

# Preparation of Highly Dispersed Copper Particles in Zeolite

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## Abstract

Temperature programmed reduction and desorption techniques have been used to investigate the reduction process of CuY. The reduction of  $\text{Cu}^{2+}$  ions in zeolite with  $\text{H}_2$  occurs via a two-step mechanism in which  $\text{Cu}^+$  is first formed and then reduced to metal. In the first step of reduction  $\text{NH}_3$  was used as the reducing agent instead of  $\text{H}_2$ . Cu particles in the reduced CuY with  $\text{NH}_3$  pretreatment were uniformly dispersed compared with those of CuY without one. The average particle size of Cu metal was estimated to be 8.4 nm for the former and 18.5 nm for the latter. The detailed mechanism of reduction process of CuY has been discussed by the physico-chemical measurements, such as mass spectrometry, transmission electron microscope, infrared spectroscopy and electron spin resonance.

## Introduction

$\text{Cu}^{2+}$  ions in Y type zeolite can be readily reduced to monovalent form in the presence of mild reducing agents such as carbon monoxide and ammonia (1-3). The  $\text{Cu}^{2+}$  ions in low Cu content sample are mainly located on the site I and I' (4, 5), and moved to supercage by the interaction with  $\text{NH}_3$  to form  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex (8, 9). Recently, the reduction process of  $\text{Cu}^{2+}$  ions in CuY has been investigated by means of temperature programmed reduction and ESR measurements by many authors (10-12).

Metal particle size is one of the important factors for supported metal catalysts. The effect of preliminary treatment with ammonia on metal particle size in CuY has been investigated in this work. Furthermore, IR and ESR spectra have been measured to reveal the roles of  $\text{NH}_3$  treatment.

## Experimental

A supported CuY catalyst was prepared by ion exchange of NaY zeolite

(Union Carbide, Linde type, SK-40) with 0.1 M copper (II) acetate solution. The pH in the solution was controlled between 5.5 and 5.8 during ion exchange. The ion exchange was repeated three times. The exchanged zeolite was filtered, washed repeatedly with distilled water to remove the excess salt, and dried at 383 K in an oven. The dried sample was pelletized without a binder, crushed and sieved to 16-32 mesh before use. Sample was stored in a desiccator with a saturated ammonium chloride solution. The fluorescent X-ray analysis showed that 80.1% of  $\text{Na}^+$  ions were replaced by  $\text{Cu}^{2+}$  ions in this procedure. Oxygen, anhydrous ammonia, carbon monoxide and helium were of high purity grade. Hydrogen, 99.9999% purity, was used without further purification.

The pretreatment, temperature programmed reduction with  $\text{H}_2$  (TPR) were carried out by conventional static system which includes high speed circulation pump, cold trap kept at liquid nitrogen temperature, a pressure transducer and quartz U-type reactor. By varying the pumping speed it was demonstrated that diffusion in the catalyst bed did not limit the rate of reduction. The volume of the circulating system was 231.0  $\text{cm}^3$ .

Zeolite sample was first evacuated at room temperature and then heated slowly to 523 K at an increment of 3 K  $\text{min}^{-1}$ . The evacuation was continued at final temperature for 60 min. The dehydrated sample showed a greenish blue color. TPR experiment was carried out as follows;  $\text{H}_2$  was adsorbed on dehydrated sample at room temperature for 30 min and then the sample was heated to 723 K at a rate of 3 K  $\text{min}^{-1}$ . The initial pressure of  $\text{H}_2$  was about 80 torr. The consumption of  $\text{H}_2$  was followed by measuring the pressure drop as a function of temperature. The accuracy in this system was 1  $\mu\text{mole}$ . The rate of reduction was obtained from the gas consumption curves by graphical differentiation with a simple computer system.

The  $\text{NH}_3$  pretreatment was carried out as follows;  $\text{NH}_3$  was adsorbed on the dehydrated sample at room temperature for 2 hrs and then sample was heated to 673 K at a rate of 3 K  $\text{min}^{-1}$ . The evolved gases during the  $\text{NH}_3$  pretreatment were monitored by a Quadrupole Mass Spectrometer (Ulvac, MSQ 150A) as a function of temperature. The details in this method were described elsewhere (13). CO pretreatment was carried out by the similar manner used for the  $\text{NH}_3$  pretreatment. Initial pressure of CO was c.a. 200 torr. Other conditions in the CO pretreatment, i.e., heating rate, treatment temperature and evacuation, were similar to those in  $\text{NH}_3$  pretreatment.

ESR spectra during the  $\text{NH}_3$  pretreatment were measured with JEOL JES-PE1X spectrometer. All spectra were measured in the X-band region at room temperature.  $\text{Mn}^{2+}$  in  $\text{MgO}$  was used as a reference standard to calculate the  $g$  value. The 0.3 g of sample was set in 5 mm o.d. quartz tube, and connected to circulating system. Sample was degassed at room temperature for 1 hr, then heated to 673 K at a rate of  $3 \text{ K min}^{-1}$ , and kept at this temperature for at least 30 min. About 400 torr of  $\text{NH}_3$  was introduced to the degassed sample. It was kept at room temperature overnight, heated at a rate of  $3 \text{ K min}^{-1}$  to the final temperature, and then evacuated for 15 min at this temperature.

Infrared spectra during the  $\text{NH}_3$  pretreatment were measured in a vacuum infrared cell which consisted with a Pyrex cell fitted with KBr windows and heater. The sample wafer was prepared as follows; 10 mg of CuY powder was pressed into wafer (o.d. = 20 mm) between stainless steel plates using a pressure of 10 tons.

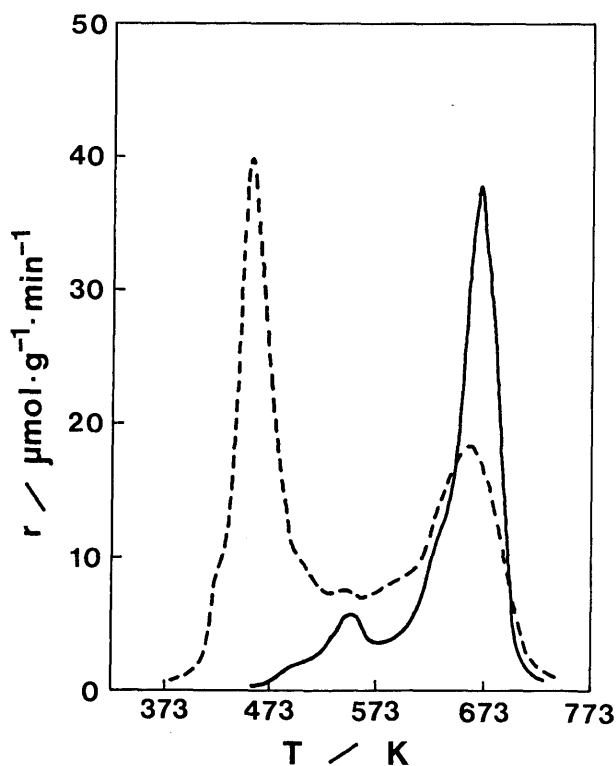


Fig. 1. TPR spectra of CuY. Solid curve, CuY with  $\text{NH}_3$  pretreatment; broken curve, CuY without  $\text{NH}_3$  treatment.

## Results

The result of TPR experiments is shown in Fig. 1. The broken curve shows the reduction rate of the fresh CuY zeolite with H<sub>2</sub>. Two distinct maxima were observed in the reduction rate around 450 and 660 K. It has been already shown that the reduction of Cu<sup>2+</sup> ions in zeolite occurs by a two-step mechanism, via Cu<sup>+</sup> ions to Cu metal (9). Therefore, the first maximum can be associated with the formation of Cu<sup>+</sup> ions, while the second maximum may suggest Cu metal formation. These assignments are further substantiated by the color changes of the sample during the TPR experiment, i.e., the greenish blue sample turns white when the first maximum is appeared, and then it turns reddish brown above 660 K.

The H<sub>2</sub> consumption of CuY with NH<sub>3</sub> pretreatment is shown by the solid curve in Fig. 1. In this case, only one maximum was observed around 670 K corresponding to the second maximum in the case of fresh CuY sample. The deep blue sample turns to white during the treatment with NH<sub>3</sub>. The NH<sub>3</sub> pretreatment is, therefore, due to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> ions. No appreciable difference of H<sub>2</sub> consumption in the process of Cu<sup>+</sup> ions to Cu metal is observed between these TPR experiments. In all cases examined a small peak was observed near 550 K, as shown in Fig. 1. This might be the reduction of small portion of Cu<sup>2+</sup> ions which could not be reduced with NH<sub>3</sub> or H<sub>2</sub> in the first step of the reduction. These Cu<sup>2+</sup> ions are presumably located in the S<sub>1</sub> positions of Y zeolite (3).

The evolved gases during programmed heating (TPD) of CuY adsorbed NH<sub>3</sub> were investigated by mass spectrometry. The NH<sub>3</sub> desorption curves are shown in Fig. 2. Solid curve and broken curve shows the desorption spectra for the first and second TPD experiment, respectively. In each run, NH<sub>3</sub> was mainly desorbed around 390 K. It should be noted that a height of the peak around 390 K decreased in the second run. When NH<sub>3</sub> was adsorbed on Cu<sup>2+</sup> ions, Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> complex forms (6-8). Upon first TPD experiment, Cu<sup>2+</sup> ions were changed into Cu<sup>+</sup> ions as shown in color. In second run, therefore, Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> complex forms when NH<sub>3</sub> was adsorbed on Cu<sup>+</sup> ions (2). The decrease of peak height supposed to be due to the difference of these complexes.

The N<sub>2</sub> desorption curves for CuY treated with NH<sub>3</sub> are shown in Fig. 3. Solid and broken curve shows TPD spectrum for the first and the second run, respectively. In the first run, two peaks were observed around 440 and 540 K. In the second run, however, the peak at the higher temperature

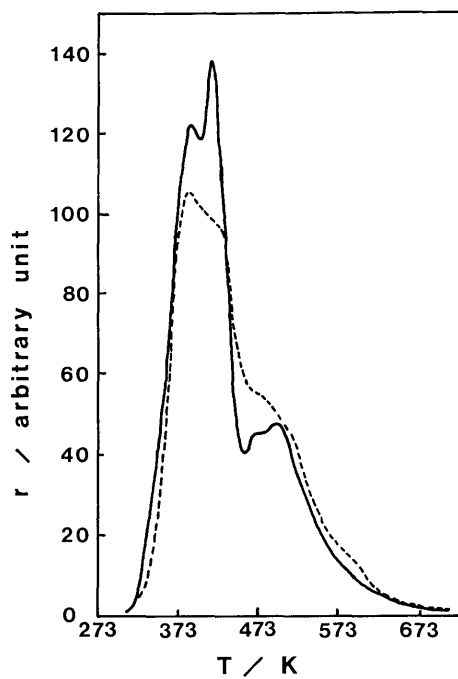


Fig. 2. TPD spectra of NH<sub>3</sub> adsorbed on CuY. Solid curve, first run ; broken curve, second run.

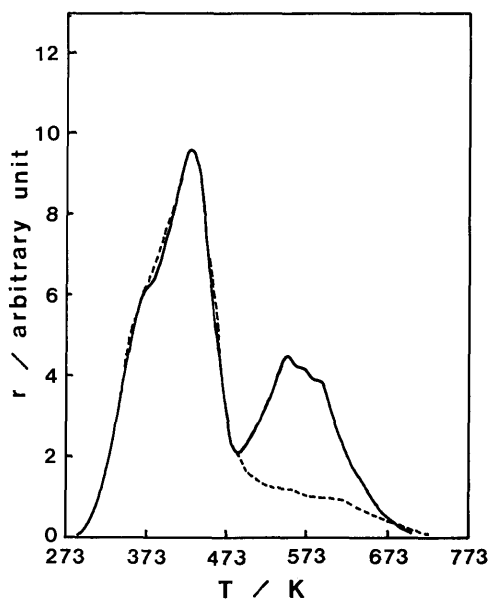


Fig. 3. TPD spectra of N<sub>2</sub> for NH<sub>3</sub> adsorbed on CuY. Solid curve, first run ; broken curve, second run.

completely disappeared. Therefore, at the temperature of second maximum,  $\text{Cu}^{2+}$  ions were reduced into  $\text{Cu}^+$  ions. The third TPD examination was carried out at the same condition, the result was similar to that in the second run. The reduction from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  was almost completed the first treatment. The peak at the lower temperature is considered to be the decomposition of the copper-ammine complex.

The dispersion state of Cu metal on zeolite was investigated by transmission electron microscope (TEM). Typical TEM photographs of the reduced CuY with and without  $\text{NH}_3$  pretreatment are shown in Figs. 4 (A) and (B), respectively. Homogeneous Cu particles were observed in the former case, while several sizes of Cu particles were observed in the latter case. The size distribution of the Cu particles was estimated from these photographs, and the histograms are shown in Fig. 5. Cu particles in the latter are distributed in a wide range of the size, whereas those in the former are distributed in a narrow range below 20 nm. The average particle size were estimated to be 8.4 nm for the former and 18.5 nm for the latter.

The results of ESR measurement during the  $\text{NH}_3$  pretreatment are shown in Fig. 6 and Table 1. Curve (a) shows the dehydrated sample and (b) shows the CuY adsorbed  $\text{NH}_3$  at room temperature. The absorption peak shifted to higher magnetic field and intensity decreased upon the adsorption of  $\text{NH}_3$ . The  $g$  value decreased from 2.165 to 2.093. These results were similar to those of Y. Huang et al. (7). ESR spectrum of CuY

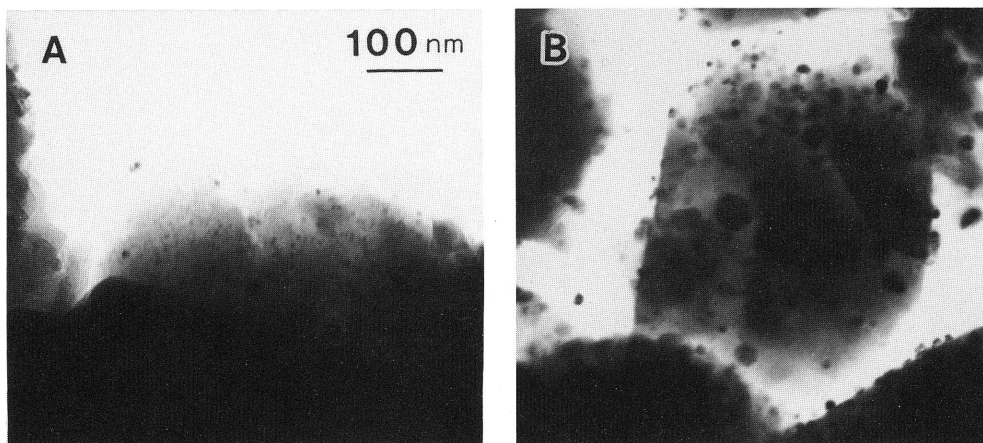


Fig. 4. TEM photographs of reduced CuY : (A) with  $\text{NH}_3$  pretreatment ; (B) without  $\text{NH}_3$  treatment.

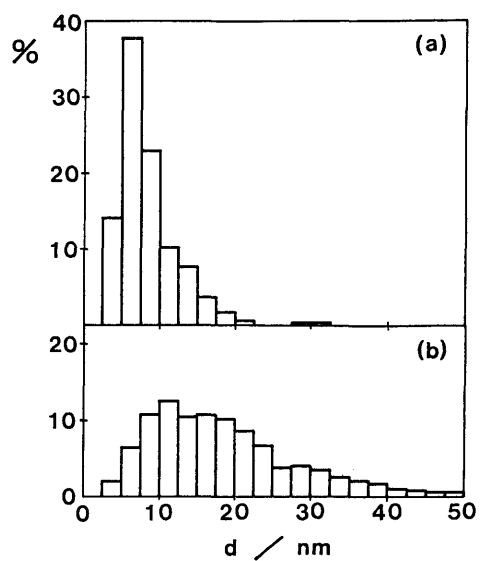


Fig. 5. Particle size histograms of Cu metal on CuY : (a) with  $\text{NH}_3$  pretreatment ; (b) without pretreatment.

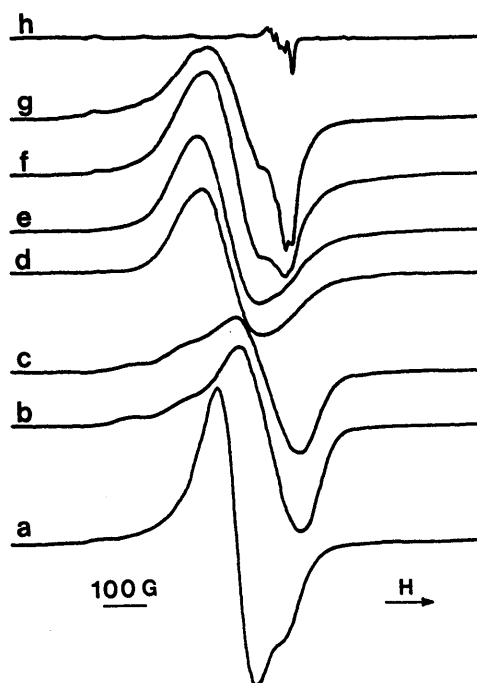


Fig. 6. ESR spectra of CuY recorded at room temperature. (a) dehydrated CuY ; (b)  $\text{NH}_3$  adsorbed on (a) at room temperature ; (c), (d), (e), (f), (g) and (h) treated (b) at 373, 423, 473, 523, 573 and 673 K, respectively.

Table 1. Magnetic parameters of CuY

Temp. of NH <sub>3</sub> treatment/K	g value	$2A\omega_{msl}/\text{Gauss}$
—	2.165	126.6
293	2.093	211.1
373	2.101	220.7
423	2.177	205.7
473	2.183	206.2
523	2.157	273.4
573	2.153	273.1

treated with NH<sub>3</sub> at 373 K is shown in Fig. 6 (c), which was similar to (b). When the sample was treated at 423 K, ESR spectrum was shifted to lower magnetic field, and the *g* value was 2.177. The color of the sample changed from deep blue to greenish blue. The circumstance around Cu ions in the sample of (d) was varied.

It is thought that the NH<sub>3</sub> molecules on Cu<sup>2+</sup> desorbed at 390 K. This is supported by the results of TPD experiment (Fig. 3). The changes between spectrum (c) and (d) was corresponded to the first peak in TPD experiment. Spectrum (e) was similar to (d). The Cu<sup>2+</sup> ion in Y zeolite treated from 423 K to 473 K remained unchanged. Upon the treatment at 673 K, ESR spectrum strongly changed. The intensity was decreased and hyperfine structure appeared. This spectrum is similar to low Cu content sample (14). Therefore, most Cu<sup>2+</sup> ions disappeared by the treatment with NH<sub>3</sub> at 673 K. Therefore, N<sub>2</sub> desorption peak around 570 K in TPD (Fig. 3) was associated with the reduction from Cu<sup>2+</sup> to Cu<sup>+</sup> ions in zeolite. ESR spectrum at 673 K may correspond the Cu<sup>2+</sup> ions located in hidden cages.

TPR experiment of CuY treated with CO was carried out to confirm roles of the NH<sub>3</sub> treatment. As shown in Fig. 7, two broad peaks were appeared at 543 and 693 K. The latter shows the reduction from Cu<sup>+</sup> to Cu metal. During the first step in this treatment, greenish blue sample changed to white, indicating Cu<sup>2+</sup> ions in the zeolite were reduced to Cu<sup>+</sup> ions with the CO treatment (3).

The TEM photograph of reduced CuY with CO pretreatment is shown in Fig. 8. The histogram of particle size is shown in Fig. 9. The Cu particles in CuY with CO pretreatment was distributed in a wide range of the size compared with NH<sub>3</sub> pretreatment, which had strong resemblance to those in the untreated sample. Average particle size of this sample is estimated to be 19.5 nm. This value almost equal to that of untreated sample (18.5 nm).

IR spectra of CuY during the NH<sub>3</sub> pretreatment were observed and the results are shown in Fig. 10. After the addition of NH<sub>3</sub> at room temperature, distinct adsorptions were observed at 1615, 1455 and 1275 cm<sup>-1</sup>. These



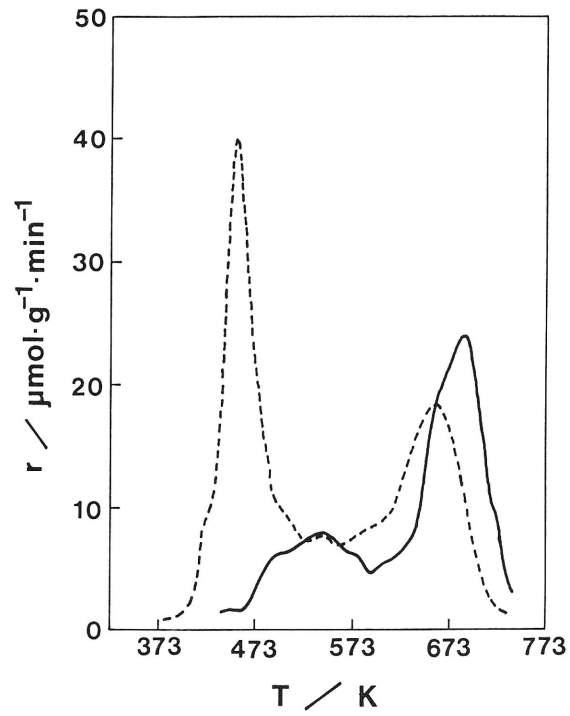


Fig. 7. TPR spectra of CuY. Solid curve, CuY with CO treatment; broken curve, CuY without pretreatment.

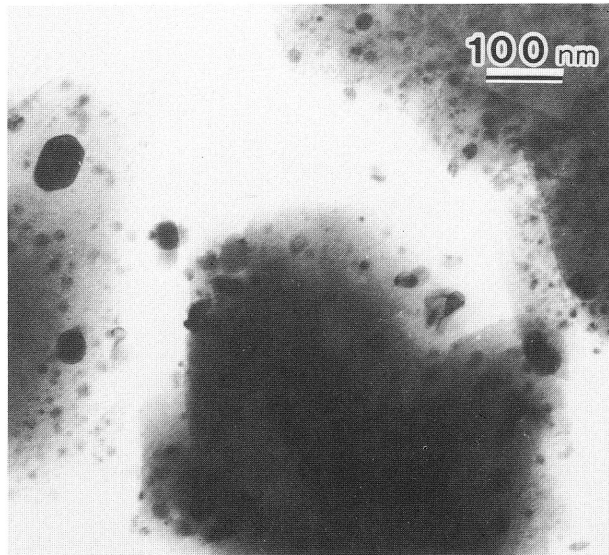


Fig. 8. TEM photograph of reduced CuY with CO treatment.

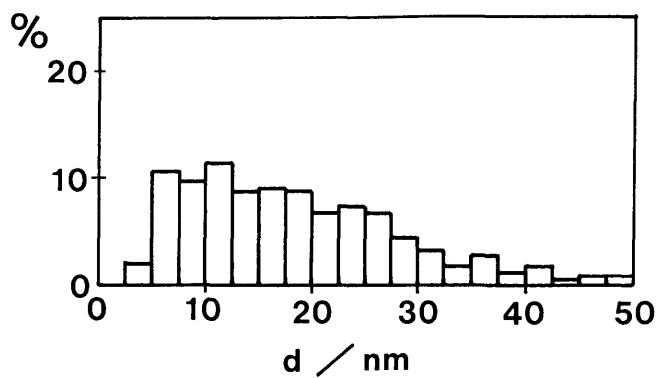


Fig. 9. Particle size histogram of Cu metal on reduced CuY treated with CO.



Fig. 10. IR spectra for CuY during NH<sub>3</sub> treatment.

absorptions correspond to  $\text{NH}_3$  deformation (6),  $\text{NH}_4^+$  ions and  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex (8), respectively. The absorptions at 1615 and 1275  $\text{cm}^{-1}$  decreased with the increase of temperature. At 673 K, the band at 1275  $\text{cm}^{-1}$  disappeared, and that at 1615  $\text{cm}^{-1}$  became very weak. The  $\text{NH}_3$  molecules in the Cu complex desorbed at 540 K. However, an appreciable absorption band of  $\text{NH}_4^+$  ions at 1455  $\text{cm}^{-1}$  was still observed above 673 K.

### Discussion

The reduction of  $\text{Cu}^{2+}$  ions in CuY with  $\text{H}_2$  occurs via two step reduction, i.e.,  $\text{Cu}^+$  ions to Cu metal. If a weak reducing agent such as  $\text{NH}_3$  or CO is used in the reduction,  $\text{Cu}^+$  species are formed selectively. In this study CuY was reduced with  $\text{H}_2$  followed by the  $\text{NH}_3$  treatment. Homogeneous small particles of Cu metal can be obtained by this treatment (Fig. 4). The reduction from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  with  $\text{NH}_3$  occurred around 570 K. It is speculated that when the  $\text{NH}_3$  is introduced on the dehydrated CuY,  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex is formed and  $\text{Cu}^{2+}$  ions are moved from small cavity to supercage (6-8). With increasing the temperature of  $\text{NH}_3$  treatment, ESR spectra were varied between 373 and 423 K, i.e.  $g$  values were changed from 2.101 to 2.177 (table 1). The latter value is similar to that of dehydrated sample, although the intensity and shape of the peak decreased. From results of TPD, the maximum desorption of  $\text{NH}_3$  was observed at this temperature range of 373-423 K (Fig. 3). Therefore, it is considered that since the  $\text{NH}_3$  molecules adsorbed on  $\text{Cu}^{2+}$  ions decreased the circumstances around  $\text{Cu}^{2+}$  ions were become to be similar to those of the dehydrated sample. Upon the treatment above 423 K, the peak area decreased with the increase of temperature. It is speculated that  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^+$  with  $\text{NH}_2$  at the elevated temperature (12). This speculation is also confirmed by the result of TPD experiment (Fig. 3), i.e., the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  takes place at 473-573 K. Upon the treatment at higher range of temperature above 673 K, the peak decreased strongly in its intensity, and is similar to that of low Cu content zeolite (14, 16). This small peak corresponds, therefore,  $\text{Cu}^{2+}$  ions located at the site I in the structure of Y zeolite. These results are also explained in terms of motional narrowing, i.e., the width of ESR signal becomes narrow, which is due to the mobility of electron spin momentum. Although the changes of intensity and width of peak are occurred by other cause such as the increase of temperature, all ESR spectra in this study were measured at same temperature (room

temperature). The peak widths ( $2\Delta\omega_{msl}$ ) of CuY treated with  $\text{NH}_3$  below 373 K were 210–220 G. These values were much larger than that of dehydrated sample (126.6 G). Therefore, the mobility of  $\text{Cu}^{2+}$  ions may be lower. Below 373 K,  $\text{Cu}^{2+}$  ions form  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex in supercage (7, 8), and their mobility is lower than the bare  $\text{Cu}^{2+}$  ions. Upon the treatment at 473 K, the  $g$  value of the  $\text{NH}_3$  treated sample is almost equal to that of the untreated sample, and the peak width of the untreated CuY is small compared with that of the sample treated at 373 K. It is considered that the mobility of  $\text{Cu}^{2+}$  ions increases by the treatment at 473 K, because  $\text{NH}_3$  in the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex is eliminated. Upon the treatment at 573 K, the peak width distinctly increased (273 G). According to the TPD experiments, an appreciable amount of  $\text{Cu}^{2+}$  ions is reduced to  $\text{Cu}^+$  at this temperature. At the same time,  $\text{NH}_4^+$  ions formed by the interaction between  $\text{NH}_3$  and  $\text{H}^+$  sites in the zeolite. The mobility of  $\text{Cu}^{2+}$  ions is presumably restricted by the presence of these bulky  $\text{NH}_4^+$  ions.

In order to reveal the adsorbed  $\text{NH}_3$  in zeolite, IR experiments were examined. The distinct three absorption bands were observed at lower temperature, while at only one band assigned  $\text{NH}_4^+$  was observed at higher temperature (673 K). It is considered, therefore, that an appreciable amount of  $\text{NH}_4^+$  ions are located in zeolite lattice. When CuY is reduced with  $\text{H}_2$ ,  $\text{Cu}^0$  species forms and then migrates in the lattice. In the reduced sample with  $\text{NH}_3$  pretreatment, however, the  $\text{NH}_4^+$  ions restrict moving of  $\text{Cu}^0$  species. Consequently, Cu metal can not be agglomerated to large particles. On the other hand, the bulky  $\text{NH}_4^+$  ions are absent in the reduced CuY without  $\text{NH}_3$  pretreatment. The migration of Cu metal occurred in an appreciable extent, and large particles are generated on the zeolite. In order to confirm the above consideration, CuY was reduced to  $\text{Cu}^+$  with CO instead of  $\text{NH}_3$ . CO molecules cannot remain in the structure. The TEM result was similar to those of CuY without  $\text{NH}_3$  pretreatment. It is concluded, therefore, that the reason why the homogeneous particles are formed on the zeolite with  $\text{NH}_3$  treatment is due to the formation of  $\text{NH}_4^+$  ions in zeolite.

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