Operando XAFS studies of supported copper oxides for catalytic ammonia combustion

Satoshi HINOKUMA a,*,†, Yusuke KAWABATA, Saaya Kiritoshi, Shun Matsuki and Masato Machida

Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2–39–1 Kurokami, Chuo-ku, Kumamoto 860–9037, Japan

Abstract: Local structures around copper oxides (CuO/Al2O3) supported on aluminum oxide borates (10A2B) during the NH3 combustion reaction were studied by operando XAFS. Although CuO/Al2O3 supported catalysts are known to have similar local structures, their partial reduction behavior has not been clarified. In contrast, CuAl2O4 was formed after thermal aging of CuO/Al2O3 at 900°C for 100 h in air, local structures of which were preserved during NH3 combustion at 600°C.

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In order to elucidate the actual dynamics of catalysis, the investigation of the local structures during catalytic reactions is essential. Recently, operando X-ray absorption fine structure (XAFS) measurements have made dramatic progress for use as a powerful technique to study the local structures of catalysts under reaction conditions.11) Kornienko et al. revealed a molecular model of an amorphous cobalt sulfide catalyzing hydrogen evolution reactions by operando XAFS and Raman.9) Li et al. developed a novel micro-reactor compatible with operando XAFS and scanning transmission electron microscopy (STEM) observation to obtain complex structural dynamics of nanocatalysts.7) Operando XAFS study of metal oxide catalysts during the water–gas shift reaction was proposed by Rodrigues et al., who also reported their partial reduction behavior.11) Foronklin et al. elucidated the local structures of iron- and copper-containing zeolites during the selective catalytic reduction (SCR) of NOx by NH3, and finally concluded their catalysis and SCR mechanism from the operando XAFS study.3) Therefore, operando XAFS has a great impact on the study of the actual local structures during catalytic reactions as well as the reaction mechanisms.

NH3 has recently been regarded as a renewable and carbon-free energy source due to its high energy density,13) but it has problems including high ignition temperature and N2O/NOx production, in comparison with fossil fuels. Previously, we proposed novel catalytic NH3 combustion systems that enable low ignition temperatures as well as negligible N2O/NOx emissions,14)15) and reported that the NH3 combustion activity of metal oxides increases with the decrease of their metal–oxygen bond energy.14) In addition, a novel catalyst, copper oxide (CuO) supported on aluminum oxide borates (10Al2O3·2B2O3: 10A2B) with high performance for NH3 combustion, was successfully prepared.15) Although CuO-based catalysts have also been widely studied for the selective oxidation of NH3 emissions to reduce air pollution,17)18) there are no published studies of the catalytic local structures during NH3 combustion and/or the oxidation reaction over the well-known supported CuO. Therefore, in this study, the local structures around Cu in the previously developed CuO/10A2B and in the conventional CuO/Al2O3 under NH3 combustion reaction conditions were elucidated by operando XAFS for the first time. Finally, taking our previous reports into account, the catalysis process is discussed.

CuO/10A2B and CuO/Al2O3 were prepared by a conventional impregnation method, the details of which are shown in the Supporting Information. To evaluate their thermal stability, the as-prepared catalysts were thermally aged at 900°C for 100 h in air. Operando XAFS for Cu K-edge was obtained at the BL9A station of the Photon Factory (PF), High Energy Accelerator Research Organization (KEK). The sample was placed in a temperature-controlled cell (Figure S1) and heated from room temperature to 600°C at a heating rate of 10°C min−1 in a gas mixture of NH3 (1.0%), O2 (1.5%), and He (balance) at a flow rate of 100 cm3 min−1. The O2-excess ratio of NH3 combustion was expressed as λ = (pO2/pNH3)stoichio/(pO2/pNH3)baseline (λ = 2). The Cu K-edge XAFS spectra were recorded during the catalytic NH3 combustion at reaction temperatures of 200, 400, and 600°C for 30 min. These spectra were measured in the transmission mode using an ionization chamber filled with N2 for the incident beam, another chamber filled with 75% N2 þ 25% Ar for the transmitted beam, and a Si(111) double-crystal monochromator. Reference samples (Cu2O, CuO) and CuAl2O4 were mixed with boron nitride (BN) powder to achieve an appropriate absorbance at the edge energy. The XAFS data were processed using the IFEFFIT software package (Athena and Artemis). EXAFS oscillations were extracted by fitting a cubic spline function through the post-edge region. The k2-weighted EXAFS oscillation in the 2.0–15.0 Å−2 region was Fourier transformed.

Figure 1 shows the normalized Cu K-edge X-ray absorption near edge structure (XANES) spectra for the catalysts during NH3 combustion (λ = 2) at room temperature, 200, 400, and 600°C together with the spectra for three references. Compared with the references, the XANES spectrum for as-prepared CuO/10A2B at room temperature (RT) was similar to that for CuO, which is consistent with our previous studies of their X-ray diffraction (XRD) patterns.15) Moreover, the catalysts exhibited a weak pre-
edge (at approximately 8985 eV assigned to Cu$^{2+}$ 1s → 4p + ligand, and Cu$^{2+}$ 1s → Cu$^{2+}$ charge-transfer excitation), which was observed in the XANES spectrum of CuO. Although the spectrum for CuO$_2$/10A2B at 200°C was also similar to that for CuO, the absorption energy of the XANES spectra for CuO$_2$/10A2B shifted to lower energy when increasing the combustion temperature to 400°C. Subsequently, the absorption energy of the spectrum for CuO$_2$/10A2B at 600°C exhibited a weak pre-edge assigned to Cu$^+$ 1s → 4p transition, which was observed in the spectrum for Cu$_2$O. According to linear combination fitting (Table S1), CuO in CuO$_2$/10A2B at 600°C was reduced approximately 50% to Cu$_2$O. These results imply that CuO (Cu$^{2+}$) in as-prepared CuO$_2$/10A2B was partly changed, i.e. reduced, to Cu$_2$O (Cu$^+$) during the NH$_3$ combustion reaction. We have previously demonstrated the following catalytic properties of CuO$_2$/10A2B and CuO$_2$/Al$_2$O$_3$: (1) these catalysts could be characterized by highly dispersed CuO nanoparticles, (2) their light-off curves of NH$_3$ were obtained at approximately 300°C, (3) the catalytic NH$_3$ combustions proceeded via the Mars–van Krevelen mechanism, (4) the lattice oxygen of CuO$_2$/Al$_2$O$_3$ nanoparticles reacted with NH$_3$, and therefore its surface was reduced. Such reduction behavior is in agreement with the previous X-ray photoelectron spectroscopy (XPS) analysis. Unlike the as-prepared CuO$_2$/10A2B, on the other hand, the XANES spectra for CuO$_2$/10A2B(aged) at RT and 200°C were similar to the spectrum for spinel CuAl$_2$O$_4$ due to the solid-state reaction between as-prepared CuO and 10A2B. Therefore, considering the XPS analysis, it is probable that the oxidation state of the bulk CuAl$_2$O$_4$ in CuO$_2$/10A2B(aged) was also 2$^+$ during the NH$_3$ combustion reaction, whereas the surface of CuAl$_2$O$_4$ was reduced to the lower oxidation state. Similar structures as well as trends were also observed in CuO$_2$/Al$_2$O$_3$ before and after thermal aging.

Figure 2 shows the extended X-ray absorption fine structure (EXAFS) oscillations for the catalysts during NH$_3$ combustion. In the case of as-prepared CuO$_2$/10A2B, its oscillation was similar to that for CuO, which is consistent with the results of XANES (Fig. 1) and XRD. The oscillation for CuO$_2$/10A2B at 200°C was also similar to that for CuO, whereas its oscillations at 400 and 600°C became similar to that for Cu$_2$O, which indicates that the CuO nanoparticles of as-prepared CuO$_2$/10A2B were partly reduced to Cu$_2$O during the NH$_3$ combustion reaction at temperatures higher than 300°C. Moreover, the amplitude of the oscillation for CuO$_2$/10A2B tends to decrease with increasing the reaction temperature. In contrast, in the cases of CuO$_2$/10A2B(aged), as-prepared CuO$_2$/Al$_2$O$_3$, and CuO$_2$/Al$_2$O$_3$(aged) at each reaction temperature, their oscillations were similar to that for CuAl$_2$O$_4$. However, the amplitudes of their oscillations also decrease upon reaching the reaction temperature of 400°C.

Figure 3 shows Fourier transforms (FT) of $k^3$-weighted Cu K-edge EXAFS for the catalysts. At RT and 200°C, the as-prepared CuO$_2$/10A2B displayed an intense Cu–O peak ($r$ ~ 1.95 Å) attributed to CuO. Upon reaching the reaction temperature of 400°C, the catalyst displayed an intense Cu–O peak ($r$ ~ 1.85 Å) attributed to Cu$_2$O. These results are in agreement with the XANES and EXAFS oscillations, and it is suggested that the structure of CuO in the as-prepared CuO$_2$/10A2B was partly changed (reduced) to that of Cu$_2$O during the NH$_3$ combustion reaction. On the other hand, the other catalysts, CuO$_2$/10A2B(aged) and CuO$_2$/Al$_2$O$_3$ before and after thermal aging, displayed an intense Cu–O peak ($r$ ~ 1.94 Å) attributed to CuAl$_2$O$_4$, $r$ of which were preserved.
partly changed to Cu₂O nanoparticles during NH₃ combustion. In contrast, the local structure of the bulk CuAl₂O₄ nanoparticles was preserved during the NH₃ combustion reaction. From our previous XPS analysis, however, it is considered that the surface of CuAl₂O₄ in the other catalysts was reduced during the NH₃ combustion reaction at 400°C, because NH₃ reacts with the lattice oxygen of CuAl₂O₄, and therefore the catalytic NH₃ combustion proceeds via the Mars–van Krevelen mechanism.

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Supporting Information Catalyst preparation, linear combination fitting parameters, experimental setup, and possible changes for the local structures of supported CuO.

References