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Reduction kinetics of Cu(II) species in Cu–ZSM-5 by CO

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Introduction

Cu supported in MFI zeolite (Cu–ZSM-5) is one of the most attractive catalyst for its potential of the direct decomposition and the selective catalytic reduction of an environmental pollution gas of NO. According to an enormous amount of researches concerning the Cu–ZSM-5 catalyst, it has been accepted that the Cu(II)-Cu(I) redox cycle is driven in the NO decomposition with the active center of the Cu(I) species. Because the dynamic structural change of the Cu species is, however, still unclear for the Cu–ZSM-5 catalyst, the reduction kinetics of Cu–ZSM-5 with CO is investigated by the time-resolved DXAFS spectroscopy in this study.

Experiments

The Cu–ZSM-5 powder was prepared by an ion-exchange method at ambient temperature and pH 5.2–5.8 using an aqueous solution of $Cu(NO_3)_2$ suspended by ZSM-5 (Tosoh, Si/Al = 11.9). The ZSM-5 powder adsorbed Cu(II) was filtered, washed by distilled water, dried at 393 K for 12 h in air, and calcined at 773 K in air for 1–2 h before the use.

The time-resolved DXAFS measurements were carried out at BL-NW2. The polychromatic X-rays were obtained by an Si(111) bent crystal (Bragg-type), which was cooled to 295 K by circulation of thermostatted water. The Si(111) crystal (1 mm thickness) was bent into the curvature radius of 3 m by a newly developed crystal holder. A self-scanning photodiode array coupled by a CsI(Tl)-embrocated fiber optical plate was used as the linear detector. The position of each sensing element was converted to the X-ray energy by referring the spectrum of a Cu foil to that measured at BL-10B.

The reduction process of Cu–ZSM-5 by CO was followed using a newly developed observation chamber with the polyimide windows under the *in-situ* conditions. The reaction was started by injection of CO gas with a known pressure. The XAFS spectrum was recorded with the acquisition time of 10 ms with a suitable time interval (0.04–1.2 s) to follow the entire chemical change.

Results and Discussion

The X-ray absorption spectrum apparently changes in two phases after injection of CO: the early change within 5 s and the later change after 10–20 s under the CO pressure of 3.4 kPa at 773 K. On the basis of the XANES spectra of CuO, Cu_2O, and Cu foil, two apparent changes are assigned to the conversion from Cu(II) to Cu(0) *via* the Cu(I) state as the reaction intermediate. This is also supported by the |*FT*| values of the time-resolved EXAFS data as shown in Figure 1.

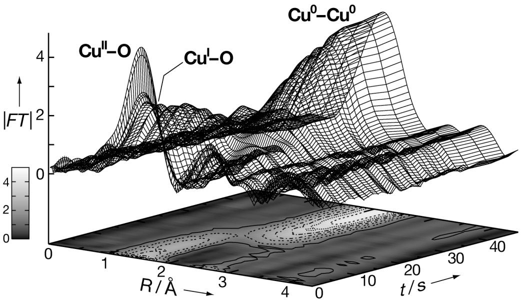

Figure 1: Time-resolved radial structure function during the reduction process of Cu–ZSM-5 by CO.

The |*FT*| peak is initially observed at 1.53 Å, which is assigned to the nearest Cu^{II}–O interactions in the CuO-like initial structure of the prepared Cu–ZSM-5 powder. This peak quickly shifts to 1.44 Å within 5 s together with the decrease in its intensity, indicating the production of the Cu(I) species. The |*FT*| functions are drastically changed after 10–20 s, and the Cu–Cu interaction peak appeares at *ca*. 2.15 Å together with the disappearance of the Cu–O interaction. The average coordination number for the Cu–Cu interaction becomes to be *ca*. 9 after *ca*. 50 s and the distance almost corresponds to that of the Cu metal.

The changes in average coordination numbers and bond distances as a function of time obtained by the time-resolved DXAFS measurements, shown in Figure 2, are well reproduced by the 5-state model, in which three states of the Cu(I) species are assumed as the reaction intermediate.

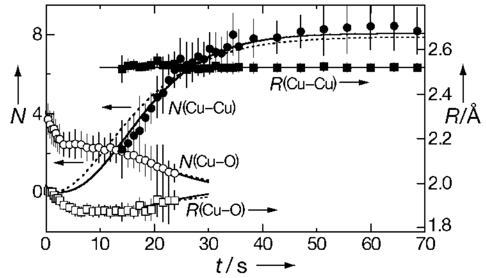

Figure 2: Change of average structure parameters.

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