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PRELIMINARY TREATMENT WITH AMMONIA IN REDUCTION OF CuY ZEOLITE

Shuji TANABE and Hiroshige MATSUMOTO*
Department of Chemistry, Faculty of Liberal Arts
Nagasaki University, Bunkyomachi 1-14, Nagasaki 852

The reduction process of CuY zeolite has been investigated in temperature programmed experiments. The reduction of Cu^{2+} ions with H_2 occurred by a two-step mechanism, via Cu^+ ions to Cu metal. In the first step of reduction NH_3 was used as the reducing agent instead of H_2. Copper particles in the reduced zeolite with the NH_3-pretreatment were uniformly dispersed compared to those without the NH_3-pretreatment. The average diameters of the particles were estimated to be 8.4 nm for the former and 18.5 nm for the latter.

Metal particle size is one of the most important factors in supported metal catalysts, since it is a measure of metal dispersion, i. e., the number of surface sites available for catalysis. The catalytic activity of metal catalysts, therefore, strongly depends on the reduction process prior to catalysis. In this work, the effect of preliminary treatment with ammonia on metal particle size and on available surface area of copper in CuY has been investigated qualitatively.

Zeolite used was commercially available synthetic faujasite (SK-40). This sample was exchanged in 0.1 mol dm^{-3} copper(II) acetate solution and washed with deionized water until Cu^{2+} ions were not detected in the filtrate. Fluorescent X-ray analysis showed that 80.1% of Na^+ ions were replaced by Cu^{2+} ions. The sample was then air dried, pelletized, sieved and stored over a saturated NH_4Cl solution. Temperature programmed reduction (TPR) was carried out in a circulation reactor consisting of a quartz U-type reactor, a high speed circulation pump, a cold trap kept at the liquid nitrogen temperature and a pressure transducer. In this way pressure change corresponding to 1 μmol could be detected. The typical TPR experiment was carried out as follows. After the sample was outgassed for 30 min at 523 K under vacuum, extra pure hydrogen at a pressure of 10 kPa was added and temperature was linearly raised at a rate of 0.05 K s^{-1} up to the final temperature of 723 K. In the treatment with ammonia prior to TPR, about 12 mmol g^{-1} of ammonia was adsorbed on the outgassed sample at room temperature, and then temperature was raised at a rate of 0.05 K s^{-1} up to 673 K. The evolved gas during the NH_3-pretreatment was monitored by a flow method described elsewhere.[1)]

It has been already shown that the reduction of Cu^{2+} ions in zeolite occurs by a two-step mechanism, via Cu^+ ions to copper metal.[2)] The solid curve in Fig.1 shows the rate of reduction of the fresh CuY. The H_2-consumption consisted of two distinct peaks around 450 and 660 K. The first and the second maximum may be asso-

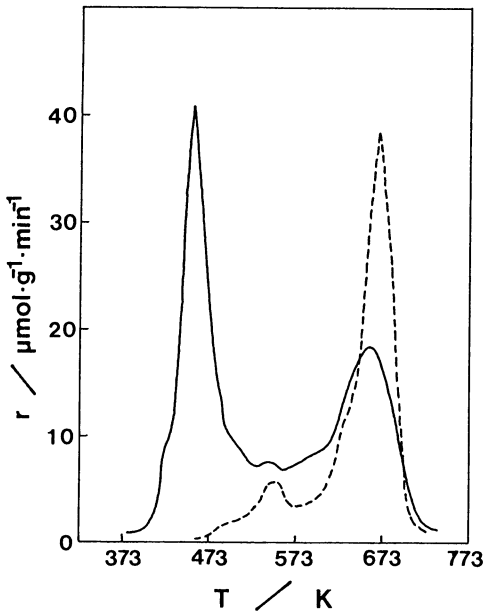

Fig.1. TPR spectra of CuY. solid curve, CuY without NH_3-pretreatment; broken curve, CuY with NH_3-pretreatment.

ciated with the formation of Cu^+ ions and metal, respectively.[2] These steps are further substantiated by the color changes of the sample during TPR, i.e., the greenish blue sample turns white when the first maximum appeared, and then it turns reddish brown above 660 K.

The rate of H_2-consumption of CuY with NH_3-pretreatment is shown by the broken curve in Fig.1. In this case only one maximum was observed around 670 K, corresponding to the second maximum in the case of CuY without NH_3-pretreatment. The sample changed from deep blue to white in color during the treatment with NH_3. The principal chemical change of Cu species during the NH_3-pretreatment is, therefore, attributed to the reduction of Cu^{2+} to Cu^+ ions. Richardson[3] reported that the reducibility of Ni^{2+} ions strongly decreased by the presence of NH_4^+ ions on the surface. With respect to the temperature where the reduction of Cu^+ ions to Cu metal occurred, however, no appreciable difference was observed between the samples without and with NH_3-pretreatment. In all cases examined a small peak was observed near 550 K, as shown in Fig.1. This might be the reduction of a small portion of Cu^{2+} ions which could not be reduced with NH_3 or H_2 in the first stage of reduction. These Cu^{2+} ions are presumably located in the S_I positions of Y zeolite.[4]

The evolved gas during programmed heating (TPD) of NH_3-CuY system was investigated by mass spectrometry. Unreacted NH_3 desorbed in a wide range of temperature from 370 to 723 K, while most of H_2O evolved between 370 and 520 K. The solid curve in Fig.2 shows the mass peak due to N_2 following NH_3 adsorption. The N_2 desorption consisted of two main peaks with maxima at 440 and 540 K, indicating that at least two kinds of decomposition took place on CuY. In order to confirm these decompositions, the NH_3-CuY system was heated repeatedly after the first reduction was accomplished, i.e., NH_3-decomposition on CuY where Cu^{2+} ions have already been reduced to Cu^+ ions. The result is shown by the broken curve in Fig.2. The N_2 peak in the higher temperature region in the first experiment almost disappeared in the second one. From these findings, it is considered that the NH_3-decomposition in the higher temperature region corresponds to the reduction of Cu^{2+} to Cu^+ ions, while that in the lower temperature region is presumably the decomposition

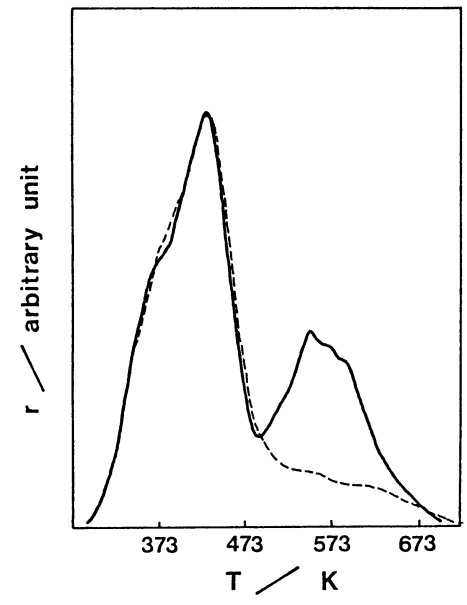

Fig.2. TPD spectra of N_2 for NH_3 adsorbed on CuY. Solid curve, first run; broken curve, second run.

of copper-ammine complexes.[5] The surface area of copper metal in reduced forms of CuY was measured by the decomposition of N_2O.[6] The N_2O decomposition was carried out at 393 K for 12 h under the initial pressure of 25.3 kPa. The available surface area of copper metal in CuY with NH_3-pretreatment was determined to be 35.7 m^2 $g\text{-}Cu^{-1}$, whereas that in untreated CuY was only 22.8 m^2 $g\text{-}Cu^{-1}$.

Measurements by transmission electron microscope (TEM) were conducted in order to observe the dispersion of copper metal. Representative TEM photographs of CuY

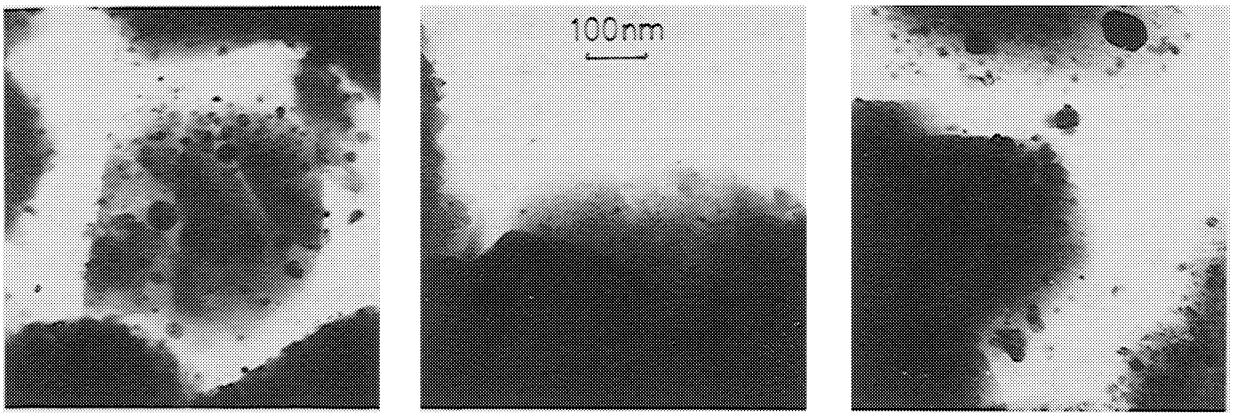

Fig.3. TEM photographs of reduced CuY, (a) without pretreatment, (b) with NH_3-pretreatment and (c) with CO-pretreatment.

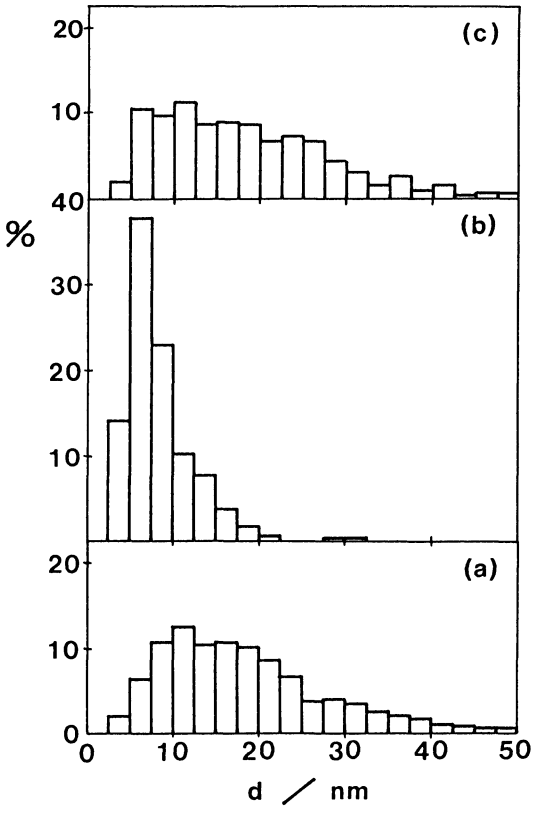

Fig.4. Crystallite size histograms of copper metal on CuY, (a) without pretreatment, (b) with NH_3-pretreatment and (c) with CO-pretreatment.

without and with NH_3-pretreatment are shown in Figs.3a and b, respectively. The copper particles in the CuY pretreated with NH_3 were distinctly small and dispersed uniformly compared to those in untreated one. Figs.4a and b show the histograms for the samples without and with NH_3-pretreatment, respectively. Copper particles in the former are distributed in a wide range of the size, while those in the latter are dispersed in a narrow range below 20 nm. The average diameters of particles are estimated to be 18.5 nm for the former and 8.4 nm for the latter.

The reason why copper particles are well dispersed in the CuY with NH_3-pretreatment is still obscure. It is, however, speculated that remaining NH_4^+ ions in the zeolite framework play an important role. When the divalent Cu ions are reduced to the monovalent Cu ions during NH_3-pretreatment, the charge balance with the framework must be compensated by the formation of H^+ sites in the presence of residual zeolitic water. In this case NH_3 could conceivably react with the H^+ sites to

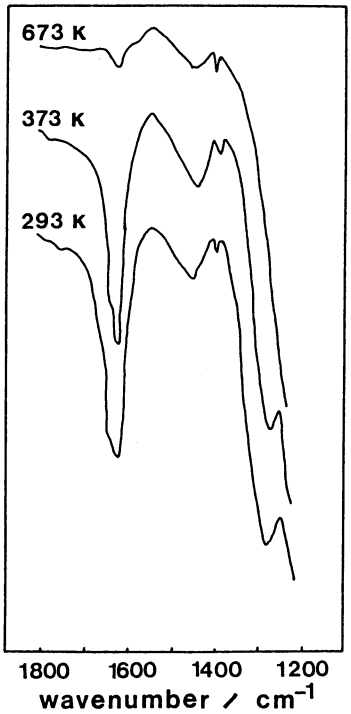

Fig.5. IR spectra for CuY during NH_3-pretreatment.

form NH_4^+ ions. Infrared spectra were measured during the NH_3-treatment, as shown in Fig.5. After addition of NH_3 distinct absorptions were observed at 1615, 1455 and 1275 cm^{-1}, corresponding to NH_3 deformation,[7] NH_4^+ ions and $Cu(NH_3)_4^{2+}$ ions,[8] respectively. The bands at 1615 and 1275 cm^{-1} decreased strongly with the increase of temperature, while that at 1455 cm^{-1} was still observed even at 673 K, where the NH_3-pretreatment had completed. This may suggest the possibility that bulky NH_4^+ ions restrict the agglomeration process of Cu species during the second reduction with H_2.

By the treatment with CO, on the other hand, Cu^{2+} ions in the zeolites are also reduced to Cu^+ ions.[9] In this case the formation of bulky species such as NH_4^+ ions are not expected on the surface. The effect of prereduction of CuY with CO was investigated to confirm this consideration. Prior to TPR, 26.7 kPa of CO was introduced to the system and then temperature was raised at a rate of 0.05 K s^{-1}. During this treatment, only CO_2 was observed as the gaseous product and the sample changed from blue to white in color. In TPR spectra of the CO-treated CuY only one maximum was recognized at 720 K. A typical photograph of the reduced CuY with CO-pretreatment is shown in Fig.3c. The histogram is shown in Fig.4c. Copper particles in this sample are distributed in a wide range. The average diameter of those particles is estimated to be 19.5 nm which is much larger than that of the NH_3-treated sample (8.4 nm) and corresponds to that of the untreated sample (18.5 nm). From these points of view, the formation of smaller particles in the CuY with NH_3-pretreatment is presumably due not to the separated two-step reduction but to the presence of bulky NH_4^+ ions on the surface. Although further experiments are needed to explain detailed mechanism of the reduction process of CuY zeolite, the NH_3-pretreatment is considered to be one of the useful methods in the preparation of highly dispersed Cu catalysts.

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