Supporting Information

Discovery of Face-Centered-Cubic Ruthenium Nanoparticles:

Facile Size-Controlled Synthesis Using the Chemical Reduction Method

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1. Experimental details

Characterization:

Transmission Electron Microscopy (TEM) images: TEM images were captured using a Hitachi HT7700 operated at 100 kV accelerating voltage.

High-resolution TEM images: High-resolution TEM images were captured using a JEOL ARM 200F STEM instrument operated at 200 kV accelerating voltage.

X-ray diffraction (XRD) measurements: The crystal structure of Ru nanoparticles was investigated by powder XRD analysis using a Bruker D8 Advance diffractometer (Cu K_{α} radiation).

In situ XRD measurements: The thermal stability of fcc Ru nanoparticles was investigated by in situ powder XRD analysis measured at the BL02B2 beamline, SPring-8. The XRD patterns of the samples sealed in a glass capillary were measured in situ with a wavelength of 0.578375(1) Å under vacuum in the temperature range between 303 K and 723 K.

Catalyst preparation: All the synthesized Ru nanoparticles were supported on γ -Al₂O₃ catalysts by wet impregnation. Each nanoparticle (equivalent to 1 wt % of γ -Al₂O₃) was ultrasonically dispersed in purified water. The γ -Al₂O₃ support has been precalcined at 1073 K for 5 h. The precalcined γ -Al₂O₃ was added into each nanoparticle solution, and then the suspended solutions were stirred for 12 h. After stirring, the suspended solutions were heated to 60 °C and dried under vacuum. The resulting powders were kept at 120 °C for 8 h for complete water removal. The obtained catalyst powders were pressed into pellets at 1.2 MPa for 5 min. The pellets were crushed and sieved to obtain grains with diameters between 180 and 250 μ m.

Catalytic characterization: For the investigation of catalytic activity in CO oxidation, each supported nanoparticle catalyst (150 mg) was loaded into a tubular quartz reactor (internal diameter, i.d. 7 mm) with quartz wool. A gas mixture of CO/O₂/He (He/CO/O₂: 49/0.5/0.5 ml min⁻¹) was passed over the catalysts at ambient temperature, and the catalysts were then heated to 100 °C. After 15 min, effluent gas was collected, and the reaction products were analyzed by gas chromatography with a thermal conductivity detector (GC-8A, Shimadzu, Japan). The catalysts were heated in increments of 10 °C to the temperature at which CO was consumed completely, and the products were analyzed at each temperature. After the reaction, the reactor was purged with He at the reaction temperature, and the catalysts were then cooled to room temperature.

2. SAED patterns and HRTEM images

Figure S1: The TEM image of sample D (a) and H (c). The selected area electron diffraction (SAED) pattern of sample D (b) and H (d). (e) and (f) are the average rotational intensity profile form a part of SAED pattern (b) and (d), respectively. The calculated kinematical (ideal) intensities are described with bars.

Figure S2. (a) The HRTEM image of the hcp Ru nanoparticle in Figure3 (b). The hcp nanoparticle was viewed in the direction of [100]. (b) The FFT image of a full region in image (a). The pattern is in good agreement with a calculated electron diffraction pattern for the hcp structure from the incident direction of [100]. (c) The atomistic model of the hcp particle in image (a) with {001}, {1-21} and {111} facets. And stacking faults observed in image (a) are not considered. (d) The simulated HRTEM image for the model (c) .The simulation was performed with using conventional multi-slice method.

Figure S3. (a) The same HRTEM image of the five-fold twinned fcc decahedral Ru nanoparticle composing with 5 tetrahedron with 4 {111} faces in Figure3 (a). The decahedral nanoparticle was viewed in [110] direction. (b) The FFT from full region of image (a). The pattern is interpreted as a super imposition of five fcc Ru diffraction pattern in incident electron direction of [110] rotating by 72° . (c) The atomistic model of the decahedral particle in image (a). In this model, the particle has only {111} facets. (d) The simulated image for the model in (c). In the simulated image, contrasts for each atomic column change between black to white depending on particle thickness. The difference between the experimental image (a) and simulated image (d) probably results in a thickness variation of amorphous carbon supporting film which induces phase shift.

3. In situ powder XRD patterns of fcc Ru nanoparticles

Figure S4. The in situ XRD patterns of fcc Ru nanoparticles measured with a wavelength of 0.578375(1) Å under vacuum in the temperature range between 303 K and 723 K.

4. Temperature dependence of the CO conversion of Ru nanoparticles supported on γ -Al₂O₃

Figure S5. The temperature dependence of the CO conversion of Ru nanoparticles supported on γ -Al₂O₃ (blue: fcc Ru, red: hcp Ru).

4. Comparison of the particle size with the crystal size

The crystal sizes calculated from XRD by using the Scherrer equation are rather smaller than those detected by TEM. The difference is considered to be based on the defects and/or the twin structure.

Table S1. The comparison of the particle size with crystal size of prepared samples

Sample	Structure	Particle size (TEM) / nm	Crystal size (XRD) / nm
A	fcc	2.4	1.6
B	fcc	3.5	2.6
C	fcc	3.9	2.7
D	fcc	5.4	2.8
E	hcp	2.2	1.6
F	hcp	3.5	1.8
G	hcp	3.9	1.9
H	hcp	5.0	2.4