

## Temperature Dependence of Reduction Processes of Cu Species Supported in Zeolite Measured by DXAFS

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### Introduction

The Cu species supported in MFI zeolite (Cu-ZSM-5) have been characterized by the XAFS spectroscopy and it has been clarified that the CuO-like state existed initially is reduced by CO to the metal-like Cu(0) state. The dynamic processes have been directly monitored by using the time-resolved dispersive XAFS (DXAFS) instrument at 773 K, and the transient Cu(I) states are demonstrated to exist during the reduction process. The CO pressure dependence of the conditional rate constants derived by the kinetic analyses reveals the reaction mechanism in the atomic scale. In this study, the time-resolved DXAFS measurements have been carried out at various temperatures to determine the activation parameters of the component processes. Although the determination of parameters has not been finished yet, an interesting reduction behavior is observed at lower temperature.

### 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<sub>3</sub>)<sub>2</sub> 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 the NW2A beamline using an Si(111) bent crystal (Bragg-type) and a self-scanning photodiode array coupled by a CsI(Tl)-embrocated fiber optical plate.

The reduction processes of Cu-ZSM-5 by CO were followed at 523–773 K under various pressures of CO. The reaction was initiated by an injection of CO gas with a known pressure. The XAFS spectrum was recorded with the acquisition time of 4–8 ms depending on the ring current.

### Results and Discussion

The observed time-resolved XANES spectra are shown in Figure 1. At 773 K, the reduction proceeds in two phases, i.e., the initial Cu(II) state is finally reduced to Cu(0) via the Cu(I) states as the transient species, as reported previously. While at lower temperature at 523 K, the final state is not Cu(0) and the reduction is found to be terminated at the Cu(I) state. No further reduction from Cu(I) to Cu(0) was checked by the static XAFS measurement at 1 h after the initiation of the reaction, indicating that the reduction from Cu(I) to Cu(0) is

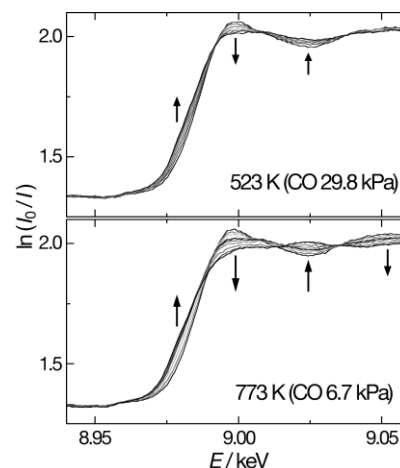


Figure 1: Time-resolved XANES spectra during the reduction of Cu-ZSM-5 by CO at 523 and 773 K.

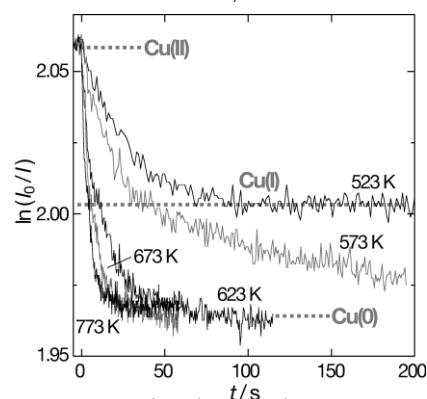


Figure 2: X-ray absorbance change at 8.998 keV and various temperatures. The absorbance of 2.060, 2.005, and 1.965 corresponds to the Cu(II), Cu(I), and Cu(0) state, respectively.

thermodynamically unfavorable. In Figure 2 are shown the X-ray absorbance changes followed at 8.998 keV for the reactions with CO of 6.2–6.7 kPa except for at 523 K, for which the CO pressure is 9.2 kPa. The kinetic analyses of the data at high temperature range reveal that the reaction model with two or three Cu(I) intermediates reproduces well the observed kinetic traces. In contrast, at 523 K, the reaction seems to be proceeded by a single step as suggested by the existence of isobestic points seen in Figure 1. This is not contradicted with the results at higher temperatures, since the conversion rate between the Cu(I) species is faster than the first reduction process.

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