# Dynamic valence change of Cu in Cu–ZSM-5 during CO-NO reaction

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### Introduction

DXAFS apparatus equipping a dispersive X-ray optics and a linear detector (photodiode array) permits us to measure a XAFS spectrum dynamically in the order of ms, and it is very powerful to follow the dynamic changes in valence and structure of metal sites during the chemical reaction without the restriction of medium phase. In this study, we have applied the DXAFS methodology to the CO-NO reaction of the Cu species supported in MFI zeolite (Cu–ZSM-5), which is accepted to be active for the direct decomposition and the selective catalytic reduction (SCR) of NO. Since the prepared Cu–ZSM-5 powder possesses the CuO-like small cluster adsorbed in the intersection channel of ZSM-5, i.e., the valence of Cu is initially +2, we have aimed the simultaneous action of CO and NO as the reducing and oxidizing reagent for Cu, respectively. The monitoring of this system using the DXAFS apparatus provides the dynamic valence change of Cu in the Cu–ZSM-5 catalyst. This is very important to understand the function and mechanisms of the redox cycle of Cu, which has been suggested to be a key point for the direct decomposition and SCR of NO.

### 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. The CO-NO reactions of Cu–ZSM-5 at 773 K were measured after the injection of the CO-NO gas mixture. The XAFS spectrum was recorded with the acquisition time of 10 ms with a suitable time interval to follow the entire chemical change.

### Results and Discussion

Figure 1 shows the X-ray absorbance changes during the CO-NO reaction of Cu–ZSM-5 at a variety of compositions of gas mixture. According to the independent static XAFS measurements of CuO, $Cu_2O$, and Cu foil using the DXAFS apparatus, it is revealed that the X-ray absorbance of *ca.* 1.80, 1.73, and 1.69 at 8.998
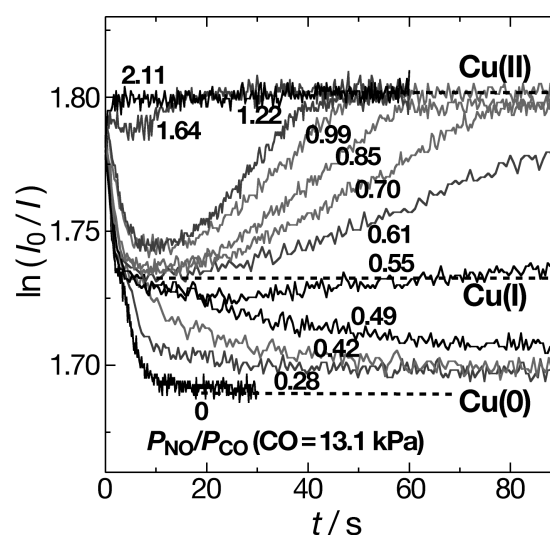


Figure 1: Change of X-ray absorbance at 8.998 keV during the CO-NO reaction of the Cu–ZSM-5 catalyst at 773 K.

keV means the Cu valence of +2, +1, and 0, respectively, and thus the observed absorbance change can be directly connected to the valence change of Cu in Cu–ZSM-5.

When only the CO gas is injected ($P_{NO}/P_{CO} = 0$), the successive reduction processes from CuO-like Cu(II) to metal-like Cu(0) *via* Cu(I) is clearly observed, and these processes are well explained by the 5-state model with three Cu(I) intermediates, as described elsewhere. If $P_{NO}$ is increased, the Cu(0) state is again formed at about 1–2 min but the reaction is strongly inhibited by the existence of NO. Under the conditions with the larger pressure of NO, the initial CuO-like Cu(II) state is perfectly regenerated after the conversion to the Cu(I) intermediate. The regeneration rate of Cu(II) is enhanced by the increase of $P_{NO}$ and the accumulated quantity of the Cu(I) intermediate is decreased. The Cu(I)-intermediate formation is apparently not observed when the $P_{NO}/P_{CO}$ value approaches to 2. These findings strongly indicate that the Cu(II)-Cu(I) catalytic cycle proceeds within 10 s under the current conditions and that the Cu(I) species contributes as the reactive intermediate for the reduction of NO. In considering the slow oxidation of reduced Cu–ZSM-5 by NO, the early intermediate formed by the reduction by CO is the most active Cu(I) intermediate.

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