

Anomalous redox properties of copper-ion-exchanged ZSM-5 prepared by microwave-assisted method

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Introduction

It is widely recognized that copper ion-exchanged ZSM-5-type zeolite (CuZSM-5) exhibits a high catalytic activity in the direct NO_x decomposition into N₂, as well as a pronounced adsorption property at room temperature for N₂ molecule. In both phenomena, there is fairly general agreement that the active center is the monovalent copper ion formed in the evacuation process. However, the states of copper ion exchanged are different depending on the conditions used in the preparation procedures, i.e., pH of solution, kind of counter ions, exchanging methods, temperatures adopted in the ion-exchange procedure, and so on. We have recently found that the CuZSM-5 sample prepared by utilizing microwave power has a prominent redox feature. In this report, we have inclined to know the reduction and oxidation behaviors of the copper ion in CuZSM-5 exchanged by different methods. From the viewpoints of controlling the properties of zeolite arbitrarily, it is important to clarify the influence of ion-exchange methods on the properties of copper ion and of the state of mother zeolite on the state of exchanged ion.

Results and discussion

Figure 1 shows the copper K-edge EXAFS and XANES spectra for the CuZSM-5(CM)-108 sample prepared by utilizing microwave power in an aqueous solution of CuCl₂, where the value, 108, represents the ion-exchange capacity in percent and the terms C and M mean chloride ion and microwave used. The sample had been evacuated at increasing temperatures in the region of 300–873 K. The first band centered at 1.52 Å (no phase-shift correction) in EXAFS spectra is attributed to the back-scattering from the nearest neighboring skeletal oxygen atoms and the resulting coordination number is estimated to be *ca.* 2.5 for the 873 K-treated sample through the least-square method by using Cu₂O as a reference substance. The prominent feature is observed in the spectra for the samples treated at above 673 K: the appearance of the distinct, new, and fairly strong band at around 2.12 Å. This band can be assigned to one due to the back-scattering from the first nearest metal species, by comparing with the spectrum for reference copper metal; the metal formation is clearly evidenced.

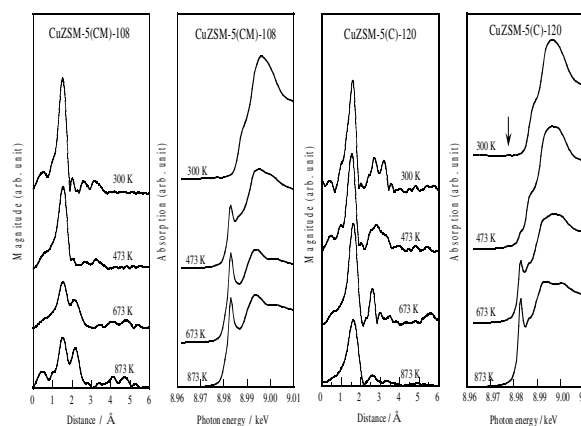
With reference to the XANES spectra, the weak shoulder at 8.978 keV observed for the sample which was evacuated at 300 K is attributable to the 1s-3d transition, indicating that the copper ion exchanged in the sample takes a divalent state. Successive pretreatments at the higher temperatures bring about strong and specific bands at 8.983 and 8.995 keV which are assigned to the 1s-4p and 1s-4p transitions in the monovalent copper ion (Cu⁺), respectively. The appearance of such two sharp bands suggests that this Cu⁺ species takes either linear or planar configuration but not tetrahedral one. The 673 K-treatment brings about a broadening of the band at around 8.983 keV,

accompanying a shoulder at lower side of this band and a new and weak band at 9.005 keV. By comparing with the spectrum of reference metal, the formation of metal species is also suggested. Further treatment at higher temperatures leads to more distinct band feature specific to the metal species, coinciding with the results obtained by EXAFS measurements. These data clearly prove that the evacuation procedure of the CuZSM-5(CM)-108 easily produces small metal clusters in zeolite.

Included in Figure 2 for comparison are EXAFS and XANES spectra for the CuZSM-5(C)-120 sample which was traditionally prepared at 363 K by using an aqueous solution of CuCl₂. As is distinct from the spectra shown in Figure 1, it is clearly evidenced that the bands being ascribable to the metal species were not observed in both EXAFS and XANES spectra.

In addition, ESR spectrum of the sample treated at above 673 K for CuZSM-5(CM) gave a new and sharp band at a *g* value of 2.002, which can be assigned to the free electron trapped in the defect site, accompanied with the extremely weak bands due to the divalent copper species. On the other hand, this new band was not observed for the 673 K-treated CuZSM-5(C) sample.

As a result, it has also become apparent that each sample shows different propensities for reducibility from the divalent copper ion to the monovalent or zerovalent one; 673 K-treatment of the CuZSM-5(CM)-108 sample results in a drastic increase in the band intensity at 2.12 Å and the appearance of a shoulder band at around 8.983 keV, whereas the CuZSM-5(C)-120 sample scarcely exhibits both bands. These facts can be interpreted as follows: the formation of the defect sites due to the poor crystallinity of the sample, which was assisted in the ion-exchange process with microwave-assisted method, is a dominant factor in the reducibility of Cu²⁺ to zerovalent species.



Figures 1 and 2 EXAFS and XANES spectra.

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