Operando XAFS study of Cu/CeO₂ for automotive three-way catalysts

Three-way catalysts (TWCs) can promote the simultaneous purification of three harmful gas emissions, that is, carbon monoxide (CO), unburned hydrocarbons (HCs), and nitrogen oxides (NOx), from automotive engines. The TWCs are placed under the floor and/or beside the engine, and their devices are installed in exhaust pipes. Each TWC comprises (i) precious metals such as platinum (Pt), rhodium (Rh), and palladium (Pd), (ii) supports for dispersing these precious metal particles on the nanometer scale, and (iii) catalytic promoters. In particular, the precious metals are pivotal components since they function as a source of catalytic active sites that detoxify harmful components. Recently, owing to the rising concern for global environmental protection, emission regulations have been strengthened step by step on a world scale. In line with this trend, the demand for automotive catalysts has been increasing yearly, increasing the consumption of precious metals. Therefore, the finite availability of precious metals has inspired us to develop catalysts comprising base metals, which are economical and abundantly available.

This study is intended to clarify a catalytic mechanism of NO reduction over a base metal catalyst and an optimum reaction condition for maximizing the catalytic activity for NO reduction, utilizing *operando* XAFS (X-ray absorption fine structure) analysis. The NO reduction reaction is considered as the most difficult reaction in threeway conversions. Herein, we show an important mechanism of an improved NO reduction reaction over the base metal catalyst Cu/CeO₂ under a periodic (rich/lean cycling) reaction condition [1].

Operando XAFS analysis provides the chemical states and molecular structures of catalysts in their working states as well as their catalytic activities. This methodology has been well established along with the use of intense synchrotron radiation sources. Figure 1 shows the high-speed operando XAFS system that we are using for catalysis at the Toyota beamline BL33XU. The gas transfer unit comprises three independent gas supply lines using 15 types of gas cylinders. The high-speed gas switching system is used to rapidly change between three gas lines, in order to simulate actual auto exhausts that always vary with the engine operation. The mass analyzer can analyze 5 gas species every 50 ms. We evaluated the catalytic activity on-line using the gas analyzer. The operando cell was specially designed for transient X-ray detection while minimizing the dead volume. A combination of a servo-motor-driven Si channel-cut monochromator with a tapered undulator enables rapid acquisitions of high-quality data of quick-scanning XAFS (QXAFS) [2]. The beamline covers an energy range from 4.0 to 46.0 keV. We applied the operando XAFS technique at both the Cu K-edge (8.98 keV) and Ce K-edge (40.45 keV) in order to clarify the Cu-Ce interaction in Cu/CeO2 catalysts under reaction conditions. We performed an operando time-resolved QXAFS analysis at both high and low X-ray energies with a temporal resolution of one second, and revealed a unique dynamic behavior of synergistic redox properties of Cu and Ce species.

In this work, 6 wt% Cu/CeO_2 was used. Figure 2 shows changes in the Cu and Ce *K*-edges absorption edge energy under the static and periodic reaction conditions at temperatures ranging from 50 to 600°C.



Fig. 1. Experimental setup for operando XAFS in transition mode.



Fig. 2. (a) Energy shift of Cu *K*-edge as a function of temperature for the Cu/CeO₂ under the static and periodic reaction conditions. Magnified views of (b) Cu *K*-edge and (c) Ce *K*-edge absorption edge energy under the periodic condition. [1]

The static condition was obtained using a reactant gas stream consisting of 0.4% O2, 0.65% CO, 0.15% NO, 0.1% C₃H₆, ca. 3% H₂O, and He balance. On the other hand, under the periodic condition, a lean stream (oxygen excess) consisting of 0.8% O₂, 0.65% CO, 0.15% NO, 0.1% C₃H₆, ca. 3% H₂O, and He balance or a rich stream (oxygen insufficient) with the same composition as the lean gas except for 0% O₂ was alternately introduced to the in situ cell every 30 s. The time-averaged O₂ concentration under the periodic condition was the same as that under the static condition. The Cu and Ce K-edges XAFS measurements were carried out under the same operando conditions, i.e., the catalyst weight, atmospheric condition, total flow rate, and temperature ramping rate. The Cu and Ce K-edges XAFS spectra were collected every one second. As shown in Fig. 2(a), the absorption edge energy of the Cu K-edge for Cu/CeO₂ at low reaction temperatures was the same as that for CuO powder used as a reference, indicating that the initial oxidation state was Cu²⁺. The reduction of CuO under the static condition began to occur at 340°C. In contrast, the onset temperature of Cu reduction under the periodic condition was obviously low compared with that under the static condition. The Cu oxide species started to be reduced at 150°C along with the oscillation of the Cu oxidation state corresponding to the rich/lean cycling (Fig. 2(b)). In addition, the Ce oxidation state of the CeO₂ support also fluctuated under the periodic condition (Fig. 2(c)). It should be noted that the fluctuation period of the Cu oxidation state synchronized with that of the Ce oxidation state. Figure 3(a) shows the temperatures for 20% NO conversion under the static and periodic conditions. Cleary, the periodic condition leads to a significant increase in the catalytic reduction of NO. As for a conventional Cu/Al₂O₃ catalyst, an effective Cu reduction and an improvement in NO reduction were not seen under the periodic condition (data not shown). It was considered that the Cu oxide species in the Cu/CeO2 catalyst under the periodic condition were easily reduced by synchronization with the valence change of Ce⁴⁺/Ce³⁺ at the interface between the Cu particles and the CeO₂ support as shown in Fig. 3(b), and that this function improved the catalytic activity for NO reduction.

By the *operando* XAFS analysis, we discovered that the synchronization of the Cu and Ce valence change in Cu/CeO_2 under the periodic condition improves the catalytic activity for NO reduction.



Fig. 3. (a) Temperatures for 20% NO conversion for the Cu/CeO_2 under the static and periodic reaction conditions. (b) Schematic representation of the oxidation state behavior of Cu and Ce under the periodic condition. [1]

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