Structural probe of novel fcc Ru nanoparticles with enhanced CO oxidation activity

Metallic ruthenium (Ru) adopts a hexagonal close-packed (hcp) structure at all temperatures, and novel face-centered cubic (fcc) Ru nanoparticles (NPs) have attracted much attention recently as a catalyst for CO oxidation because of their higher catalytic activity than conventional hcp-type Ru NPs when the diameter is larger than 3 nm [1]. CO oxidation catalysts are required for the purification of automobile exhaust gases and for the prevention of CO poisoning in electrolyte fuel-cell systems.

The atomic-scale structures of Ru NPs have been determined by high-energy X-ray diffraction (HEXRD) coupled with Rietveld analysis, pair distribution function (PDF), and reverse Monte Carlo (RMC) modeling methods. Here we demonstrated the three-dimensional (3D) atomic arrangements of Ru metal NPs, which deviates significantly from their corresponding bulk crystalline structures [2,3].

The surface structures of the Ru metal NPs are involved in the back-donation of electrons from the metal surface to the π antibonding orbital of CO. Hence, the CO interacts with a metal atom with a higher coordination number, where electrons are more delocalized. In this study, we present the correlation between the mean and atomic-scale structure and the catalytic activity of Ru NPs as a function of the crystal structure and particle size. The origin of the CO oxidation activity of Ru NPs is discussed on the basis of Rietveld analysis as well as the short to intermediate-range structures in terms of the coordination-number and bond-angle distributions.

HEXRD measurements were performed using a two-axis diffractometer installed at SPring-8 **BL04B2**. The incident X-ray beam energy was 61.46 keV, which corresponds to a wavelength of 0.02017 nm. The synthesized fcc- and hcp-types Ru NPs were loaded into a capillary column with 1.0 mm inner diameter and measured at room temperature. Fine powders of bulk 99.9% Ru and poly(*N*-vinyl-2-pyrrolidone) (PVP) were used as the reference materials. HEXRD intensity data were corrected for the background, polarization, and absorption and were then normalized by the structure factor and Fourier transformed using the analysis software provided in beamline BL04B2. HEXRD patterns for the fcc- and hcp-types Ru NPs were analyzed using the Rietveld refinement method with a pseudo-Voigt function. The RMC modelings for 3D structures of Ru NPs were guided by the experimental structure factor. The RMC modelings were carried out using the RMC_POT software set up for the case of nonperiodic boundary conditions.

From the Rietveld refinement analysis for the mean structure of Ru NPs with a long-range order, we investigated the relationship between the *B* factor, which appears in the Debye-Waller factor related to the r.m.s. amplitude of the atomic vibration, and the particle size (Fig. 1). The *B* factor can be regarded as an indication of the relative thermal vibrational motion, which is related to the static atomic displacement. Atoms with a small *B* factor belong to a part of the structure that is well ordered. In contrast, atoms with a large *B* factor generally belong to a part of the structure that is very flexible or is more reactive to the ambient environment. By comparing fcc-type Ru NPs with hcp-type Ru NPs of a similar particle size, we found that the *B* factor of the fcc-type Ru NPs is considerably larger than that of the hcp-type Ru NPs. As a result, we suggest that the higher catalytic activity of the fcc-type Ru NPs is due to the larger lattice distortion and *B* factor.

To understand the catalytic properties of the fcc- and hcp-types Ru NP catalysts, atomic-scale structure information was obtained from HEXRD data coupled with PDF analysis and RMC modeling methods. We observed broader peak profiles in all Ru NP PDFs than in the bulk Ru, which strongly indicates that the structures of the NPs are disordered. In addition, the PDF data imply that the positions of the coordination shells are distorted owing to the size and structure of the Ru NPs.

Figure 2 shows the behavior of the calculated order parameters S_{fcc} and S_{hcp}, of Ru NPs and the bulk, evaluated by the pair correlation function and

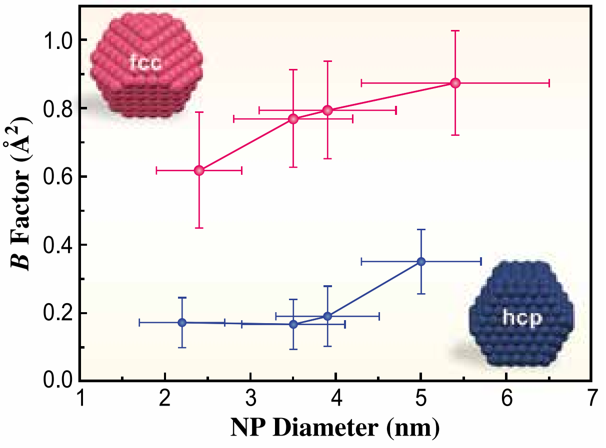

Fig. 1. Dependence of *B* factor on particle diameter.

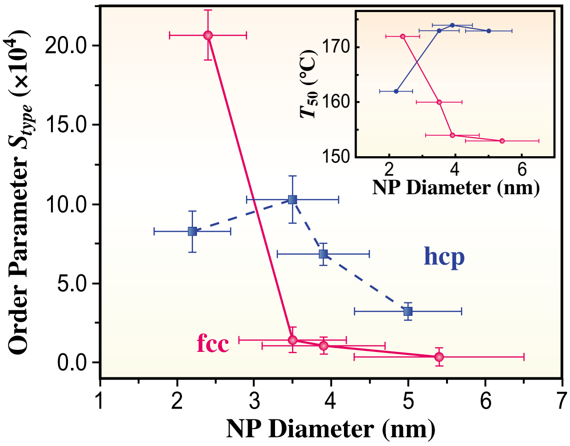

Fig. 2. NP-diameter dependence of the order parameters. The inset shows the temperature dependence for 50% conversion of CO to CO_2 (T_{50}) *vs*. particle size [1].

bond angle distribution obtained by RMC models as a function of the NP diameter. Upon comparing the fcc-type Ru NPs with the hcp-type Ru NPs, we observed that the structural parameter for the fcc-type NPs decreased with increasing NP diameter. Conversely, the order parameter for the hcp-type Ru NPs was larger than that for the fcc-type NPs for a diameter above 3 nm and above which confirmed that the catalytic activity (such as CO oxidation) was reduced as a result of the dense close-packing atomic arrangement of the larger hcp-type NPs.

We also evaluated the first-shell coordination number (CN) by counting the number of Ru atoms in a spherical shell with a radius between 0.23 and 0.32 nm around each central atom. Figure 3 shows 3D RMC models of the fcc-type Ru NPs with different CNs in highlighted colors. The 5.4 nm fcc-type Ru NP model shows a higher probability of the existence of step-edge (CN = 10) and sawtooth (CN = 11) sites as well as lower probability of containing close-packed (CN = 9) and square-planar (CN = 8) sites compared with the 5.0 nm hcp-type Ru NP model. According to the surface topologies observed through CN analysis, the newly discovered fcc-type Ru NPs are more reactive than the conventional hcp-type Ru NPs.

HEXRD coupled with the Rietveld refinement analysis, PDF analysis, and RMC modeling methods are appropriate techniques for investigating the atomic-scale structure of NPs that are much smaller than the X-ray spatial coherence length. In this study, we found that the relative thermal vibration acquired from the *B* factor of the fcc-type Ru NPs is considerably larger than that of the hcp Ru NPs. Here we demonstrated highly disordered NP structures on the basis of atomic PDF analysis and 3D NP models constructed by the RMC modeling method. In particular, the enhanced catalytic activity of the novel fcc-type Ru NPs is consistent with observed order parameters and coordination number analysis based on the RMC NP models. The advanced structural characterization technique that we have used here is expected to be a promising and helpful tool for characterizing nanostructure materials.

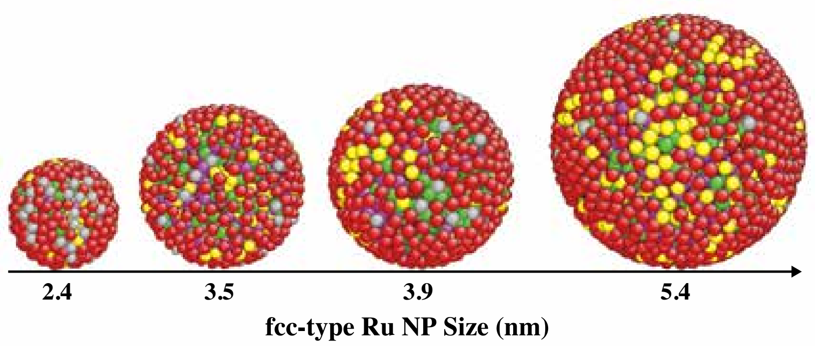

Fig. 3. RMC models of fcc-type Ru NPs with different coordination numbers in highlighted colors (gray: ≤ 4, red: 5 to 7, yellow: 8, green: 9, magenta: 10, brown: 11, and purple: ≥12).

Osami Sakata[a,b,*], Rosantha Kumara[a] and Chulho Song[a]

[a] Synchrotron X-ray Station at SPring-8,
National Institute for Materials Science (NIMS)
[b] Department of Materials Science and Engineering,
Tokyo Institute of Technology

*Email: SAKATA.Osami@nims.go.jp

References

[1] K. Kusada *et al.*: J. Am. Chem. Soc. **135** (2013) 5493.
[2] *C.H. Song, O. Sakata, L.S.R. Kumara, S. Kohara, A. Yang, K. Kusada, H. Kobayashi and H. Kitagawa: Sci. Rep.* ***6*** *(2016) 31400.*
[3] *L.S.R. Kumara, O. Sakata, S. Kohara, A. Yang, C.H. Song, K. Kusada, H. Kobayashi and H. Kitagawa: Phys. Chem. Chem. Phys.* ***18*** *(2016) 30622.*