A Temperature Programmed Reduction Profile of Activated CuY Zeolite probed by EXAFS Measurement

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An active species of CuY zeolite, formed by consecutive reduction–reoxidation treatment with H_2 and O_2 under mild conditions, was identified by temperature programmed reduction (TPR) and characterized by K-edge EXAFS analysis as small CuO clusters which easily undergo reduction.

Although the redox behaviour of Cu species in zeolites has been the subject of numerous studies[1] in the last decade, the chemical entity of the active species is still obscure because of the intricate structure of the zeolite matrix. In this report the formation and characterization of an active species have been demonstrated by temperature programmed reduction (TPR) and EXAFS measurements.

The TPR spectrum of the original CuY clearly depicts that the reduction of Cu^{2+} ions in the zeolite occurs by a two-step mechanism,[2,3] outlined in Figure 1. The first (I) and second peak (II) are associated with the reduction of Cu^{2+} to Cu^+ ions and of Cu^+ ions to Cu metal, respectively, as confirmed in previous work.[3] After a consecutive reduction–reoxidation (R–O) treatment with H_2 and O_2 under very mild conditions, a new sharp peak (III) appeared at a lower temperature. The formation of this active species (X) was markedly affected by the conditions at each stage of the R–O treatment, *i.e.*, the optimum temperatures for preliminary evacuation, reduction, and reoxidation, which were determined to be 523, 673, and 473 K, respectively. After the R–O treatment the e.s.r. signal due to Cu^{2+} ions was markedly reduced in intensity, suggesting that the original cations had been converted to an e.s.r.-insensitive species such as CuO.[4]

The *in-situ* EXAFS measurements were performed in sequence with each step of the TPR process. The measurement and analysis of EXAFS spectra have been described in detail elsewhere.[5] Fourier transforms (FT) of these EXAFS data have been carried out to obtain the radial distribution functions. From the Cu–O and Cu–Cu scatterings, the best-fit values of structural parameters were estimated by the inverse

FT of each main peak in the FT. The results are summarized in Table 1 together with those for the reference compounds. In the original CuY the Cu–O distance (r_{Cu-O}) of 1.97 Å agrees
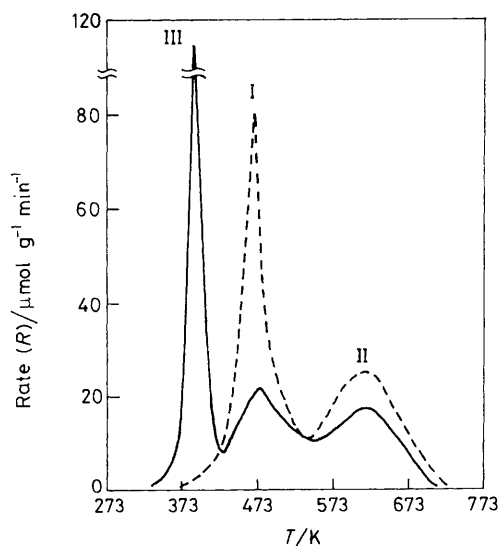
Figure 1. TPR spectra of 79%-exchanged CuY with (solid curve) and without (broken curve) R–O treatment. TPR was measured in a conventional circulation system with a temperature increment of 5 K min^{-1} and under an initial H_2 pressure of 10 kPa. R–O treatment was performed in the sequence: (1) preliminary evacuation at 523 K for 0.5 h, (2) reduction at 673 K for 2 h, and (3) reoxidation at 473 K for 2 h.

Table 1. Best-fit values of structural parameters from EXAFS data during TPR, together with data for reference compounds.

Sample	T/K	Bond	r/Å	N
Original CuY	298	Cu–O	1.97	3.7
	423	Cu–O	1.97	3.7
	673	Cu–Cu	2.51	10.0
CuY with R–O treatment	298	Cu–O	1.96	4.4
	423	Cu–Cu	2.52	7.0
	523	Cu–Cu	2.52	8.5
	673	Cu–Cu	2.52	8.8
Cu foil	—	Cu–Cu	2.51	12.0
CuO	—	Cu–O	1.96	4.0
Cu$_2$O	—	Cu–O	1.84	2.0

well with the reported value[6] and the co-ordination number of Cu atoms (N = 3.7) probably indicates an average value of Cu^{2+} ions in the super and sodalite cages (N = 3) and in the hexagonal prisms (N = 6). Upon reduction at 673 K the $r_{Cu–O}$ peak in the FT disappeared and a distinct peak appeared for $r_{Cu–Cu}$, which coincided with that in Cu foil (r = 2.51 Å). After the R–O treatment the main peak was recognized at 1.96 Å in the FT and N increased to 4.4. When CuY after R–O treatment was reduced at 423 K, where peak III appeared in the TPR spectrum, a distinct peak in the FT was observed at 2.52 Å due to the Cu–Cu metal bond. It clearly shows the dramatic influence of the R–O treatment, *i.e.*, the species X is reduced directly to Cu metal at low temperature, where the original Cu^{2+} ions remain unchanged in the TPR and EXAFS measurements. However, in this metal N (7) is small in comparison with that in Cu foil (N = 12). The discrepancy between these values is attributed mainly to the difference in size of the metal, *i.e.*, N in small particles is smaller than that

in large crystals because of the high proportion of surface atoms. The particle size, therefore, increases slightly with temperature in the TPR process, probably because of sintering. Applying the theory by Greegor–Lytle[7] and assuming a spherical particle shape, the diameter of Cu metal particles formed in CuY with the R–O treatment is estimated to be 5—8 Å. From these observations, the species X (the precursor of metal clusters) is considered to consist of small clusters of CuO which are directly reduced to Cu metal at low temperature.

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