

Speciation of Cu species in Cu-ZSM-5 before calcination

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Introduction

It has been pointed out that Cu supported in MFI zeolite (Cu-ZSM-5) is useful for the direct decomposition and the selective catalytic reduction of NO gas. A large number of studies about the Cu-ZSM-5 catalyst reveals that the catalytic reactivity is affected by the state of Cu species in the zeolite framework. In this study, the local structure around the Cu center is evaluated by the conventional XAFS technique and it has been clarified that the Cu state in ZSM-5 is mainly explained by the Cu(II) species existed in aqueous solution during the ion-exchange process for its preparation.

Experiments

The Cu-ZSM-5 samples were prepared by an ion-exchange method at ambient temperature using an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ or $\text{Cu}(\text{CH}_3\text{COO})_2$ suspended by ZSM-5 (Tosoh, Si/Al = 11.9). The pH value of the aqueous solution was varied in the range of 2.8–9.1 using NH_3 or NaOH as the Brønsted base. The ZSM-5 powder adsorbed Cu(II) was filtered, washed by distilled water, and dried at 393 K for 12 h in air.

The conventional EXAFS spectra at the Cu K edge were measured at BL-12C and NW2. The incident and transmitted X-ray intensities were measured by ionization chambers. The XANES spectra were recorded at BL-10B. Both measurements were carried out at ambient temperature. The X-ray energy was calibrated using the spectrum of a Cu foil. The XAFS spectra of aqueous solutions of Cu^{2+} and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and the CuO powder were also measured for comparison.

Results and Discussion

Figure 1 shows the first derivatives of the observed XANES spectra and the Fourier transform magnitudes of the EXAFS oscillation function. The XANES spectra of all the Cu-ZSM-5 samples are characteristic of Cu(II) species and there is no evidence to contain the Cu(I) and Cu(0) species. Under acidic conditions (pH < 5), the XANES spectra and the $|FT|$ functions are perfectly in agreement with those of Cu^{2+} in water, indicating that the Cu(II) ion is adsorbed in ZSM-5 as the aqua complex. In considering the molecular radius (*ca.* 3–4 Å) of $[\text{Cu}(\text{OH}_2)_4(\text{OH}_2)_2]^{2+}$, the aqua complex is inserted in the intersection channel of ZSM-5 with the cavity radius of *ca.* 4.5 Å. If pH is adjusted using NH_3 to alkaline condition (pH > 8), the XANES spectra are similar to that

of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, while it can be seen a contribution from

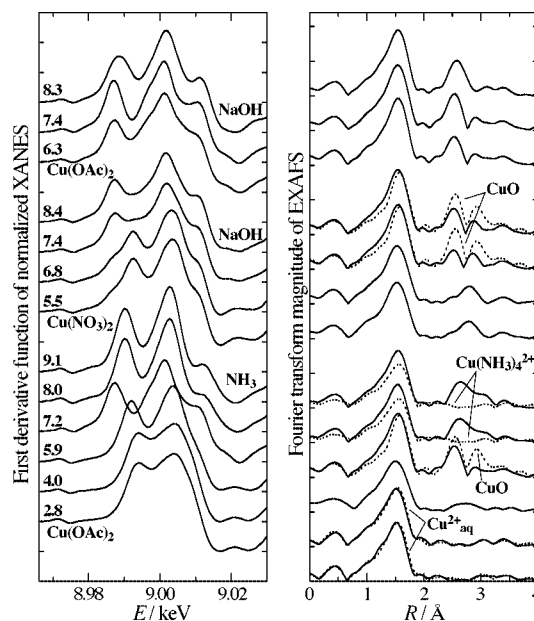


Figure 1: First derivative functions of XANES and Fourier transform magnitudes of EXAFS for a series of Cu-ZSM-5.

CuO in the $|FT|$ data. This is quite reasonable, since the ammine complex is predominant in the aqueous solution under such conditions with the minor component of the hydrolyzed species. This interpretation is supported by the cases where NaOH is used as the pH-adjusting reagent, for which the contribution from $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is not observed. It is clearly seen that CuO-like structure is formed in Cu-ZSM-5 prepared under the near neutral conditions ($6 < \text{pH} < 8$) without using NH_3 . Taking into account the hydrolysis and polymerization constants reported for Cu(II) [1], the $\text{Cu}_2(\text{OH})_2^{2+}$ species formed in aqueous solution (*ca.* 90 % under our experimental conditions) is adsorbed in the intersection channel of ZSM-5, and it is then dehydrated by the drying at 393 K to form the CuO-like state.

Reference

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