

# Dynamic behavior of Rh species in Rh/Al<sub>2</sub>O<sub>3</sub> model catalyst during three-way catalytic reaction: An *operando* X-ray absorption spectroscopy study

Heterogeneous catalysts have been used in various essential chemical transformations in petrochemistry, ammonia production, and environmental catalysis. Catalysts for the production of useful chemicals are usually used under ideal conditions. On the other hand, so-called catalytic converters, such as three-way catalysts (TWCs), are often exposed to nonideal conditions, such as severe time variations of oxidative and reductive atmospheres or high temperatures, which can easily induce degradation and change the structure-activity relationship during reactions. Therefore, it is essential to elucidate the dynamic behavior of structural and electronic states of a catalyst under working conditions to understand its catalysis and improve catalytic activity and stability.

Essential components of TWCs are the platinum group metals (PGMs) such as Rh, Pd, and Pt. They are vital for the purification of harmful gases in automobile exhausts, such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and hydrocarbons (HCs). Because of the scarcity of PGMs and strict regulations on automobile exhausts, the reduction of PGM used in TWCs has been one of the urgent global issues arising in response to the trend of increasing demand for automobiles worldwide and the need to protect the global environment.

In this work [1], the dynamic behavior of Rh species in a model catalyst, 1 wt% Rh/Al<sub>2</sub>O<sub>3</sub>, under a TWC reaction was examined by *operando* study using conventional quick scanning X-ray absorption spectroscopy (XAS) performed at a public beamline, SPRING-8 BL01B1, as follows. The Rh/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a common impregnation method was placed into a heating XAS cell. The catalyst was pretreated under He flow at 400°C for 30 min. Immediately after the pretreatment, a model feed gas (100 mL·min<sup>-1</sup>) containing NO (1000 ppm), CO (1000 ppm), C<sub>3</sub>H<sub>6</sub> (250 ppm), and O<sub>2</sub> (912.5–1337.5 ppm) with He balance was introduced into the XAS cell. The concentration of O<sub>2</sub> was varied between 912.5 and 1337.5 ppm during the reaction. The stoichiometric condition was achieved when the concentration of O<sub>2</sub> was set to 1125 ppm on the basis of the chemical equation shown below.



The dynamic behavior of Rh species during the TWC reaction was analyzed by Rh *K*-edge XAS spectra in combination with various gas analyzers, a high-sampling-rate TCD-GC, a NO<sub>x</sub> meter, and

a Q-mass spectrometer. A schematic view of the *operando* XAS setup is shown in Fig. 1.

The catalytic reaction and state of Rh profiles during the TWC reaction over 1 wt% Rh/Al<sub>2</sub>O<sub>3</sub> are summarized in Fig. 2. The pretreatment with He gas induced the reduction of some of the Rh species. Initially, 80% of NO is converted to N<sub>2</sub> with the oxidative model feed gas, but the reduction activity declined to 60% as the Rh species was oxidized. After the first-feed-gas condition, the conversion rate of NO to N<sub>2</sub> increased as the feed gas was changed to the stoichiometric condition in a stepwise manner. When the feed gas was changed to a reductive gas 1 hour after the beginning, the conversion rate of model pollutant gases, CO, NO, and C<sub>3</sub>H<sub>6</sub>, exhibited no change, but the Rh species was rapidly reduced to its metallic state. Monitoring of the following condition variation between oxidative and reduction feed gases suggested reproducible catalytic behavior of the catalyst under the present conditions. From the findings concerning the reduction of NO of high catalytic activity under reductive and oxidative conditions in the beginning period, we confirmed the importance of the surface state of the catalytically active species. The time resolution of the NO<sub>x</sub> meter was the highest among effluent gas analyzers and the NO<sub>x</sub> profile can be tied to the redox state of the surface of Rh species. With the stepwise decrease in the oxygen concentration of the feed gas, the NO<sub>x</sub> profile exhibited a discontinuous change. On the other hand, with the stepwise increase in the oxygen concentration, the NO<sub>x</sub> profile showed a sigmoidal curve. In brief, this behavior was explained by two-step autocatalytic oxidation and simple one-step pseudo-

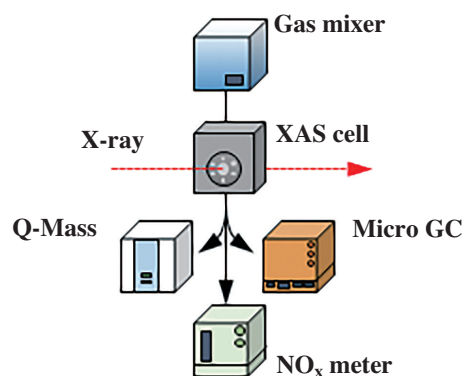


Fig. 1. Simplified view of *operando* XAS setup.

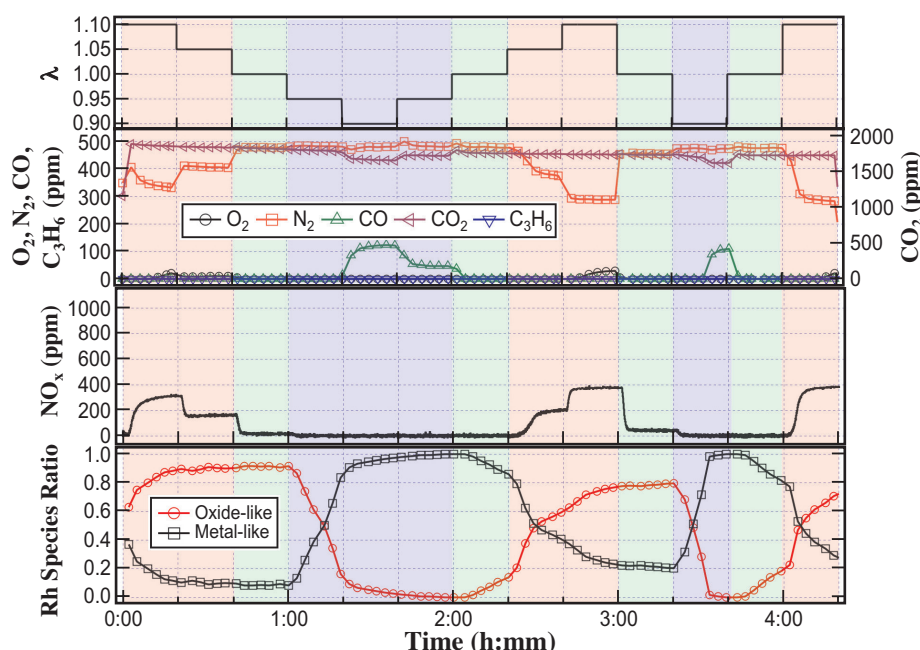


Fig. 2. GC,  $\text{NO}_x$  profiles of the effluent gases and redox behavior of Rh species during TWC reaction over 1 wt%  $\text{Rh}/\text{Al}_2\text{O}_3$ , and  $\lambda$ , the  $\text{O}_2$  concentration indicator. ( $\lambda = ([\text{NO}]_a + [\text{CO}]_a + [\text{O}_2]_a \times 2) / ([\text{NO}]_s + [\text{CO}]_s + [\text{O}_2]_s \times 2)$ , where  $[X]_y$  is the concentration of X under the actual ( $y=a$ ) or stoichiometric ( $y=s$ ) condition. [1])

first-order kinetics during oxidation and reduction processes on the basis of the results of curve fitting analysis of the  $\text{NO}_x$  profiles.

The dynamic behavior of Rh species during feed gas switching is summarized in Fig. 3. We assumed that the sizes of the Rh nanoparticles were almost unchanged because the intensities of the Fourier transforms of the EXAFS spectra (not shown) were similar. Considering the reduction process of Rh species, the surface of the oxide-like Rh species was easily reduced to the metallic state swiftly and randomly. On the other hand, in the oxidation process of Rh species, surface oxidation of Rh species proceeded via random and autocatalytic growth by oxide-like Rh site generation.

In summary, we successfully performed *operando* XAS measurement of the  $\text{Rh}/\text{Al}_2\text{O}_3$  model catalyst

during TWC and found that the reaction steps of oxidation and reduction of surface Rh species involve two-step autocatalytic oxidation and simple one-step pseudo-first-order kinetics. We also demonstrated the implementation of a powerful *operando* XAS system for heterogeneous catalytic reactions and its importance for understanding the dynamic behavior of active metal species of catalysts. It is also promising that a more brilliant X-ray source will enable the clarification of the local structure and electronic states of the target elements with higher temporal, spatial, and energy resolutions, thus contributing to the further understanding of functional materials.

#### Reduction process



#### Oxidation process

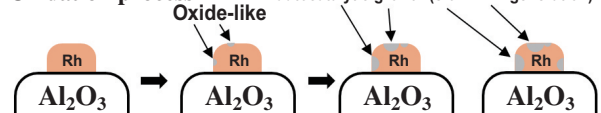


Fig. 3. Redox behavior of Rh species when the gas composition is switched. [1]

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#### References

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