated MnO. The catalyst with calcined at 600°C is disintegrated into bulky copper and MnO. The peak at 248°C was attributed to the reduction of bulky copper.

5. Ammonia TPD

Ammonia TPD was used to characterize acid sites and acidic strength of Cu/Mn/SiO$_2$ catalysts. As shown in Fig. 10, three kinds of acid sites were found. Weak-acid site appears near at 170°C. This site was observed for all catalysts. The amount and strength of the weak acid site were nearly constant regardless of the doping of either Cu or Cu/Mn. Intermediate acid site appears near at 420°C. This site becomes a little but stronger when Mn is additionally doped on Cu/SiO$_2$. However, its intensity successively decreases with increasing Mn loading over Cu/SiO$_2$. Strong acid site at 900°C observed with silica becomes negligible when either Cu or Cu/Mn is doped on silica. In Fig. 2(b), the selectivity of cyclohexanone is increased sharply with the addition of Mn to Cu/SiO$_2$. This can be related to the decreased intensity of ammonia TPD peak that corresponds to the reduction in intermediate acid sites responsible for cyclohexene formation upon the addition of Mn to Cu/SiO$_2$. Therefore, it can be concluded that the dehydration product, cyclohexene, is believed to be intermediate acid site.

6. XPS

The composition of Cu, Mn and Si measured with XPS for three Cu/Mn/SiO$_2$ catalysts is shown in Table 3. The surface composition of copper decreases after the activity test at 390°C probably due to either copper migration into bulk or copper sub-

Table 3. The surface atomic ratios of Cu/Si, Mn/Si, and Mn/Cu for Cu/Mn/SiO_2 catalysts determined by XPS analyses

Cu/Mn/SiO_2	$[Cu]/[Si] \times 10^2$			$[Mn]/[Si] \times 10^2$			[Mn]/[Cu]		
(wt%)	Calcination1)	Reduction2)	Use3)	Calcination	Reduction	Use	Calcination	Reduction	Use
6/0/94	2.10	2.22	0.81						
6/2/92	1.20	1.37	1.07	0.67	1.12	1.22	0.56	0.81	1.14
6/18/76	2.15	1.56	0.85	2.15	1.56	3.00	1.00	1.00	3.57

1)after calcination for 12 hr at 300 °C. 2)after reduction for 5 hr at 250 °C. 3)after reaction for 5 hr at 390 °C.

limation. When Mn is introduced into Cu/SiO_2, there seems to be enrichment of manganese at surface after use. As shown in Table 3, 6 wt% Cu/18 wt% Mn/SiO_2 catalyst has a ratio of Mn to Cu equals to nearly 1 in the oxidized and reduced state whereas the ratio becomes above 3 after the activity test at 390 °C. Compared to 6 wt% Cu/18 wt% Mn/SiO_2 catalyst, 6 wt% Cu/2 wt% Mn/SiO_2 catalyst having lower Mn content shows only 40 % increase in the Mn/Cu ratio after the reaction test. Anyhow, a significant amount of bulk Mn seems to migrate into surface at the reaction temperature of 390 °C and the migration of manganese seems to result in the enrichment of manganese at the surface.

A similar surface enrichment of manganese on Cu-Mn catalyst was reported in both supported system [Castro et al., 1987; Yang et al., 1991] and alloy system [Veprek et al., 1986; Yoon and Cocke, 1988a, 1988b]. In Cu/MnO_2 catalyst [Castro et al., 1987], the ratio of Mn to Cu increases with the temperature of reduction and a drastic increase of the ratio occurs at the reduction temperature of CuO to Cu (i.e. reduced Cu metal diffused into the substrate). This phenomenon was explained by either diffusion of copper into substrate or agglomeration of metallic copper. Yang et al. [1991] reported that the surface enrichment in the order Mn>Cu>Co was found in mixed Cu, Mn, and Co. Yoon and Cocke [1988a] reported that the ratio of Mn to Cu increased with increasing the temperature of oxidation, partial pressure of oxygen and temperature of annealing for air-exposed Cu-Mn alloy catalyst.

In oxidized state, copper in bulk is mainly CuO (identified by XRD). But in the XPS spectrum, any of 'shake up' satellite doesn't appear in oxidized state. When a core electron leaves the atom, a valence electron may be simultaneously excited to the conduction band (shake up). Unlikely to Cu, CuO and Cu_2O must appear 'shake up' satellite [Schon, 1973]. 6 wt% Cu/18 wt% Mn/SiO_2 catalyst after activity test at 390 °C shows the peak with 641.7 eV assigned MnO phase [Wollner et al., 1993] and after reduction, 642.2 eV assigned MnO_2 phase. The binding energy of Cu $2P_{3/2}$ electron in oxidized Cu/Mn/SiO_2 catalysts obtained here, 933.6 eV, may be compared to the valence 933.9 eV that in CuO reported by Wollner et al. [1993].

CONCLUSIONS

The influence of addition of Mn to Cu/SiO_2 catalyst on the catalytic activity for the dehydrogenation of cyclohexanol and the catalyst characterization was investigated. Addition of manganese to Cu/SiO_2 enhances the temperature of reduction of copper oxide, and increases the dispersion of copper metal but the loading change of manganese over 2 wt% Mn of Cu/Mn/SiO_2 catalyst does not affect the dispersion of copper metal, and decreases the selectivity of cyclohexene. Dehydration of cyclohexanol to cyclohexene occurred in the intermediate acidic sites of catalyst. At low loading of manganese (below 2 wt%) of Cu/SiO_2 catalysts, manganese increases the conversion of cyclohexanol and selectivity of dehydrogenation to cyclohexanone. At high loading of manganese of Cu/Mn/SiO_2 catalysts and high temperature of reaction, manganese decreases the conversion of cyclohexanol sharply compared to that of Mn-free Cu/SiO_2 catalyst. Manganese is more enriched on the surface of used catalyst compared to that of freshly-calcined or reduced catalysts at high temperature of reaction. This may be the cause of sharp decrease of the conversion of cyclohexanol. For copper manganate supported on silica, it shows little activity. Copper manganate decomposes into copper metal and MnO upon reduction. As a result, high activity can be obtained due to decomposition of copper manganate under hydrogen atmosphere.

ACKNOWLEDGEMENT

The authors wish to thanks the Research Center for Catalytic Technology of POSTECH for providing financial support.

REFERENCES

Anderson, J. R., "Structure of Metallic Catalysts", Academic Press, London (1975).

Bartley, G. J. J., Burch, R. and Chappel, R. J., "Investigation of the Dispersion of Supported Copper Catalysts by Oxygen Adsorption and Nitrous Oxide Decomposition", *Appl. Catal.*, **43**, 91 (1988).

Busca, G., "FT-IR Study of the Surface of Copper Oxide", *J. Mol. Catal.*, **43**, 225 (1987).

Castro, V. D., Furlani, C., Gargano, M. and Rossi, M., "XPS Characterization of the CuO/MnO_2 Catalyst", *Appl. Surface Sci.*, **28**, 270 (1987).

Chen, W.-S., Lee, M.-D. and Lee, J.-F., "Nonoxidative Dehydrogenation of Cyclohexanol over Copper-Iron Binary Oxides", *Appl. Catal. A:General*, **83**, 201 (1992).

Chinchen, G. C., Hay, C. M., Vandervell, H. D. and Waugh, K. C., "The Measurement of Copper Surface Areas by Reactive Frontal Chromatography", *J. Catal.*, **103**, 79 (1987).

Cocke, D. L. and Veprek, S., "First Direct Evidence of a Solid State Charge Redox System $Cu^{+2}+Mn^{+3}=Cu^{+1}+Mn^{+4}$ in Copper Manganese Oxide", *Solid State Commun.*, **57**, 745 (1986).

Cubberley, A. H. and Mueller. M. B., "Equilibrium Studies on the Dehydrogenation of Primary and Secondary Alcohols. II. Cyclohexanol", *J. Am. Chem. Soc.*, **June**, 1535 (1947).

Emelyanov, N. P., Bel'skaya, R. I. and Semyachko, R. Ya., "Catalyst for Dehydrogenation of Cyclohexanol to Cyclohexanone" U.S. Patent, 3 652 460 (1972).

Fridman, V. Z., Bedina, L. N. and Petrov, I. Y., "Catalytic Properties and Structure of Copper-Chromium Catalysts for the Dehydrogenation of Cyclohexanol", *Kinet. Katal.,* **29**, 621 (1988).

Guczi, L., Solymosi, F. and Tetenyi, P., "New Frontiers in Catalysis : B", Budapest (1992).

Hino, M. and Arata, K., "Dehydrogenation of Cyclohexanol to Cyclohexanone Catalyzed by Tin Oxide and Sulfated Tin Oxide", *Chem. Lett.,* 1737 (1990).

Jeon, G. S. and Chung, J. S., "Active and Selective Copper Catalyst Supported on Alkali-Doped Silica for the Dehydrogenation of Cyclohexanol to Cyclohexanone", *Korean J. Chem. Eng.,* **12**, 132 (1995).

Jeon, G. S. and Chung, J. S., "Preparation and Characterization of Silica-Supported Copper Catalysts for the Dehydrogenation of Cyclohexanol of Cyclohexanone", *Appl. Catal. A: General,* **115**, 29 (1994).

Jeon, G. S., Seo, G. and Chung, J. S., "Dehydrogenation of Cyclohexanol to Cyclohexanone over Cu/SiO$_2$ Catalysts : Dispersion and Catalytic Activity", *Korean J. Chem. Eng.,* **13**, 412 (1996b).

Jeon, G. S., Seo, G. and Chung, J. S., "Variation of Deactivation with Support in the Dehydrogenation of Cyclohexanol over Supported Copper Catalyst", *HWAHAK KONGHAK,* **34**, 605 (1996a).

Jeon, G. S., "The Dehydrogenation of Cyclohexanol over Silica-Supported Copper Catalysts", Pohang University of Science and Technology, 1995.

Klier, K., "Methanol Synthesis", *Adv. Catal.,* **31**, 243 (1982).

Komarov, V. S., Bel'skaya, R. I., Skruko, O.F. and Taborissakaya, E. A., "Catalyst for Dehydrogenation of Cyclohexanol to Cyclohexanone", U.S.S.R Patent, 411 888 (1974).

Leith, I. R. and Howden, M. G., "Temperature-Programmed Reduction of Mixed Iron-Manganese Oxide Catalysts in Hydrogen and Carbon Monoxide", *Appl. Catal.,* **37**, 75 (1988).

Lin, Y.-M., Wang, I. and Yeh, C.-T., "Activity and Stability of Copper (II) Oxide-Zinc (II) Oxide Catalysts for Oxidative Dehydrogenation of Cyclohexanol to Cyclohexanone", *Appl. Catal.,* **41**, 53 (1988).

Lockwood, W. H. and Frazer, J. C. W., "High Temperature Catalysts for Carbon Monoxide Oxidation", *J. Phys. Chem.,* **38**, 735 (1934).

Parris, G. E. and Klier, K., "The Specific Copper Surface Areas in Cu/ZnO Methanol Synthesis Catalysts by Oxygen and Carbon Monoxide Chemisorption : Evidence for Irreversible CO Chemisorption Induced by the Interaction of the Catalyst Components", *J. Catal.,* **97**, 374 (1986).

Robertson, S. D., McNicol, B. D., de Baas, J. H., Kloet, S. C. and Jenkins, J. W., "Determination of Reducibility and Identification of Alloy in Copper-Nickel-on-Silica Catalysts by Temperature-Programmed Reduction", *J. Catal.,* **37**, 424 (1975).

Schon, G., "ESCA Studies of Cu, Cu$_2$O and CuO", *Surface Sci.,* **35**, 96 (1973).

Schwab, G. M. and Kanungo, S. B., "The Catalytic Promotion in Hopcalite", *J. Phys. Chem.,* **107**, 109 (1977).

Sermon, P. A. and Bond, G. C., "Hydrogen Spillover", *Cat. Rev.-Sci. Eng.,* **8**, 211 (1974).

Sinha, A. P. B., Sanjana, N. R. and Biswas, A. B., "The Crystalline Structure of Copper Manganite", *J. Phys. Chem.,* **62**, 191 (1958).

Sivaraj, C., Reddy, B. M. and Rao, P. K., "Selective Dehydrogenation of Cyclohexanol to Cyclohexanone on Cu-ZnO-Al$_2$O$_3$ Catalysts", *Appl. Catal.,* **45**, L11 (1988).

Sivaraj, C., Srinvas, S. T., Rao, V. N. and Rao, P. K., "Selective Dependence on the Acidity of Copper-Alumina Catalysts in the Dehydrogenation of Cyclohexanol", *J. Mol. Catal.,* **60**, L 23 (1990).

Takezawa, N., Kobayashi, H., Kamegai, Y. and Shimokawabe, M., "Characterization of Copper/Silica Catalysts in Reduced States", *Appl. Catal.,* **3**, 381 (1982).

Uemichi, Y., Sakai, T. and Kanazuka, T., "Dehydrogenation of Cyclohexanol to Cyclohexanone on Supported Nickel Catalysts", *Chem. Lett.,* 777 (1989).

Vandenberghe, R. E., "Comment on Neutron Diffraction Studies of the Spinel Oxide CuMn$_2$O$_4$", *Phys. Stat. Sol.(a),* **50**, K85 (1978).

Veprek, S., Cocke, D. L., Kehl, S. and Oswald, H. R., "Mechanism of the Deactivation of Hopcalite Catalysts Studied by XPS, ISS, and Other Technique", *J. Catal.,* **100**, 250 (1986).

Wagner, C. D., Riggs, W. H., Davis, L. E. and Mullenberg, G. E., "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer Co., Minnesota (1979).

Wang, I. and Lin, Y.-M., "Method of Producing Cyclohexanone from Cyclohexanol through Oxidative Dehydrogenation", U. S. Patent, 4 198 239 (1990).

Wollner, A., Lange, F. and Knozinger, H., "Characterization of Mixed Copper-Manganese Oxides Supported on Titania Catalysts for Selective Oxidation of Ammonia", *Appl. Catal. A: General,* **94**, 181 (1993).

Yang, B. L., Chan, S. F., Chang, W. S. and Chen, Y. Z., "Surface Enrichment in Mixed Oxides of Cu, Co and Mn, and Its Effect on CO Oxidation", *J. Catal.,* **130**, 52 (1991).

Yoon, C. and Cocke, D. L., "Oxidation Studies of Copper-Manganese Alloy-A Basis for Model Catalyst Preparation", *Appl. Surface Sci.,* **31**, 118 (1988a).

Yoon, C. and Cocke, D. L., "The Design and Preparation of Planar Models of Oxidation Catalysts. I. Hopcalite", *J. Catal.,* **113**, 267 (1988b).