Dynamic observations of surface behavior of Rh nanoparticles under reaction conditions by environmental transmission electron microscopy

Hiromochi Tanaka[a,*], **Masaoki Iwasaki**[b], **Shigeo Arai**[c], **Hirohito Hirata**[a], **Shunsuke Muto**[c]
[a]*Toyota Motor Corporation,1, Toyota-cho, Toyota, Aichi ,471-8572, Japan*
[b]*Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi, 480-1192, Japan*
[c]*Nagoya University, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan*
**Corresponding author: +81-565-72-0502, hiromochi_tanaka@mail.toyota.co.jp*

Abstract: The structural changes of Rh nanoparticles supported on ZrO_2 substrate were observed under reaction conditions using environmental transmission electron microscopy. With increasing temperature in a 1 vol% NO gas atmosphere (diluted by Ne) at a total pressure of 50 Pa, rhodium oxide layers as thick as a few nm were formed on the particle surface below 200 °C while the layer thickness drastically shrank eventually with a metastable oxide mono-layer retained above 300 °C. These results should help establishing a new model for NO dissociation on a Rh nanoparticle surface.

Keywords: Environmental Transmission Electron Microscopy, NO_x dissociation, Rhodium nanoparticle

1. Introduction

The call for global environment protection has driven the continued demands for development of higher-performance catalysts for purification of nitrogen oxides (NO_x) from automobile exhaust gas. To this end, it is essential to clarify the catalytic reaction mechanism to promote research and development of better catalyst materials. Supported rhodium catalysts are typically applied to NO_x purification [1]. In the present study, we observed the atomic scale structural changes of Rh nanoparticles supported on zirconia substrates (Rh/ZrO_2 model catalyst) under model reaction conditions using an ultra-high voltage environmental transmission electron microscope (E-UHV-TEM) to understand how Rh particles behave in catalytically active states.

2. Experimental

The model catalyst was prepared by the evaporation-to-dryness method of a mixture of a Rh colloidal solution and ZrO_2 powder while stirring. The loading of Rh amounted to 2 wt.%, where the diameter of the Rh particles ranged over 3-20 nm. E-UHV-TEM observations were performed by a JEOL JEM-1000K RS [2] of Nagoya University, operated at 1 MV. Figure 1(a) shows how it looks. To simulate an automotive environment, a specially designed environmental cell and a specimen heating holder were implemented, as shown in Figure 1(b). We observed the surface structural change of Rh particles with atomic resolution, gradually heating to 700 °C in a 1 vol% NO gas atmosphere (total pressure of 50 or 95 Pa). Prior to observation, the Rh particles were reduced to the metallic state at 200 °C in vacuum (10^{-3} Pa).

3. Results and discussion

Figures 2(a) and (b) show TEM images of the same Rh particle in NO (50 Pa) at 200 °C and 300 °C, respectively. Rh oxide layers appeared immediately after NO injection and grew to the thickness of 2-3 nm at 200 °C. At 300 °C, the thickness of the layers shrank, though the Rh oxide mono-layers (~0.3 nm thick) still covered the surface. It is noted that the edges of the mono-layers repeatedly grew and shrank with time as shown in Figure 3. This dynamic motion suggested the local steady state of redox reactions near the ridges of the surface oxide mono-layers. At the pressure of 95 Pa, on the other hand, thicker oxide layers remained even at 700 °C. These results will help establishing a new model for NO dissociation on a surface of Rh nanoparticle, depending on the gas pressure.

4. Conclusions

The metastable behavior of the Rh particle surface in the presence of NO gas (50 Pa) was observed for the first time using E-UHV-TEM. Although it has been conventionally assumed that NO_x decomposition occurs on the pure *metallic* Rh surface, our results suggest that at lower gas pressures the NO decomposition reaction proceeds via a surface redox process likely triggered at the ridges of Rh *oxide* mono-layers.

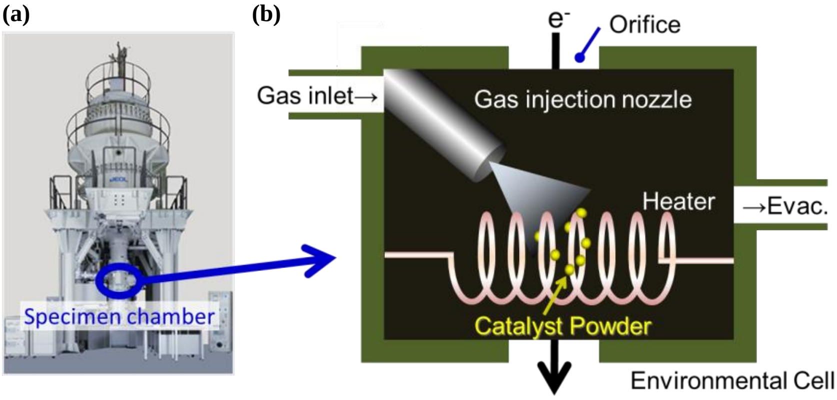

Figure 1. Schematic illustrations of the environmental ultra-high voltage transmission electron microscope (E-UHV-TEM; JEOL JEM-1000K RS). (a) Outer view of the instrument. (b) Schematic of the environmental control cell. The catalyst powder is heated and reactive gas is injected.

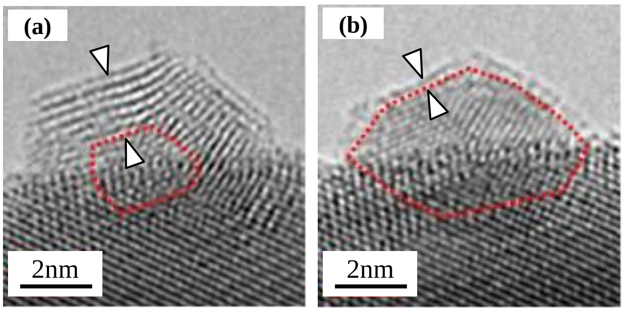

Figure 2. TEM images of the same Rh particle in NO gas (50 Pa). (a) Thick Rh oxide layer appeared at 200 °C. (b) Rh oxide mono-layers remained even above 300 °C.

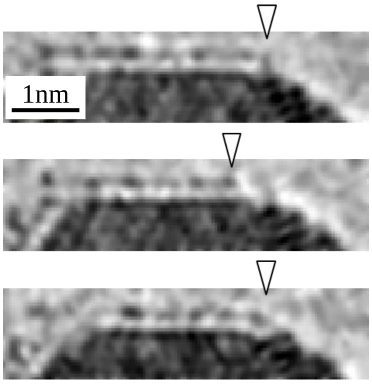

Figure 3. The dynamic motion of the oxide mono-layer. The arrows indicate the ridge of the mono-layer. The time interval between the images was approximately 33 ms (video frame rate: 30 frames per second).

A part of this work was supported by Nagoya University microstructural characterization platform as a program of "Nanotechnology Platform" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

1. H. Shinjoh, T. Tanabe, K. Yokota and M. Sugiura, *Topics in Catalysis* 30-31 (2004) 319.
2. N. Tanaka, J. Usukura, M. Kusunoki, Y. Saito, K. Sasaki, T. Tanji, S. Muto and S. Arai, *Microscopy* 62 (2013) 205.