

## Operando XAFS study of highly active Au-Ni bimetallic clusters for NO-CO reaction in simulated automobile exhaust

Exhaust-gas catalysts can promote the simultaneous purification of harmful automotive exhaust components, such as carbon monoxide (CO), unburned hydrocarbons (HCs), and nitrogen oxide (NO<sub>x</sub>) from automotive engines. The catalytic converters are placed under the floor and/or beside the engine, and their devices are installed in exhaust pipes. These catalysts typically comprise (i) platinum group metals (PGMs), i.e., Pt, Pd, and Rh, (ii) oxide supports (Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, etc.) to disperse these precious metal particles at the nanometer scale, and (iii) catalytic promoters. In particular, the PGMs are essential components since they provide catalytically active sites that remove harmful emissions. Recently, owing to the growing need for global environmental protection, exhaust gas regulations have gradually become stricter worldwide. Corresponding to this trend, the demand for automotive catalysts has increased year after year, increasing in the consumption of PGMs. Therefore, the scarcity of PGM resources has inspired us to develop an alternative catalyst to PGMs. Achieving sufficient catalytic activity with a non-PGM catalyst has been considered to be difficult, especially for the NO reduction reaction.

In the process of our research and development, we discovered that a Au-Ni bimetallic cluster catalyst exhibited high NO purification activity matching that of PGMs in the NO-CO reaction under simulated automobile exhaust conditions. Bimetallic clusters have been identified as one possibility for non-PGM catalysts. Although several studies have been carried out on the use of Au-Ni bimetallic system in some applications, to the authors' knowledge, there have been few studies on its use for automobile exhaust purification reactions.

In this study, we attempted to clarify the catalytic mechanism of the high NO-CO activity of the Au-Ni bimetallic clusters utilizing the *operando* XAFS (X-ray Absorption Fine Structure) method [1]. *Operando* XAFS analysis can provide the chemical states and molecular structures of catalysts in their working states as well as their catalytic activity. This methodology has been well established along with intense synchrotron radiation sources. We have constructed a high-speed and high-sensitivity *operando* XAFS system for catalysis at the Toyota beamline BL33XU, SPRING-8 [2]. The gas transfer unit is made up of three independent gas supply lines to simulate actual auto exhausts, whose compositions vary instantaneously with the engine operation. Its mass analyzer can analyze five gas species at intervals of 50 ms. The *operando* cell was specially designed for the transient XAFS method while minimizing the dead

volume. This *operando* system can enable the real-time visualization of the catalytic working state.

In this work, we prepared Au, Ni, and Au-Ni metal nanoparticles via the liquid-phase reduction method. The loadings of Au and Ni in the Au-Ni cluster/SiO<sub>2</sub> were 1.92 wt% and 0.61 wt%, respectively. Rh/SiO<sub>2</sub> as a reference PGM-containing catalyst was also prepared by the conventional wet impregnation process. Figure 1 shows the NO purification conversion as a function of temperature for the NO-CO reaction over the catalysts studied herein. The conversion of NO on both the monometallic Au cluster/SiO<sub>2</sub> and the Ni cluster/SiO<sub>2</sub> was less than 10% up to 600°C. These results indicate that Au or Ni alone on a SiO<sub>2</sub> support has only negligible activity for the NO-CO reaction. In contrast, the Au-Ni cluster/SiO<sub>2</sub> shows significantly higher NO reduction activity over the entire temperature range than both monometallic cluster samples. Furthermore, NO conversion over the Au-Ni cluster/SiO<sub>2</sub> began at less than 300°C, which is comparable to the light-off temperature of the Rh/SiO<sub>2</sub> catalyst. It is assumed that the high NO purification activity over the Au-Ni cluster/SiO<sub>2</sub> is caused by the Au-promoted reduction of NiO to metallic Ni. This hypothesis can be probed by time-resolved *operando* XAFS, which can show the correlation between catalytic activity and the oxidation state of an active site via analysis of the X-ray Absorption Near Edge (XANES) region under actual reaction conditions. Figure 2 shows the energy shift ( $\Delta E$ ) of the Ni *K*-edge under the *operando* NO-CO conditions, along with serial time-resolved Ni *K*-edge XANES spectra of the Au-Ni cluster/SiO<sub>2</sub> and the Ni cluster/SiO<sub>2</sub>. The  $\Delta E$  values of the Ni *K*-edge for both samples at low temperatures were almost equivalent to that for

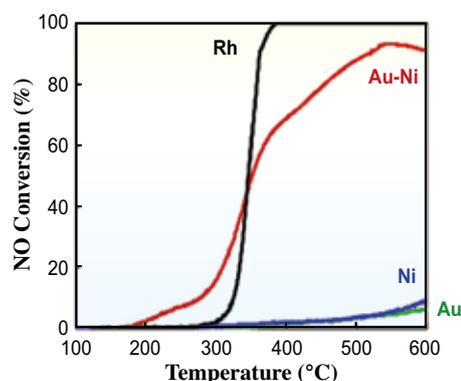


Fig. 1. NO conversion as a function of the reaction temperature under a NO-CO feed: 3000 ppm NO, 4000 ppm CO after pretreatment in 10% O<sub>2</sub> (N<sub>2</sub> bal.) at 350°C.

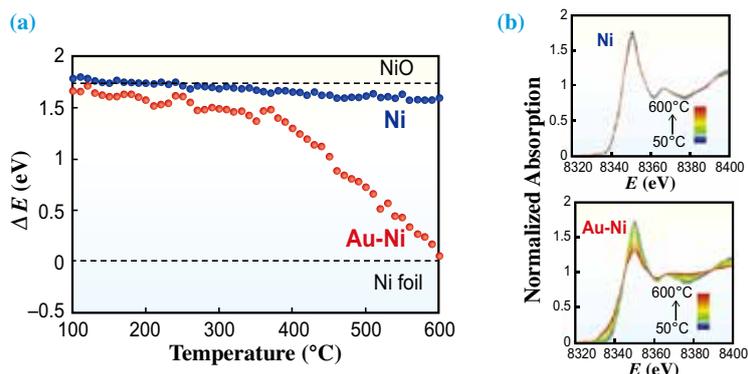


Fig. 2. (a) Energy difference ( $\Delta E$ ) calculated by subtracting the Ni *K*-edge absorption energy for Ni foil (base) from that for the Au-Ni cluster/SiO<sub>2</sub> (red) and the Ni cluster/SiO<sub>2</sub> (blue) under a NO-CO feed. (b) Normalized XANES spectra of the Ni *K*-edge during the NO-CO reaction.

NiO powder, indicating that the initial oxidation state was Ni<sup>2+</sup>. The  $\Delta E$  value of the Ni cluster/SiO<sub>2</sub> slightly decreased with increasing temperature. Moreover, it should be noted that the Au-Ni cluster/SiO<sub>2</sub> catalyst exhibited a more significant shift towards metallic Ni. These results suggest that Ni<sup>2+</sup> is more easily reduced to a metallic Ni active site for NO reduction in the Au-Ni cluster/SiO<sub>2</sub> than the monometallic Ni cluster/SiO<sub>2</sub>. To investigate the correlation between the structure of the supported Au-Ni clusters and the NO purification activity under a NO-CO feed, Au *L*<sub>3</sub>-edge XAFS analysis was also performed on the Au-Ni cluster/SiO<sub>2</sub>. As shown in Fig. 3, the XANES spectrum of the Au cluster/SiO<sub>2</sub> under NO-CO at 600°C hardly changed. On the other hand, the peak height of the white line at 11,929 eV for the Au-Ni cluster/SiO<sub>2</sub> significantly increased. As

already reported, the increase in the Au white line intensity at 11,929 eV reflects the formation of the Au-Ni alloy species. It is clear that the increase in the Au white line intensity of the Au-Ni/SiO<sub>2</sub> is due to the formation of the Au-Ni alloy in the NO-CO reaction.

In conclusion, the Au-Ni cluster/SiO<sub>2</sub> exhibited the same level of NO purification activity as the Rh/SiO<sub>2</sub>, whereas the Au cluster/SiO<sub>2</sub> and the Ni cluster/SiO<sub>2</sub> showed very low activity. *Operando* XAFS analysis revealed that the reduction of NiO in the Au-Ni cluster/SiO<sub>2</sub> was significantly promoted under the NO-CO reaction despite the initial separation of NiO and Au particles. It is suggested that the easy formation of Au-Ni alloy species shows a synergistic effect of the metallic Ni as a dissociative adsorption site for NO and the Au as an oxygen release site in the NO purification reaction.

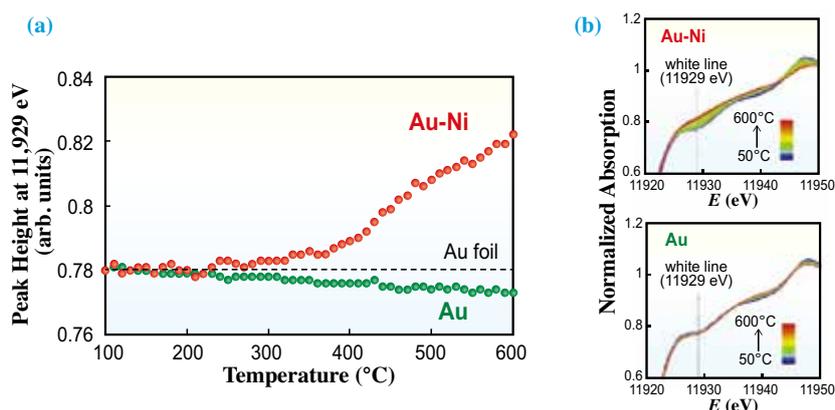


Fig. 3. (a) Peak height at 11,929 eV for the Au *L*<sub>3</sub>-edge XANES spectrum under a NO-CO feed. (b) Normalized XANES spectra of the Au *L*<sub>3</sub>-edge during the NO-CO reaction.

Yasutaka Nagai<sup>a,\*</sup> and Shogo Shirakawa<sup>b</sup>

<sup>a</sup>TOYOTA Central R&D Labs., Inc.

<sup>b</sup>TOYOTA Motor Corporation

Email: e1062@mosk.tytlabs.co.jp

## Reference

- [1] S. Shirakawa, M. Osaki, Y. Nagai, Y.F. Nishimura, K. Dohmae, S. Matsumoto, H. Hirata: *Catalysis Today* **281** (2017) 429.
- [2] Y. Nagai: *SPring-8 Research Frontiers* (2013) 110.