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Research Report

Operando XAFS Study of Automotive Exhaust Catalysts

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■**ABSTRACT**|| Synchrotron-based analysis techniques allow an improved understanding of catalysts. *Operando* time-resolved X-ray absorption fine structure (XAFS) spectrometry is an especially powerful technique for uncovering the actual state of the catalyst under catalytic reaction conditions. This methodology is thus well-suited to the analysis of automotive exhaust catalysts. Exhaust gases exiting from engines change quickly and dramatically, and the reaction temperature and atmospheric conditions to which automotive catalysts are exposed vary with time during operation of the vehicle. It is therefore very important to track the dynamic behavior of the catalytic active sites during operation so as to understand the working principles of the catalysis. In this paper, we present the results of our latest fundamental study involving the *operando* XAFS analysis of automotive catalysts. We initially investigated the catalytic activation process at low temperatures during the total oxidation of C_3H_6 over a Pt/ Al_2O_3 catalyst. Subsequently, we examined catalytic NO reduction over Cu/ CeO_2 under periodic (rich/lean cycling) or static reaction conditions. These studies generated new information concerning the nature of the catalytic active sites under working conditions, and provided important insights that will be helpful in designing better catalysts.

■**KEYWORDS**|| Automotive Catalyst, X-ray Absorption Spectroscopy, C_3H_6 Oxidation, NO_x Reduction, Platinum Group Metal, Base Metal

1. Introduction

Automotive three-way catalysts (TWCs) can promote the simultaneous removal of three harmful gas emissions from automotive engines: carbon monoxide (CO), unburned hydrocarbons (HCs), and nitrogen oxides (NO_x). TWCs were commercialized for vehicular exhaust emission control in both the U.S. and Japan in 1977⁽¹⁾ and, since then, the use of TWC systems has spread rapidly. Presently, these systems are used in almost all gasoline powered vehicles around the world. Each TWC comprises (i) a platinum group metal (PGM; Pt, Pd or Rh), (ii) supports for dispersing these PGM particles on the nanometer scale, and (iii) catalytic promoters. The PGMs are vital since they function as the source of catalytic active sites to remove harmful exhaust components. An ever-increasing appreciation of the damage that noxious gas emissions are doing to our environment has led to increasingly stringent legislation designed to combat such pollution. As a result, the demand for automotive catalysts has been increasing yearly,

causing a rise in the consumption of PGMs. The finite nature of PGM resources has inspired us to develop advanced catalysts that have reduced PGM contents or that use alternative technologies that are both economical and abundantly available. Central to technological progress in this sense is a fundamental understanding of the behavior of PGMs or alternative materials as catalytic active sites during the catalytic reaction.

The recent progress in analytical techniques such as synchrotron radiation analysis has generated remarkable breakthroughs, and has allowed us to gain a better understanding of catalysts.^(2,3) *Operando* (meaning ‘at work’) X-ray absorption fine structure (XAFS) analysis is a particularly powerful technique for uncovering the real state of the catalyst under working conditions.⁽⁴⁻⁷⁾ This methodology has been well established in conjunction with the use of intense synchrotron radiation sources, assisting us in performing XAFS experiments on catalysts loaded with small amounts of PGMs (up to 1 wt%), applying short measurement times. *Operando* XAFS can

provide both the chemical states and molecular structures of catalysts under reaction conditions, in addition to their catalytic activities. Exhaust gases exiting from gasoline engines change quickly and dramatically, and the reaction temperatures and atmospheric conditions to which automotive catalysts are exposed thus vary with time during operation of the vehicle. It is consequently very important to understand the dynamic behavior of automotive catalysts under operational conditions to allow the development of more efficient and durable catalysts. **Figure 1** shows the *operando* XAFS system that we are using for the analysis of catalysis at the Toyota beamline BL33XU at SPring-8.^(8,9) The combination of a gas transfer unit with a high-speed gas switching system allows us to create simulated auto exhausts that mimic the variations that occur with engine operation. The *operando* cell of this system has been specially designed for transient X-ray detection while minimizing the dead volume. During analyses, the self-supported catalyst disk is placed in the cell and the reactant gas mixture is introduced into the cell while a portion of the effluent gas from the cell is transferred to a mass spectrometer. XAFS analysis provides information concerning the chemical states and molecular structures of the catalytic active sites and the gas analyzer determines the on-line catalytic activity. This *operando* system thus permits the real-time visualization of the catalytic working state.

In this review, we present the latest results of our fundamental studies applying *operando* to the XAFS analysis of PGM catalysts, and we also discuss base metal catalysts as an alternative to PGM catalysts. This technique has provided new information concerning the nature of the catalytically active sites under working conditions. We hope that this knowledge will provide a wider perspective on this field and assist other researchers in their work.

2. *Operando* Observations of a Pt/Al₂O₃ Catalyst for the Total Oxidation of C₃H₆

In this section, we report the results of *operando* experiments using the XAFS technique with Pt/Al₂O₃ catalysts for the total oxidation of C₃H₆,⁽¹⁰⁾ which is typically detected in automotive exhaust gases at a considerable concentration. The main objective of this work was to probe the catalyst activation process during the reaction. Many properties are needed for an automotive catalyst to achieve highly efficient exhaust purification, and the catalyst activation behavior is one of the most important so as to allow the exhaust purification system to function at lower temperatures. Because the catalyst is originally at ambient temperature at the start-up of an automotive engine, it must be capable of being activated at as low a temperature as possible.

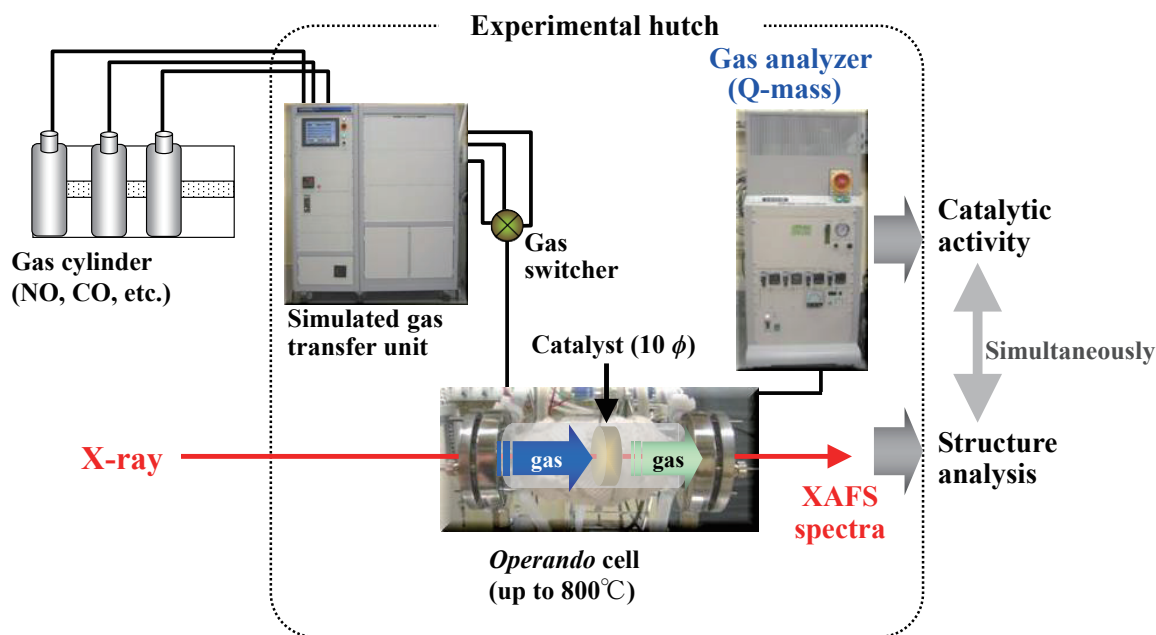


Fig. 1 Typical experimental setup for *operando* XAFS in the transition mode (Toyota beamline, BL33XU of SPring-8).

The *operando* XAFS experiments were carried out at the BL01B1 and BL16B2 beamlines of SPring-8. In this work, 1 wt% Pt/ γ -Al₂O₃ was used, and both the Pt oxidation state and the catalytic reaction progress were monitored simultaneously as the temperature was increased. **Figure 2(a)** shows the changes in the XANES (X-ray absorption near edge structure) spectra at the Pt L₃-edge (11.5 keV) during the ramping up of the temperature throughout the C₃H₆ oxidation reaction. During these trials, a lean stream (that is, with a slight oxygen excess) consisting of 0.6% O₂, 0.1% C₃H₆ and He as the balance was introduced into the *operando* cell in which the catalyst disk was held.

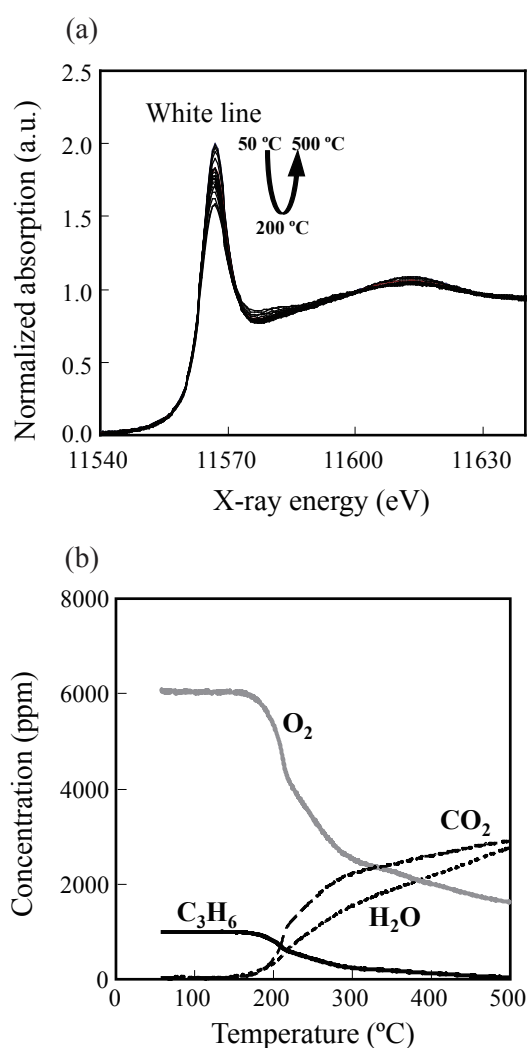


Fig. 2 (a) Pt L₃-edge XANES spectra acquired during C₃H₆ oxidation in a gas mixture (0.6% O₂ and 0.1% C₃H₆ in He, total flow of 100 mL/min) over Pt/Al₂O₃ (35 mg). (b) The concentrations of C₃H₆, O₂, CO₂ and H₂O measured during the C₃H₆ oxidation reaction over Pt/Al₂O₃ as a function of temperature.

The steeply rising absorption edge in the Pt L₃-edge XANES spectrum is referred to as a “white line” and its maximum height reflects the vacancy in the 5d orbitals of the Pt atoms.⁽¹¹⁾ An intense white line peak is observed for oxidized Pt, while a low peak height is associated with reduced Pt, and so this line may be used to estimate the valence state of the Pt. In the present work, the white line peak height was found to vary with reaction temperature, although the change was not monotonic. The reduction of Pt species evidently proceeded as the temperature was ramped up to 200°C, above which the Pt species were re-oxidized. During these *operando* XAFS experiments, both the XAFS spectra and the on-line mass spectra of the effluent gas species H₂O (*m/z* 28), O₂ (*m/z* 30), C₃H₆ (*m/z* 41), and CO₂ (*m/z* 43) were simultaneously acquired. The concentration changes of each species as functions of the temperature of the Pt/Al₂O₃ are plotted in Fig. 2(b). The concentrations of C₃H₆ and O₂ evidently began to decrease at approximately 160°C while, at the same time, CO₂ and H₂O began to form. These results indicate that the catalytic C₃H₆ oxidation reaction started at this approximate temperature.

Figure 3 shows the relationship between the fraction of metallic Pt and the resulting C₃H₆ conversion rate as a function of temperature, as a means of assessing the catalyst activation behavior during C₃H₆ oxidation over the Pt/Al₂O₃ catalyst. The fraction of metallic Pt was estimated from the XANES spectra in

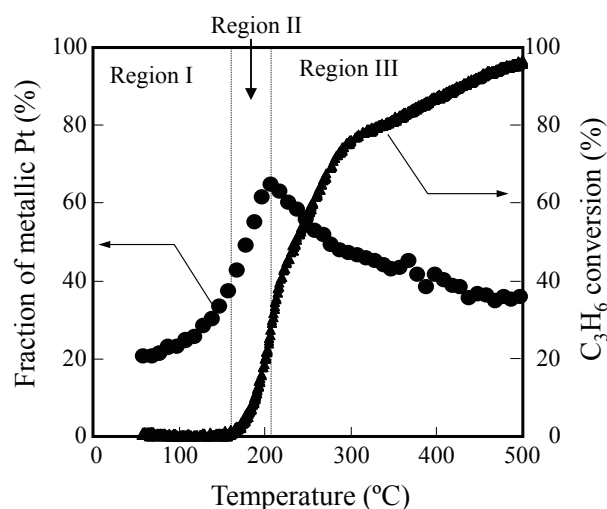


Fig. 3 The temperature dependencies of the metallic Pt fraction and conversion rate during the catalytic C₃H₆ oxidation over Pt/Al₂O₃. Legend: metallic Pt fraction (circle), C₃H₆ conversion (triangle).

Fig. 2(a), based on the assumption that there is a linear relationship between the white line intensity and the valence state of Pt on certain metal oxide supports.⁽¹²⁾ Based on this assumption, the white line peak heights of PtO₂ powder and Pt foil were assigned to 0% and 100% metallic Pt, respectively. It is generally believed that metallic Pt is the active site for the automotive catalytic reaction.⁽¹³⁾ The C₃H₆ conversion rates were calculated from the effluent concentrations of C₃H₆ shown in Fig. 2(b). The catalytic activation process can be divided into three regions according to reaction temperature. In region I, the Pt metal fraction slowly increases without any catalytic C₃H₆ conversion. In region II, the Pt metal fraction increases rapidly in conjunction with the onset of the C₃H₆ oxidation reaction. In region III, the C₃H₆ conversion rapidly progresses up to 500°C while, in contrast, the Pt metal fraction decreases. A scheme summarizing the catalyst activation behavior in each temperature region based on the results described above is presented in Fig. 4.

In region I, the fraction of metallic Pt increases although no C₃H₆ conversion is observed based on analysis of the gas phase. Kinetic studies of the C₃H₆-O₂ reaction over a Pt catalyst have shown that the reaction order is negative with regard to C₃H₆ and positive with regard to oxygen.⁽¹³⁾ This suggests a self-poisoning effect during the C₃H₆-O₂ reaction over Pt catalysts, through preferential adsorption of C₃H₆ on the surface of Pt compared with O₂. The adsorbed C₃H₆ is expected to reduce the oxidized Pt but no net catalytic reaction is observed because the temperature is not high enough to break the C-C bonds in the adsorbed C₃H₆. In this region, the adsorbed C₃H₆

should dominate the surfaces of the Pt particles.

In region II, the oxidation of C₃H₆ is observed in the gas phase and the conversion rate increases as the temperature is increased. The overall reaction is believed to be kinetically controlled in this region because the conversion rate is below 30%; thus, the reaction rate should be the product of the number of active sites multiplied by their turnover frequency. All the active sites should contribute equally to the reaction in this stage. The XAFS observations of the Pt valence state can therefore be discussed based on the observed conversion seen in the gas phase and resulting from the catalytic reaction. In this stage, the Pt dispersion in the Pt/Al₂O₃ was 55% as determined by the CO pulse adsorption method. If the creation of metallic Pt proceeds from the surfaces of Pt particles, a specific value of metallic Pt fraction will correspond to a monolayer of Pt particles. In fact, a metallic fraction of approximately 75% would correspond to a monolayer reduction of Pt particles, since a 20% metallic fraction was found prior to the reaction and 55% dispersion was determined by CO adsorption. This suggests that the metallic Pt fraction in region II amounts to less than a monolayer, meaning that oxidized and metallic Pt would coexist on the surfaces of the Pt particles, as shown in Fig. 4. As the metallic Pt fraction increases with increasing temperature in region II, the net catalytic reaction on the surfaces of the Pt particles and the creation of active sites occur simultaneously. Thus the catalyst activation is a coupled process, combining the creation of active sites and the catalytic reactions at these sites.

In region III, the metallic Pt fraction decreases with

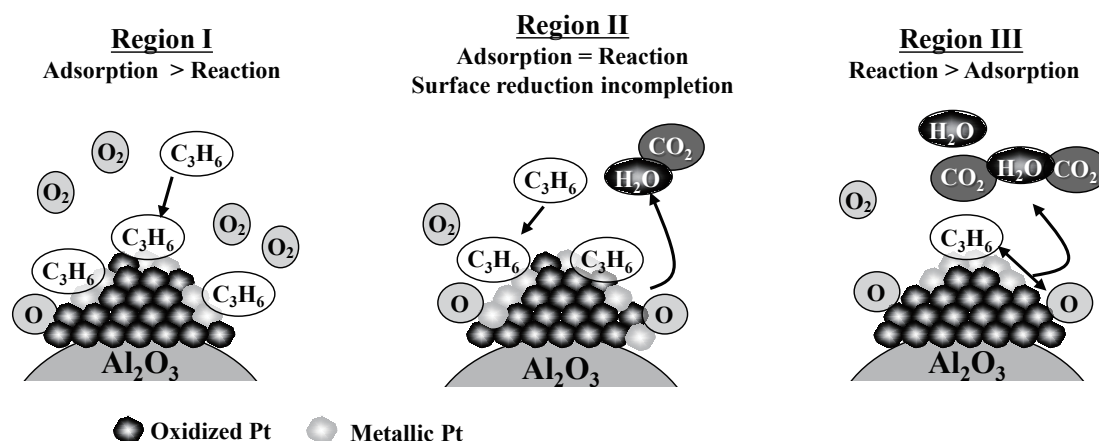


Fig. 4 Proposed mechanisms for the catalysis of the C₃H₆ oxidation reaction over Pt/Al₂O₃ in regions I, II and III.

increasing temperature. In this region, the conversion rate is greater than 30% and the overall reaction is not kinetically controlled, meaning that the active sites in the catalyst do not contribute equally to the reaction. A portion of the active sites will therefore determine the catalytic reaction while the other active sites will not contribute. In this scenario, the XAFS observation of Pt valence states cannot be discussed in conjunction with the observed overall catalytic reaction. Some Pt is expected to be oxidized by residual oxygen following the reaction under oxidizing conditions, as shown in Fig. 4, and this oxidized Pt will not contribute to the catalytic reaction. This explains why the fraction of metallic Pt decreases with increasing reaction temperature in region III.

3. Operando Investigations of Catalytic NO Reduction over Cu/CeO₂

This fundamental study was intended to clarify the catalytic mechanism of NO reduction over a base metal catalyst as an alternative to PGM catalysts, and to determine the optimum reaction conditions for maximizing the catalytic activity for NO reduction, utilizing *operando* XAFS. The NO reduction reaction is considered to be the most difficult reaction in three-way (CO and HC oxidation/NO_x reduction) conversion systems. In this work, we elucidate the important mechanism of an improved NO reduction reaction over the base metal catalyst Cu/CeO₂ under periodic (rich/lean cycling) reaction conditions. Ceria-based oxide is widely utilized in automotive catalysts as both supports and promoters, because of its oxygen storage/release capabilities based on the reversible Ce⁴⁺/Ce³⁺ redox reaction. In the present study, 6 wt% Cu/CeO₂ was used and the *operando* XAFS experiments were carried out at the Toyota beamline (BL33XU) of SPring-8, spanning 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 CuO-CeO₂ interactions in Cu/CeO₂ catalysts under reaction conditions. **Figure 5** summarizes the changes in the Cu and Ce *K* absorption edge energies under both static and periodic reaction conditions at temperatures ranging from 50 to 600°C. 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, with He as the balance. In contrast,

under the periodic condition, a lean stream (oxygen rich) consisting of 0.8% O₂, 0.65% CO, 0.15% NO, 0.1% C₃H₆, ca. 3% H₂O, with He as the balance and a rich stream (oxygen poor) with the same composition as the lean gas except with 0% O₂ were alternately introduced to the in situ cell every 30 seconds. 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 of catalyst weight, atmosphere, total flow rate, and temperature ramp rate. The Cu and Ce *K*-edges XAFS spectra were collected at one second intervals. As shown in Fig. 5(a), the absorption edge energy of the Cu *K*-edge for Cu/CeO₂ at low reaction temperatures was the same as that for the CuO powder used as a reference, indicating that the initial oxidation state was Cu²⁺. The reduction of CuO under

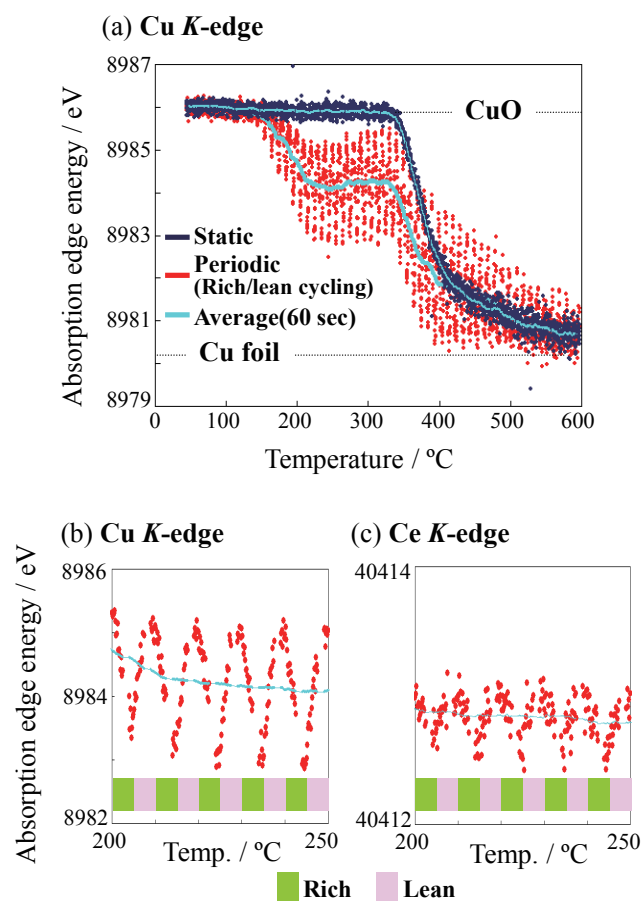


Fig. 5 (a) The Cu *K*-edge energy shifts as functions of temperature for Cu/CeO₂ under static and periodic reaction conditions. Magnified views of the (b) Cu *K*-edge and (c) Ce *K*-edge absorption edge energies under the periodic condition.

the static condition began at 340°C. In contrast, the onset temperature for Cu reduction under the periodic condition was significantly lower. The Cu oxide species began to be reduced at 150°C, accompanied by an oscillation of the Cu oxidation state corresponding to the rich/lean cycling (Fig. 5(b)). In addition, the Ce oxidation state in the CeO₂ support also fluctuated under the periodic condition (Fig. 5(c)). The important point to note is that the fluctuation period of the Cu oxidation state was synchronized with that of the Ce oxidation state. Martínez-Arias et al. investigated the interfacial redox processes in Cu/CeO₂ under CO/O₂ using electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) and concluded that the reduction begins at the copper oxide/ceria interface.⁽¹⁴⁾ Based on that investigation, we believe that the synchronized redox oscillation observed in our system starts at CuO/CeO₂ interface positions at low temperatures. In addition, the conventional Cu/Al₂O₃ catalyst does not exhibit effective Cu reduction at low temperatures under the periodic condition (Fig. 6). Based on the thermodynamic phase diagram, it is generally held that the Al oxidation state in the Al₂O₃ support remains as Al³⁺ under both reductive and oxidative conditions at temperatures up to and above 1000°C. The present results lead to the conclusion that the coexistence of Cu (Cu²⁺, Cu⁺ and Cu⁰) and Ce (Ce⁴⁺ and Ce³⁺), which have mutually variable oxidation states, is fundamental to the synergistic redox characteristics of Cu/Ce interfaces resulting from a strong CuO-CeO₂

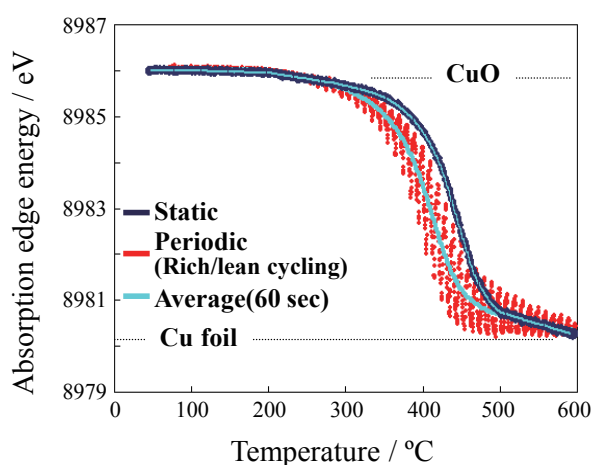


Fig. 6 The Cu *K*-edge energy shifts as functions of temperature for Cu/Al₂O₃ under static and periodic reaction conditions.

interaction.

Figure 7 shows the catalytic NO conversions over Cu/CeO₂ under static and periodic operation. To facilitate the comparison between static and periodic operation, the average NO conversion over 60 seconds is used as an index of the catalytic activity in Fig. 7(a). The temperature at 20% NO conversion under periodic operation was significantly lower than that under static operation. As with the Cu reduction, an improvement in NO reduction was not observed when using Cu/Al₂O₃ under the periodic condition (data not shown). Clearly, periodic operation of Cu/CeO₂ is the main factor leading to the significant increase in the catalytic NO reduction. The NO conversion under periodic operation starts to increase at approximately 200°C. This onset temperature is close to that at which the redox oscillations of the Cu and Ce valence states occur. These data suggest that the oxygen vacancies in CeO₂ and the reduced Cu⁰ and/or Cu⁺ species generated under the rich condition are the driving forces improving the catalytic NO reduction under periodic operation, as shown in **Fig. 8**. A similar observation has been reported by Chen et al., who performed NO-temperature programmed desorption (TPD) measurements of Cu/SiO₂, CeO₂, and Cu/CeO₂ samples after reductive pretreatment, and concluded that oxygen vacancies in both ceria and metallic copper are active for NO dissociation.⁽¹⁵⁾ To summarize our results; the synchronization of Cu and Ce valence changes under periodic operation improves the catalytic activity for NO reduction at low temperatures. Even when the time-averaged O₂ concentration is the same between the static and periodic operations, a partially-rich atmosphere can produce active species at the reduced CuO_x/CeO_y interface for NO reduction at low temperatures, and consequently, periodic operation improves the average catalytic NO reduction compared with the static condition.

4. Concluding Remarks

In this study, we applied modern *operando* XAFS techniques to the dynamic observation of automotive catalysts under working conditions. A conventional PGM Pt/Al₂O₃ catalyst was investigated to probe the catalytic activation process during the total oxidation of C₃H₆. The reduction of oxidized Pt species was observed prior to the activation of the catalytic reaction while increasing the catalyst temperature.

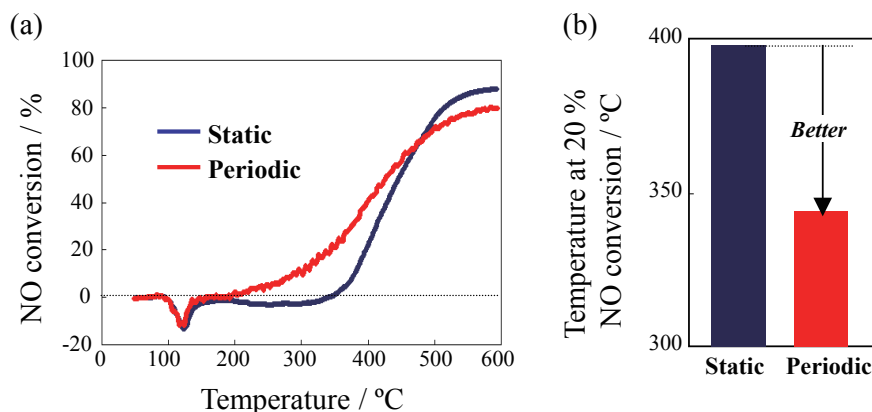


Fig. 7 (a) Temperature dependencies of average NO conversion rate over 60 seconds and (b) 20% NO conversion temperatures over the Cu/CeO₂ catalyst.

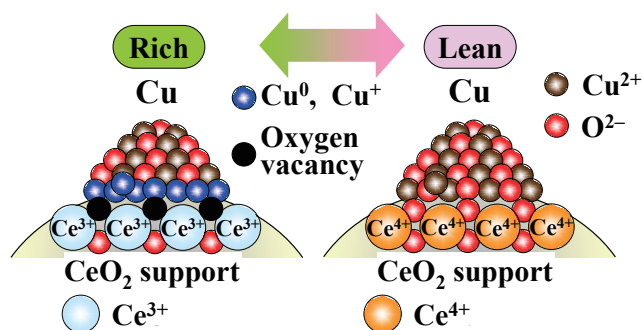


Fig. 8 Schematic representation of the oxidation state behavior of Cu and Ce under the periodic condition.

These results demonstrate that the creation of metallic Pt sites and the activation of adsorbed C₃H₆ species on the surface of the Pt are important for the catalytic C₃H₆ oxidation reaction at low temperatures. These findings should provide important guidance with regard to the design of improved catalytic purification systems, both by developing the catalyst material and by controlling the exhaust atmosphere, so as to promote Pt reduction and suppress C₃H₆ poisoning. The advent of advanced catalysts and engine exhaust operations will allow the PGM content of catalyst systems to be reduced. In addition, we have followed catalytic NO reduction over Cu/CeO₂, a base metal catalyst, under periodic (rich/lean cycling) or static reaction conditions, and ascertained the unique dynamic behavior and synergistic redox properties of the Cu/Ce interface. The application of a partially-rich atmosphere during periodic operation evidently generates oxygen vacancies in the CeO₂ support as well as reduced Cu species, improving the catalytic activity for NO

reduction. These results are encouraging proof that alternatives to PGM catalysts are possible, although more efficient performance as well as improvements in durability are required to compete with PGM catalysts, and so these replacement materials are still a long way from practical use. The development of such catalysts will be challenging but, we believe, still feasible with continued assiduous studies using the *operando* XAFS technique. Of course, the *operando* XAFS analysis is not an all-powerful tool and so it is still important to simultaneously investigate new catalytic materials with other analytical methods.

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Figs. 2-4

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Figs. 5, 7 and 8

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