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DISCRIMINATION OF REDUCTION PROCESSES OF PARTIALLY CUPRIC ION-EXCHANGED Y ZEOLITES BY A TEMPERATURE-PROGRAMMED REDUCTION TECHNIQUE

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Four reduction processes of Cu(II) to Cu(0) in Y zeolite framework have been discernible in temperature-programmed reduction experiments with hydrogen. The reduction peaks around 473 and 593 K were proposed to correspond to the reductions of lone Cu(II) ions and Cu^{2+}-O^{2-}-Cu^{2+} species to Cu(I) ions, respectively. The generated Cu(I) ions were further reduced to Cu(0) atoms around 803 and 1153 K.

Although two-step reduction of Cu(II) exchanged in faujasite zeolites have been recognized,1) it is difficult to measure independently the processes of Cu(II) to Cu(I) and of Cu(I) to Cu(0) in static reduction experiments. A temperature-programmed reduction (TPR) technique, being useful for distinguishing two similar processes,2) has been applied to the characterization of Cu(II)-exchanged zeolites and two reduction processes have been found in the range 298-773 K.3,4) However, these processes have poorly been characterized; for example, the amounts of hydrogen consumed per Cu(II) ion and the assignments of these two processes differ significantly between the reports.3,4) We wish to report the finding and unambiguous assignment of four reduction processes of Cu(II) in Y zeolites. These results would help to understand the role and/or function of copper and oxygen ions in catalytic reactions.

Samples of CuNaY-m (m is the exchange level of Cu(II) ions), the apparatus used, and the experimental method applied were essentially the same as those previously reported.5) In all experiments, a mixture of H_2 (1.3 %) and N_2 (98.7 %) was used as the reductant.

Typical TPR spectra are shown in Fig. 1. Each spectrum consists of four peaks with peak maxima around 473, 593, 803, and 1123-1173 K. The total hydrogen consumptions per mol of Cu(II) ion in the samples between 298-1273 K were *ca.* 1.0 mol-H_2 regardless of the exchange levels of Cu(II) ions, indicating that all Cu(II) ions were reduced to Cu(0) metals. The zeolite lattices of the samples used in the experiments were shown to be completely destroyed by X-ray analyses. A NaY zeolite did not give any TPR peak in the same temperature range.

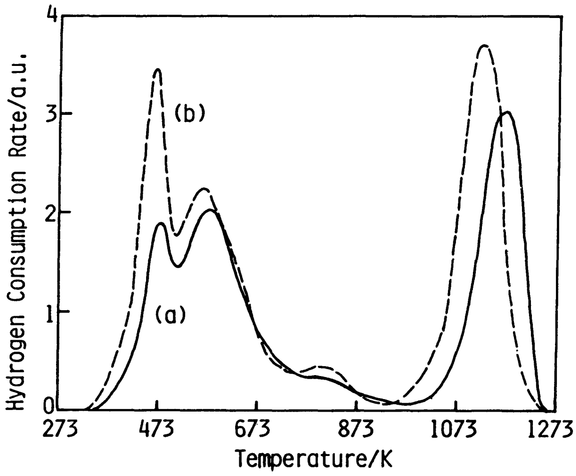

Fig. 1. TPR spectra of cupric ions in CuNaY-52(a) and -75(b). Samples were heated at a rate of 10 K/min.

It is concluded on the following bases that each Cu(II) ion is reduced to a Cu(I) ion upon the reduction between 298 and 773 K. First, the hydrogen consumptions of all CuNaY samples in above temperature range were *ca.* 0.5 mol-H_2/mol-Cu. Secondly, upon the reduction up to 773 K EPR spectra of Cu(II) ions were thoroughly eliminated and the sample color turned from greenish blue to white. In infrared study, thirdly, admission of carbon monoxide onto the sample reduced at 773 K resulted in appearance of strong absorption bands around 2135-2145 cm^{-1} attributable to Cu(I)-CO complexes.[1)]

The presence of Cu-O-Cu complexes and unpaired Cu(II) ions has been reported based on temperature-programmed desorption (TPD) experiments of oxygen.[6)] The CuNaY samples prereduced at 473 K by hydrogen gave TPD peaks of oxygen resulting from cleavage of the bridged complexes, while upon prereduction at 673 K the TPD peaks appeared no longer. In addition, the amounts of hydrogen consumed in the TPR peak at 593 K were measured to be *ca.* 0.3 mol-H_2/mol-Cu in separate experiments, which were well consistent with amounts required to reduce the whole oxygen bridged complexes (0.153 mol-O_2/mol-Cu[6)]). These observations indicate that the reducibility of the bridged Cu(II) ions is different from that of the lone Cu(II) ions and the reduction of Cu(II) to Cu(I) in CuNaY samples proceeds as follows;

$$2Cu^{2+} + H_2 \rightarrow 2Cu^{+} + 2H^{+} \quad \text{(at 473 K)} \quad (1)$$

$$Cu^{2+}\text{-}O^{2-}\text{-}Cu^{2+} + H_2 \rightarrow 2Cu^{+} + H_2O \quad \text{(at 593 K)}. \quad (2)$$

The water possibly formed during the reaction was difficult to be detected in the present experiments because of the readsorption of water onto the zeolite structure.

Finally, the reduction peaks around 803 and 1123-1173 K will be discussed. The total amounts of hydrogen consumed in the range 773-1273 K were 0.44-0.52 mol-H_2/mol-Cu, indicating consumption of a half hydrogen molecule per copper ion. Furthermore, the characteristic IR absorption bands of Cu(I)-CO did not appear upon admission of carbon monoxide onto the samples reduced at 1173 K. The sample color turned from white to black. These facts suggest that the Cu(I) ions generated through the TPR procedure between 298 and 773 K were reduced to Cu(0) atoms, though the difference between two peaks at 803 and 1123-1173 K has remained unknown.

$$Cu^{+} + \tfrac{1}{2}H_2 \rightarrow Cu^{0} + H^{+} \quad (3)$$

Activation energies for the reductions at 803 and 1173 K were measured for CuNaY-52 by the method of Gentry *et al.*[3)] and were 155 and 179 kJ·mol^{-1}, respectively. These may be compared with values of 70 and 81 kJ·mol^{-1} which have been obtained for the respective reactions (1) and (2).[5)] It is clear that the reduction of Cu(II) to Cu(I) is easier in Y zeolite structure than that of Cu(I) to Cu(0).

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