

REDUCTION MECHANISM OF COPPER IONS EXCHANGED IN Y TYPE ZEOLITES

by

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Two distinct Cu(II) to Cu(I) processes have been discernible in temperature programmed reduction with hydrogen. The reduction peak with a maximum around 573–593 K is proposed to correspond to the reduction of $\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+}$ species locating in sodalite cages. Another peak around 473–513 K has been attributed to the reduction of unpaired Cu(II) ions.

INTRODUCTION

Much efforts for revealing reduction processes of transition metal ions in zeolites have been made in order to clarify redox cycles of metal ions during catalytic oxidations and/or to develop finely dispersed metal clusters or particles on zeolites. Particularly the behavior of oxygen over Cu(II)-exchanged Y zeolites (CuNaY)¹⁻³ and the reducibility of Cu(II) ions in zeolite structure⁴⁻⁷ have been extensively studied since copper containing zeolites exhibit high catalytic activities for various oxidation reactions. In these studies a temperature programmed reduction (TPR) technique has recently been used by two research groups and been demonstrated to be a powerful tool for characterization of catalysts.^{6,7} Both studies have agreed in terms of the appearance of two reduction processes of Cu(II) ions but there are some significant discrepancies: for example, the amounts of hydrogen consumed per Cu(II) ion and the assignment of these two processes. We therefore report in this paper the effects of

exchange levels of Cu(II) ions and of the pretreatment prior to the TPR procedure on the reduction processes, which allow us to elucidate some of the above problems.

EXPERIMENTAL

CuNaY samples were prepared by the conventional ion-exchange of NaY (Linde, SK-40) reported elsewhere.¹ The exchange levels were 13, 25, 52, and 73%. The apparatus was essentially the same as that used for temperature programmed desorption experiments.⁸ In all experiments, a mixed gas of 1.3% hydrogen and 98.7% nitrogen was employed as a reductant. After being mounted in a TPR sample tube, the sample 50 mg was subjected to the following sample conditioning at 773 K: evacuation for 1 h, exposure to oxygen at 13.3 kPa for 1 h, and re-evacuation for 30 min. After this conditioning, 13.3 kPa of oxygen was introduced at 773 K and the system was cooled in the presence of oxygen to 298 K. Being submitted to evacuation of oxygen at 298

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K for 10 min, the sample was then heated to 773 K at a rate of 5 K/min in the mixed gas flow of 35 cm³/min. The mixed gas passing through the sample bed was quenched to 195 K to remove water vapor produced in the reaction of hydrogen with zeolite oxygen and then hydrogen uptakes were measured by a thermal conductivity detector.

RESULTS AND DISCUSSION

Typical results of hydrogen uptakes (TPR spectra) are shown in Fig. 1(A) as a function of temperature. X-ray diffraction analyses indicated no destruction of zeolite framework during the present experiments. Each spectrum in Fig. 1(A) consists of two peaks separated by ca. 100

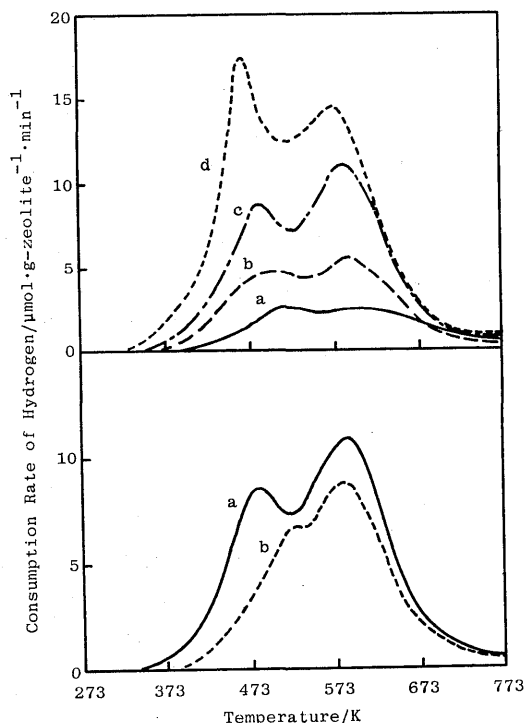


Fig. 1. TPR profiles of CuNaY zeolites. In part (A), curves a-d were obtained on CuNaY-13, -25, -52, and -73, respectively, after being cooled from 773 to 298 K in the presence of oxygen. In part (B), CuNaY-52 was cooled in the presence (a) or absence (b) of oxygen from 773 to 298 K prior to the TPR procedure.

K, in good agreement with the results of Gentry et al.⁶⁾ and Mahoney et al.⁷⁾ The temperatures of the respective peak maxima (around 473–593 K) were slightly shifted to lower temperatures with increasing exchange levels of Cu(II) ions. The total hydrogen consumptions per Cu(II) ion were 0.57, 0.56, 0.50, and 0.54, respectively, for CuNaY-13, -25, -52, and -73. These values are very close to one half, in good conformity with the other workers' results^{2,5)} using a static system. It is further confirmed in separate experiments that the EPR signal of Cu(II) ions was completely eliminated upon the present reduction treatment and that the sample color of CuNaY turned to white from greenish blue with the progress of reduction. In infrared study, admission of carbon monoxide onto the reduced sample resulted in appearance of strong absorption bands around 2135–2145 cm⁻¹, as shown in Fig. 2(c). These bands are apparent to be attributed to CuI-CO complexes reported by Huang.⁹⁾ On the basis of above findings, it is concluded that all Cu(II) ions in zeolite structure were reduced to Cu(I); namely, above observations exclude the possibility that Cu(II)

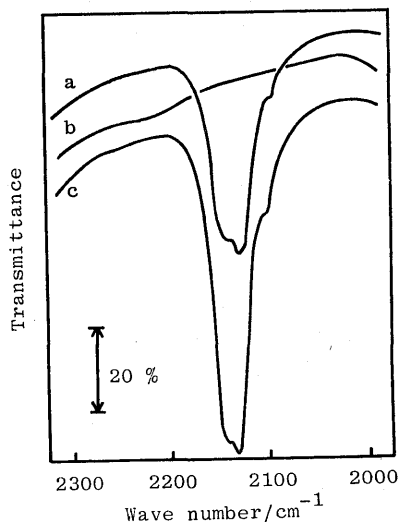


Fig. 2. IR spectra of carbon monoxide adsorbed on CuNaY-73 at 373 K following the treatment of the sample conditioning (a), cooling in O₂ (b), and the TPR procedure (c).

ions occupying hexagonal prism sites might remain unreduced⁶⁾ or that the lower and higher temperature peaks might correspond to the respective reductions from Cu(II) to Cu(I) and from Cu(I) to Cu(0).⁷⁾

From the X-ray diffraction¹⁰⁻¹²⁾ and other^{1,13)} data, Cu(II) ions show a tendency to occupy the interior sites (S_I or $S_{I'}$) in dehydrated form. When the exchange levels arise above 20-30%, a part of additional Cu(II) ions appears to be sited in the supercage sites. Therefore, the observations of two reduction processes in CuNaY-13, and -25 eliminate the possibility⁶⁾ that the two reduction processes might result from reductions of Cu(II) ions in the supercage and sodalite cages, respectively.

To gather further evidence for the origin of the two reduction processes, the influence of pretreatment prior to the TPR procedure on the TPR spectrum of CuNaY-52 were examined. The results are depicted in Fig. 1(B). Curve b in the figure was obtained after the sample was cooled in the absence of oxygen from 773 to 298 K following the sample conditioning. Evidently, the lack of oxygen treatment between 773 and 298 K diminished mainly the lower temperature reduction peak. Similar phenomenon was also observed on CuNaY-25. These results suggests that evacuation at high temperatures causes autoreduction of Cu(II) ions. This was further supported in a separate infrared experiment; appearance of absorption bands at 2135-2145 cm^{-1} (Fig. 2a) upon introduction of CO onto CuNaY-73 immediately after the sample conditioning indicates the presence of Cu(I) ions. These two findings reveal that the higher temperature process is attributed to the reduction of Cu(II) ions which are not reduced by evacuation treatment at 773 K.

In the discussion for assignment of the two reduction processes, the observations concerning extra-framework oxygen atoms reported by

several workers would be very useful. It has been described on all samples used here that ca. 60% of Cu(II) ions loaded in the zeolite framework have contributed to the formation of $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ bridges in the sodalite cages.¹⁴⁾ These bridging oxygen atoms could be desorbed from the zeolite upon heating samples above 773 K. Furthermore, these oxygen atoms were removed completely when the zeolite was exposed to hydrogen at 773 K. From these facts, it should be noted that there are at least two kinds of Cu(II) ions in Y type zeolites regardless of the occupying sites: $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ species and lone Cu(II) ions. Taking the results depicted in Fig. 1(B) and the thermostability and reactivity of the oxygen-bridged complexes into account, it is likely that the $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ species are reduced at higher temperatures with hydrogen. The proportion of Cu(II) ions bridged with oxygen (ca. 60%) is well reconciled with that the peak areas of the higher temperature reductions are larger than those of the lower temperature ones in Fig. 1(A). On the other hand, the lower temperature peak is deemed to be due to the reduction of lone Cu(II) ions since they were easily reduced upon evacuation at 773 K with little desorption of oxygen.¹⁵⁾ The proposed reduction schemes are as follows, $2\text{Cu}^{2+} + \text{H}_2 \longrightarrow 2\text{Cu}^+ + 2\text{H}^+$ (lower temperature reduction), $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+} + \text{H}_2 \longrightarrow 2\text{Cu}^+ + \text{H}_2\text{O}$ (higher temperature reduction). 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. The protons generated would become to surface hydroxyl groups.

The observations reported by other workers would support the above assignment. Gallezot et al.¹⁰⁾ reported the existence of 5 extra-framework oxygen atoms in $\text{Cu}_{16}\text{Na}_{24}\text{Y}$ after degassing at 773 K by using X-ray diffraction. Since these oxygen atoms are suggested to correspond

to several kinds of $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ species,¹⁶⁾ 63% Cu(II) ions in $\text{Cu}_{16}\text{Na}_{24}\text{Y}$ are concluded to correlate with this oxygen bridges. This value of 63% appears to agree well with the fraction of area of the high temperature peak in the total area, bearing out the above assignment. In addition, Dalla Betta et al.¹⁷⁾ reported that the amount of $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ bridges in sodalite cages decreased very slowly upon hydrogen treatment at 423 K but became negligible with ease at 673 K. This implies that such oxygen bridges are reduced around 600 K with a certain rate. Thus the reduction schemes proposed above seem to be reasonable, assuming small difference between the reducibilities of $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ and $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ bridges.

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