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TIME-RESOLVED ENERGY-DISPERSIVE XAFS STUDY OF Cu-ZSM-5 CATALYSTS DURING REDUCTION WITH HYDROGEN

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Introduction

Information on the structure of short-lived species at surface provides a clue to grasp the mechanism for chemical reactions and dynamic surface processes. EXAFS is well recognized as a useful method to investigate the structure of non-crystalline materials. The shortcoming of a conventional EXAFS is, however, that it takes several ten minutes to collect a spectrum. Recently, a novel technique called energy-dispersive XAFS (DXAFS) has been developed and applied to catalyst characterization. The advantage of this method is that the data of whole energy range are collected simultaneously and at sub-second time resolution. We have applied the DXAFS technique to study the dynamic behavior of copper species in Cu-ZSM-5 during reduction with H_2 [1-3].

Results and Discussion

DXAFS measurement was carried out using synchrotron radiation at BL-9C at KEK-PF. A triangle-shaped Si(111) bent crystal was used to focus polychromatic X-ray beam and a 1024-pixel position sensitive detector was used to record DXAFS spectra. Cu-ZSM-5 samples were prepared by ion exchange using copper nitrate solution.

Figure 1 shows Fourier transforms of Cu K-edge DXAFS spectra during the temperature-programmed reduction (TPR) of Cu-ZSM-5 in H_2 (5.3 kPa) at a heating rate of 5 K min^{-1} from 300 to 700 K. The data acquisition time for each spectrum was 1 s. Figure 2 shows coordination numbers (CN) of Cu-O and Cu-Cu as a function of reduction temperature, delivered by curve fitting analysis. At 400-450 K CN of Cu-O (0.195 nm) decreased and at 550 K Cu-Cu bonding (0.255 nm) of Cu metal particles appeared. Isolated Cu^{2+} species in the channel of ZSM-5 were reduced stepwise. According to CN and XANES analysis, Cu_{3-5} small clusters were formed initially followed by particle growth.

The reduction process of Cu-ZSM-5(CuO), which involves big CuO particles on the outer surfaces of the ZSM-5, was completely different from that of the isolated Cu^{2+} species in the channels of ZSM-5. According to Fourier transforms of the DXAFS data for Cu-ZSM-5(CuO) during TPR, at 300 K Cu-O and Cu-(O)-Cu peaks ascribed to CuO particles were observed. These bonds drastically disappeared around 450 K, and Cu-Cu bonding due to Cu^0 particles appeared. The DXAFS study demonstrates that the big CuO particles were readily reduced to big Cu^0 particles around 450 K.

The dynamic change of catalytic active sites during pretreatment was successfully monitored DXAFS technique.

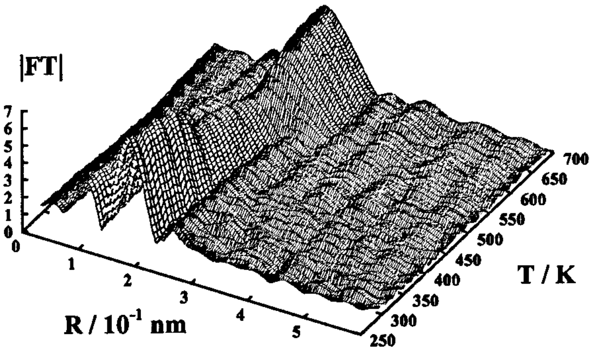

Figure 1 Fourier transforms of DXAFS spectra of Cu-ZSM-5 during temperature-programmed reduction

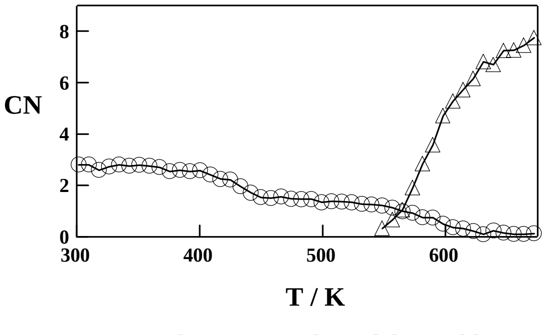

Figure 2 Coordination numbers delivered by curve fitting analysis

References

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