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Active Species of CuY Zeolite Catalyst in CO Oxidation at Low Temperatures

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The formation and catalytic behavior of active species in CuY zeolite were investigated with aids of TPR and EXAFS measurements. The active species formed during a reduction-reoxidation treatment was directly and reversibly reduced to Cu metal clusters with CO, indicating that the CO oxidation on the zeolite proceeded via the redox mechanism of active CuO clusters.

In the last decade the characterization of Cu-exchanged zeolites has been the subject of numerous studies.[1)] The entity of active species in this catalyst is, however, still obscure. Among various techniques to investigate unknown species the temperature programmed reduction (TPR) is one of the simplest methods, as shown elsewhere.2) On the other hand, particles of the metal species formed in zeolites are generally so small that a conventional methods, such as X-ray diffraction, is incompetent to characterize them. The extended X-ray absorption fine structure (EXAFS) spectroscopy is well suited for this purpose since it can pursue changes of local structure around specific atoms.2,3) In this work, the formation of a species active for CO oxidation was demonstrated by TPR and the characterization of this species was performed by EXAFS measurements.

The catalyst used was 59.6% exchanged CuY zeolite. The TPR measurements were carried out in a circulation system, as shown in the previous reports.4) The kinetic experiments were performed in a differential reactor of the conventional flow system. The measurements and analysis of the EXAFS spectra were described in detail elsewhere.5)

It has already been known that the reduction of Cu^{2+} ions in the Y-zeolite with H_2 occurs by a two-step mechanism, via Cu^+ ions to Cu metal.4,6) The two-step mechanism could be recognized directly from the TPR spectra obtained under suitable conditions, as shown by broken curves in Fig.1. The first (peak I) and second peak (peak II) are associated with the reduction of Cu^{2+} to Cu^+ ions and Cu^+ ions to Cu metal, respectively.4) After the consecutive reduction-reoxidation (R-O) treatment with H_2 and O_2 under mild conditions a new sharp peak (peak III) appeared at a lower temperature. The formation of this active species (species III) strongly depended on the conditions of each step in the pretreatment such as evacuation, reduction and reoxidation. Effects of temperature in these steps are shown by solid curves in Fig.1, indicating the optimum temperatures for evacuation, reduction and reoxidation are 523, 673, and 473 K, respectively. The ESR signal due to Cu^{2+} ions in CuY was remarkably reduced after the R-O treatment, suggesting

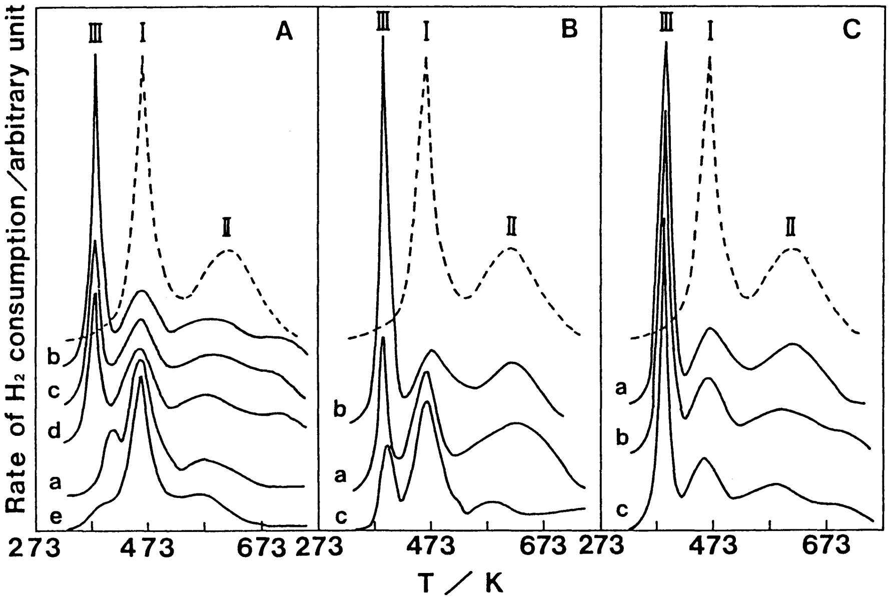

Fig.1. TPR spectra of CuY with various R-O treatments. The initial pressure of H_2, 10 kPa, and temperature increment, 5 K min^{-1}.

A; evacuated for 0.5 h at 293(a), 523(b), 573(c), 673(d), 773(e) K (reduced for 2 h at 673 K and reoxidized for 2 h at 673 K).

B; reduced for 2 h at 573(a), 673(b), 773(c) K (evacuated for 0.5 h at 523 K and reoxidized for 2 h at 473 K).

C; reoxidized for 2 h at 473(a), 573(b), 673(c) K (evacated for 0.5 h at 523 K and reduced for 2 h at 673 K).

that the original Cu^{2+} ions converted to ESR-insensitive species, such as CuO.[7)]

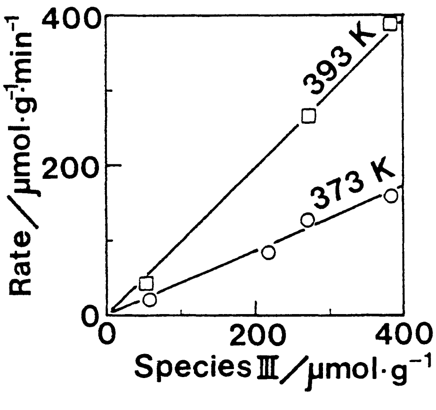

Fig.2. Activity dependence of CuY on the species III.

In order to investigate the catalytic roles of species III the CO oxidation with O_2 was performed in the low-temperature range from 373 to 433 K under atmospheric pressure. The original CuY showed no substantial CO conversion under the present conditions. The R-O treatment remarkably induced the catalytic activity of CuY, which exceeded by far that of a conventional CuO-SiO_2 catalyst. In Fig.2 the rates of CO oxidation are plotted against the amount of species III, which is estimated from the area of peak III in the TPR spectra of CuY with various treatments. The rate increases proportionally with the amount of species III. The apparent activation energy of the reaction was, however, virtually independent of the amount of species III and determined to be 42 kJ mol^{-1}, which was extremely smaller than that by CuO-SiO_2 catalyst (81 kJ mol^{-1}). The peak III in the TPR spectra completely disappeared upon reduction with CO and regenerated upon reoxidation with O_2 at the reaction temperature. From these points of view, it is plausible that the CO oxidation on CuY with R-O treatment proceeds via the redox process of species III at low temperatures.

The EXAFS study was performed to confirm the redox behavior described above. The spectra were measured in the sequence during the pretreatment and catalysis.

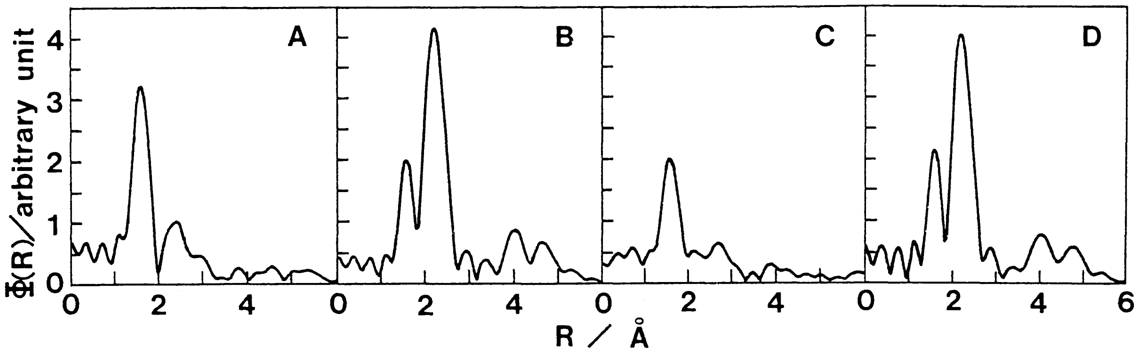

Fig.3. Fourier transforms of EXAFS spectra of CuY in the sequence of consecutive treatments.

A; after the R-O treatment in the optimum condition.
B; after the reduction of A with CO for 2 h at 423 K.
C; after the oxidation of B with O_2 for 2 h at 423 K.
D; after the reduction of C with CO for 2 h at 423 K.

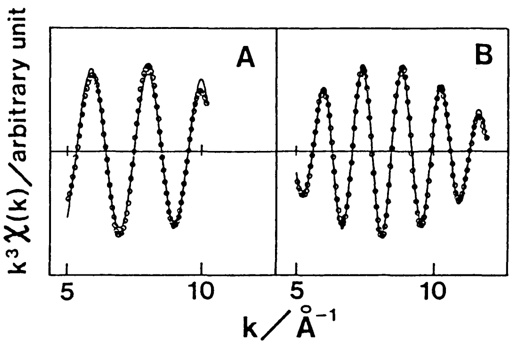

Fig.4. Comparison of the inverse Fourier transforms of the main peaks of Fig.3A(A) and Fig.3B(B) with the best-fit curve assuming Cu-O and Cu-Cu scatterings, respectively.

Fourier transforms of the EXAFS data at each stage are shown in Fig.3, where the peaks are displaced slightly from true interatomic distances because of the phase shift. Furthermore, the best-fit values of structural parameters by the inverse Fourier transforms of main peaks in the radial distribution functions are summarized in Table 1 with those of reference compounds. In the evacuated CuY the Cu-O distance (R_{Cu-O}) of 1.97 Å agrees with the reported value8) and the coordination number (N=3.7) probably indicates an average value of Cu^{2+} ions in the super and sodalite cages (N=3) and the hexagonal prisms (N=6). R_{Cu-Cu} in the reduced CuY is 2.51 Å which bears close resemblance with that in Cu foil (2.50 Å). The Fourier transforms of the sample with R-O treatment exhibits a single peak at 1.96 Å (Fig.3A). The inverse Fourier transform of this peak coincides with the calculated value assuming Cu-O scattering, as shown in Fig. 4A. Upon the reduction of the pretreated sample with CO at the reaction temperature of 423 K, a distinct peak appeared at R_{Cu-Cu} with small one at R_{Cu-O} (Fig.3B) and the calculated curve for the main peak assuming the Cu-Cu scattering well reproduces the inverse Fourier transform (Fig.4B). It clearly shows the dramatic influence of the R-O treatments, since in the case of untreated CuY no changes are observed in the EXAFS data and TPR spectra upon the CO-reduction at this temperature. Upon the CO-reduction, that is, the species III is reduced directly to Cu metal at low temperatures, while the original Cu^{2+} ions are reduced to Cu^+ ions at much higher temperatures.4) After the CO-reduced sample again reoxidized with O_2 a single small peak appeared at R_{Cu-O}, as shown in Fig.3C. Upon the further CO-reduction (Fig.3D and Table 1) this reoxidized sample

Tabel 1. Best-fit Values of Structural Parameters from EXAFS Data in the Sequence of Consecutive Pretreatment and Catalysis

Sequence	Sample and treatment	Neighboring atoms	R/Å	N
1	CuY evacuated at 523 K	Cu-O	1.97	3.6
2	CuY reduced with H_2 at 673 K	Cu-Cu	2.51	10.0
3	CuY oxidized with O_2 at 473 K	Cu-O	1.96	4.4
4	CuY reduced with CO at 423 K	Cu-Cu	2.52	5.0
5	CuY oxidized with O_2 at 423 K	Cu-O	1.96	4.2
6	CuY reduced with CO at 423 K	Cu-Cu	2.52	4.9
——	Cu foil	Cu-Cu	2.50	12.0
——	CuO powder	Cu-O	1.96	4.0
——	Cu_2O powder	Cu-O	1.84	2.0

regains the similar reduced state of Cu species to that in the sample with the first CO-reduction (Fig.3C and Table 1). This reversible behavior well agrees with that observed in the TPR experiment, as described before.

Thus, the species III is reversibly reduced to Cu metal with R_{Cu-Cu}=2.52 Å upon the CO-reduction at the reaction temperature. However, N of Cu atoms in the metal formed is 5.0, which is extremely smaller than that in the bulk phase (N=12). The discrepancy between these values is mainly attributable to the difference in the size of metal,[3,9] i.e., the coordination number in small particles is smaller than that in large crystals because of the high proportion of surface atoms.[2,3,10] Since it could be presumed that the number of Cu atoms in the metal clusters is substantially retained during the redox treatment with CO and O_2 (Table 1), the species III, the precursor to the metal clusters, is considered to be small CuO clusters. In the CO oxidation at low temperatures, therefore, the CuO clusters in the zeolite could function as the active species via the redox mechanism.

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