

Determination of Active Cu Species of Cu/BaO/La₂O₃ Catalyst for the Simultaneous Removal of Carbon Soot and Nitrogen Oxides

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1 Introduction

Diesel engines that operate under lean conditions have been widely employed in numerous kinds of vehicles because of their high fuel efficiency, high export power, and excellent durability. However, the exhausts of diesel engines contain carbon soot (particulate matter), which is composed of aggregated carbonaceous soot and adsorbed hydrocarbons with particle sizes less than 2.5 μm, and NO_x gas; these particulates and gas have been causing severe damage to the environment and human health. Therefore, a technique that can efficiently remove carbon soot and NO_x emissions is particularly desired to satisfy upcoming diesel emission standards.

We have developed a novel Cu/BaO/La₂O₃ catalyst for the simultaneous removal of carbon particulates and NO gas from diesel exhaust. In this study, local structure of the active Cu species was evaluated by XAFS.

2 Experiment

X-ray absorption fine structure (XAFS) spectra were recorded at room temperature in fluorescence mode at the BL-9A facilities. A Si(111) double crystal was used. In a typical experiment, a sample was loaded into an in situ cell with plastic windows. The EXAFS data were examined using an EXAFS analysis program, Rigaku EXAFS. The pre-edge peaks in the X-ray absorption near edge structure (XANES) regions were normalized for atomic absorption on the basis of the average absorption coefficient of the spectral region. Fourier transformation (FT) of *k*³-weighted normalized EXAFS data was performed over the 3.5 Å < *k*/Å⁻¹ < 11 Å range to obtain the radial structure function.

3 Results and Discussion

Fig. 1 shows the Cu K-edge XANES spectra of the Cu/BaO/La₂O₃, Cu/BaO/Al₂O₃, and Cu/La₂O₃ as well as those of Cu foil, Cu₂O, and CuO as reference copper compounds. The different edge energies and edge shapes of the three standards provide important information for identifying the oxidation state and local structure of copper. A small pre-edge peak of the CuO standard at 8.974 keV is ascribed to the dipole-forbidden electronic transition of 1s → 3d for Cu²⁺; the more intense peaks between 8.982–8.986 keV are attributed to the dipole-allowed 1s → 4p electron transition of Cu⁺ and Cu²⁺, respectively, which are indicative of the copper oxidation state. The spectrum of Cu/BaO/La₂O₃ (**Fig. 1(d)**) indicated that this catalyst exhibit the same edge energy as the CuO standard, which suggests that the copper

species exist in a 2+ oxidation state. In addition, the absence of the edge transition peak, the greater white line intensity, and the different shape of the catalyst spectrum can be attributed to a strong interaction between the copper species and the BaO phase on the La₂O₃ support. Either Cu ions are incorporated within the BaO lattice, thereby leading to a different electronic environment from that of the CuO standard, or isolated copper ions that strongly interact with BaO and form a mixed copper barium oxide with electronic and structural properties that differ from those of the CuO standard. On the basis of the edge energy, the copper species in Cu/BaO/Al₂O₃ and Cu/La₂O₃ also exist in a 2+ oxidation state (**Fig. 1(e) and (f)**); however, the white line intensity of the Cu/La₂O₃ is slightly weaker than those of the Cu/BaO/La₂O₃ and Cu/BaO/Al₂O₃.

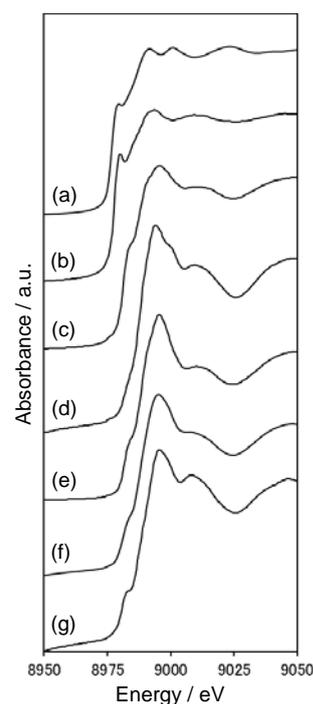


Fig. 1 Cu K-edge XANES spectra of (a) Cu foil, (b) Cu₂O, (c) CuO, (d) Cu/BaO/La₂O₃, (e) Cu/BaO/Al₂O₃, (f) Cu/La₂O₃, and (g) recovered Cu/BaO/La₂O₃.

The FTs of Cu K-edge EXAFS data are depicted in **Fig. 2**. The peak positions of the Cu/BaO/La₂O₃ are similar to those of CuO but differ from those of the Cu foil and Cu₂O, indicating that most copper species exists as CuO.

However, compared to the spectrum of the reference CuO standard, the second peaks in the spectrum of the Cu/BaO/La₂O₃ are substantially more intense (**Fig. 2(d)**). This peak is attributable to the contiguous Cu–O–Cu bonds due to CuO₆ octahedra. The increased intensity of the Cu/BaO/La₂O₃ in this region can be explained by the formation of Cu–O–Ba bonds due to the strong interaction between small CuO_x clusters and the BaO phase. The formation of these bonds is indicated by the absence of the edge transition peak, the greater white line intensity, and the different shape in the XANES spectrum of the Cu/BaO/La₂O₃. Such unique phenomena cannot be observed in cases of Cu/BaO/Al₂O₃ and Cu/La₂O₃ (**Fig. 2(e) and (f)**), where the peak positions and relative intensity coincide with those of the CuO standard. We concluded that the CuO phase formed on the BaO/La₂O₃ support is completely different from those on the BaO/Al₂O₃ and on the original La₂O₃.

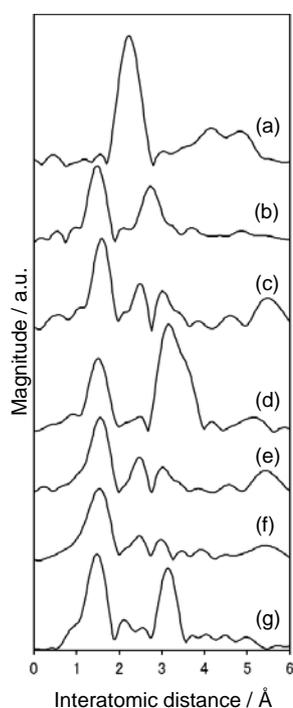


Fig. 2 Cu K-edge FT-EXAFS spectra of (a) Cu foil, (b) Cu₂O, (c) CuO, (d) Cu/BaO/La₂O₃, (e) Cu/BaO/Al₂O₃, (f) Cu/La₂O₃, and (g) recovered Cu/BaO/La₂O₃.

References

- [1] K. Mori, Y. Iwata, M. Yamamoto, N. Kimura, A. Miyauchi, G. Okamoto, T. Toyoshima, and H. Yamashita, *J. Phys. Chem. C*, **2014**, 118, 9078-9085.