Operando XAFS studies of supported copper oxides for catalytic ammonia combustion

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Local structures around copper oxides (CuO_x) supported on aluminum oxide borates (10A2B) during the NH_3 combustion reaction were studied by *operando* XAFS. Although CuO_x in as-prepared $\text{CuO}_x/10\text{A2B}$ at room temperature can be assigned to CuO , the CuO was partly reduced to Cu_2O during NH_3 combustion at 400°C . In contrast, CuAl_2O_4 was formed after thermal aging of $\text{CuO}_x/10\text{A2B}$ at 900°C for 100 h in air, local structures of which were preserved during NH_3 combustion at 600°C .

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Key-words : *Operando* XAFS, Supported catalysts, Copper oxides, Ammonia combustion

[Received March 31, 2017; Accepted May 3, 2017]

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.^{1)–12)} Kornienko et al. revealed a molecular model of an amorphous cobalt sulfide catalyzing hydrogen evolution reactions by *operando* XAFS and Raman.⁶⁾ 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 prospected by Rodriguez et al., who also reported their partial reduction behavior.¹¹⁾ Doronkin et al. elucidated the local structures of iron- and copper-containing zeolites during the selective catalytic reduction (SCR) of NO_x by NH_3 , 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.

NH_3 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 $\text{N}_2\text{O}/\text{NO}_x$ production, in comparison with fossil fuels. Previously, we proposed novel catalytic NH_3 combustion systems that enable low ignition temperatures as well as negligible $\text{N}_2\text{O}/\text{NO}_x$ emissions,^{14)–16)} and reported that the NH_3 combustion activity of metal oxides increases with a decrease in their metal–oxygen bond energy.¹⁴⁾ In addition, a novel catalyst, copper oxide (CuO_x) supported on aluminum oxide borates ($10\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$: 10A2B) with high performance for NH_3 combustion, was successfully prepared.¹⁵⁾ Although CuO_x -based catalysts have also been widely studied for the selective oxidation of NH_3 emissions to reduce air pollution,^{17),18)} there are no published studies of the catalytic local structures during NH_3 combustion and/or the oxidation reaction

over the well-known supported CuO_x . Therefore, in this study, the local structures around Cu in the previously developed $\text{CuO}_x/10\text{A2B}$ and in the conventional $\text{CuO}_x/\text{Al}_2\text{O}_3$ under NH_3 combustion reaction conditions were elucidated by *operando* XAFS for the first time. Finally, taking our previous reports into account, the catalysis process is discussed.

$\text{CuO}_x/10\text{A2B}$ and $\text{CuO}_x/\text{Al}_2\text{O}_3$ 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-controllable cell (Figure S1) and heated from room temperature to 600°C at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in a gas mixture of NH_3 (1.0%), O_2 (1.5%), and He (balance) at a flow rate of $100 \text{ cm}^3 \cdot \text{min}^{-1}$. The O_2 -excess ratio of NH_3 combustion was expressed as $\lambda = (p\text{O}_2/p\text{NH}_3)_{\text{exp.}} / (p\text{O}_2/p\text{NH}_3)_{\text{stoichiom.}}$ ($\lambda = 2$). The Cu K-edge XAFS spectra were recorded during the catalytic NH_3 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 N_2 for the incident beam, another chamber filled with 75% $\text{N}_2 + 25\%$ Ar for the transmitted beam, and a Si(111) double-crystal monochromator. Reference samples (Cu_2O , CuO , and CuAl_2O_4) 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 k^3 -weighted EXAFS oscillation in the $2.0\text{--}15.0 \text{ \AA}^{-1}$ region was Fourier transformed.

Figure 1 shows the normalized Cu K-edge X-ray absorption near edge structure (XANES) spectra for the catalysts during NH_3 combustion ($\lambda = 2$) 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 $\text{CuO}_x/10\text{A2B}$ 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-

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[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.125.P10-1>

Fig. 1. Normalized Cu K-edge XANES spectra for the catalysts during NH_3 combustion and the references.

edge (at approximately 8985 eV assigned to $\text{Cu}^{2+} 1s \rightarrow 4p + \text{ligand}$, and $\text{Cu}^{2+} 1s \rightarrow \text{Cu}^{2+}$ charge-transfer excitation⁵⁾), which was observed in the XANES spectrum of CuO. Although the spectrum for $\text{CuO}_x/10\text{A2B}$ at 200 °C was also similar to that for CuO, the absorption energy of the XANES spectra for $\text{CuO}_x/10\text{A2B}$ shifted to lower energy when increasing the combustion temperature to 400 °C. Subsequently, the absorption energy of the spectrum for $\text{CuO}_x/10\text{A2B}$ at 600 °C exhibited a weak pre-edge assigned to $\text{Cu}^+ 1s \rightarrow 4p$ transition,⁵⁾ which was observed in the spectrum for Cu_2O . According to linear combination fitting (Table S1), CuO in $\text{CuO}_x/10\text{A2B}$ at 600 °C was reduced approximately 50% to Cu_2O . These results imply that CuO (Cu^{2+}) in as-prepared $\text{CuO}_x/10\text{A2B}$ was partly changed, i.e. reduced, to Cu_2O (Cu^+) during the NH_3 combustion reaction. We have previously demonstrated the following catalytic properties of $\text{CuO}_x/10\text{A2B}$ and $\text{CuO}_x/\text{Al}_2\text{O}_3$: (1) these catalysts could be characterized by highly dispersed CuO_x 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_x nanoparticles reacted with NH_3 , and therefore its surface was reduced.¹⁵⁾ Such reduction behavior is in agreement with the previous X-ray photoelectron spectroscopy (XPS) analysis.¹⁵⁾ Unlike the as-prepared $\text{CuO}_x/10\text{A2B}$, on the other hand, the XANES spectra for $\text{CuO}_x/10\text{A2B(aged)}$ at RT

Fig. 2. Cu K-edge EXAFS oscillations for the catalysts during NH_3 combustion and the references.

and 200 °C were similar to the spectrum for spinel CuAl_2O_4 due to the solid-state reaction between as-prepared CuO and 10A2B. Therefore, considering the XPS analysis,¹⁵⁾ it is probable that the oxidation state of the bulk CuAl_2O_4 in $\text{CuO}_x/10\text{A2B(aged)}$ was also 2+ during the NH_3 combustion reaction, whereas the surface of CuAl_2O_4 was reduced to the lower oxidation state. Similar structures as well as trends were also observed in $\text{CuO}_x/\text{Al}_2\text{O}_3$ before and after thermal aging.

Figure 2 shows the extended X-ray absorption fine structure (EXAFS) oscillations for the catalysts during NH_3 combustion ($\lambda = 2$). In the case of as-prepared $\text{CuO}_x/10\text{A2B}$, its oscillation was similar to that for CuO, which is consistent with the results of XANES (Fig. 1) and XRD. The oscillation for $\text{CuO}_x/10\text{A2B}$ at 200 °C was also similar to that for CuO, whereas its oscillations at 400 and 600 °C became similar to that for Cu_2O , which indicates that the CuO nanoparticles of as-prepared $\text{CuO}_x/10\text{A2B}$ were partly reduced to Cu_2O during the NH_3 combustion reaction at temperatures higher than 300 °C. Moreover, the amplitude of the oscillation for $\text{CuO}_x/10\text{A2B}$ tends to decrease with increasing the reaction temperature. In contrast, in the cases of $\text{CuO}_x/10\text{A2B(aged)}$, as-prepared $\text{CuO}_x/\text{Al}_2\text{O}_3$, and $\text{CuO}_x/\text{Al}_2\text{O}_3(\text{aged})$ at each reaction temperature, their oscillations were similar to that for CuAl_2O_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 $\text{CuO}_x/10\text{A2B}$ displayed an intense Cu–O peak ($r \sim 1.95 \text{ \AA}$) attributed to CuO. Upon reaching the reaction temperature of 400 °C, the catalyst displayed an intense Cu–O peak ($r \sim 1.85 \text{ \AA}$) attributed to Cu_2O . These results are in agreement with the XANES and EXAFS oscillations, and it is suggested that the structure of CuO in the as-prepared $\text{CuO}_x/10\text{A2B}$ was partly changed (reduced) to that of Cu_2O during the NH_3 combustion reaction. On the other hand, the other catalysts, $\text{CuO}_x/10\text{A2B(aged)}$ and $\text{CuO}_x/\text{Al}_2\text{O}_3$ before and after thermal aging, displayed an intense Cu–O peak ($r \sim 1.94 \text{ \AA}$) attributed to CuAl_2O_4 , r of which were preserved

Fig. 3. Fourier transforms of k^3 -weighted Cu K-edge EXAFS for the catalysts during NH_3 combustion and the references.

after heating at 600°C. These results indicate the catalysts also form spinel CuAl_2O_4 during the NH_3 combustion reaction.

Based on the present and previous results, the local structures of supported CuO_x during catalytic NH_3 combustion ($\lambda = 2$) can be suggested, as depicted in Figure S2. CuO_x in the as-prepared $\text{CuO}_x/10\text{A2B}$ can be assigned to CuO nanoparticles before the combustion, whereas the structure of CuO was partly changed to that of Cu_2O during the NH_3 combustion. These results imply that a mixture of CuO and Cu_2O nanoparticles exists during the combustion, and the catalytic NH_3 combustion over CuO nanoparticles in the catalysts probably proceeds by redox cycling between CuO and Cu_2O . On the other hand, the CuAl_2O_4 nanoparticles in other catalysts preserved the local structure of its spinel CuAl_2O_4 even during the NH_3 combustion. However, because the reduction of surface CuAl_2O_4 was obtained after the NH_3 combustion reaction from previous XPS analysis, it is probable that the catalytic NH_3 combustion over CuAl_2O_4 nanoparticles proceeds by redox cycling of surface CuAl_2O_4 .

In conclusions, the local structures around CuO_x nanoparticles in $\text{CuO}_x/10\text{A2B}$ and $\text{CuO}_x/\text{Al}_2\text{O}_3$ during the catalytic combustion ($\lambda = 2$) of NH_3 were studied by means of *operando* Cu K-edge XANES and EXAFS. From the XANES spectra, the nanoparticles of CuO (Cu^{2+}) in the as-prepared $\text{CuO}_x/10\text{A2B}$ were reduced by approximately 50% to Cu_2O (Cu^+) at a reaction temperature of 600°C, whereas the oxidation state of the bulk CuAl_2O_4 nanoparticles in the other catalysts was barely changed. According to the profiles of EXAFS oscillations and FT-EXAFS, similar behaviors of catalytic reductions were obtained. In addition, the local structure of CuO nanoparticles in the $\text{CuO}_x/10\text{A2B}$

partly changed to Cu_2O nanoparticles during NH_3 combustion. In contrast, the local structure of the bulk CuAl_2O_4 nanoparticles was preserved during the NH_3 combustion reaction. From our previous XPS analysis, however, it is considered that the surface of CuAl_2O_4 in the other catalysts was reduced during the NH_3 combustion reaction at 400°C, because NH_3 reacts with the lattice oxygen of CuAl_2O_4 , and therefore the catalytic NH_3 combustion proceeds via the Mars–van Krevelen mechanism.

Acknowledgements This research was supported by JST, PRESTO (JPMJPR1344). *Operando* XAFS experiments were performed at the BL9A with the approval of PF, KEK (Proposal No. 2016G527).

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

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