Supporting Information

Carbon-supported Pt–Ru nanoparticles prepared in glyoxylate-reduction system promoting precursor-support interaction

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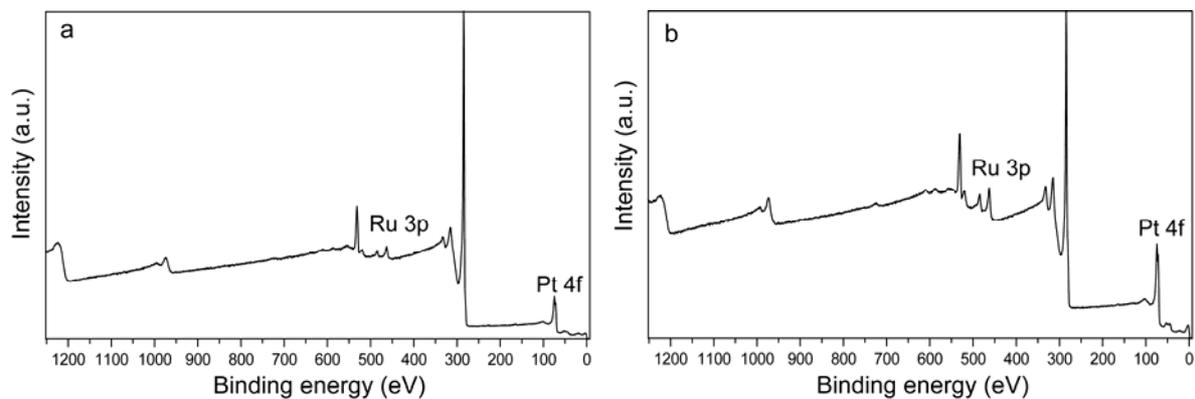[b] Nagano Techno Foundation, 1-18-1 Wakasato, Nagano 380-0928, Japan.

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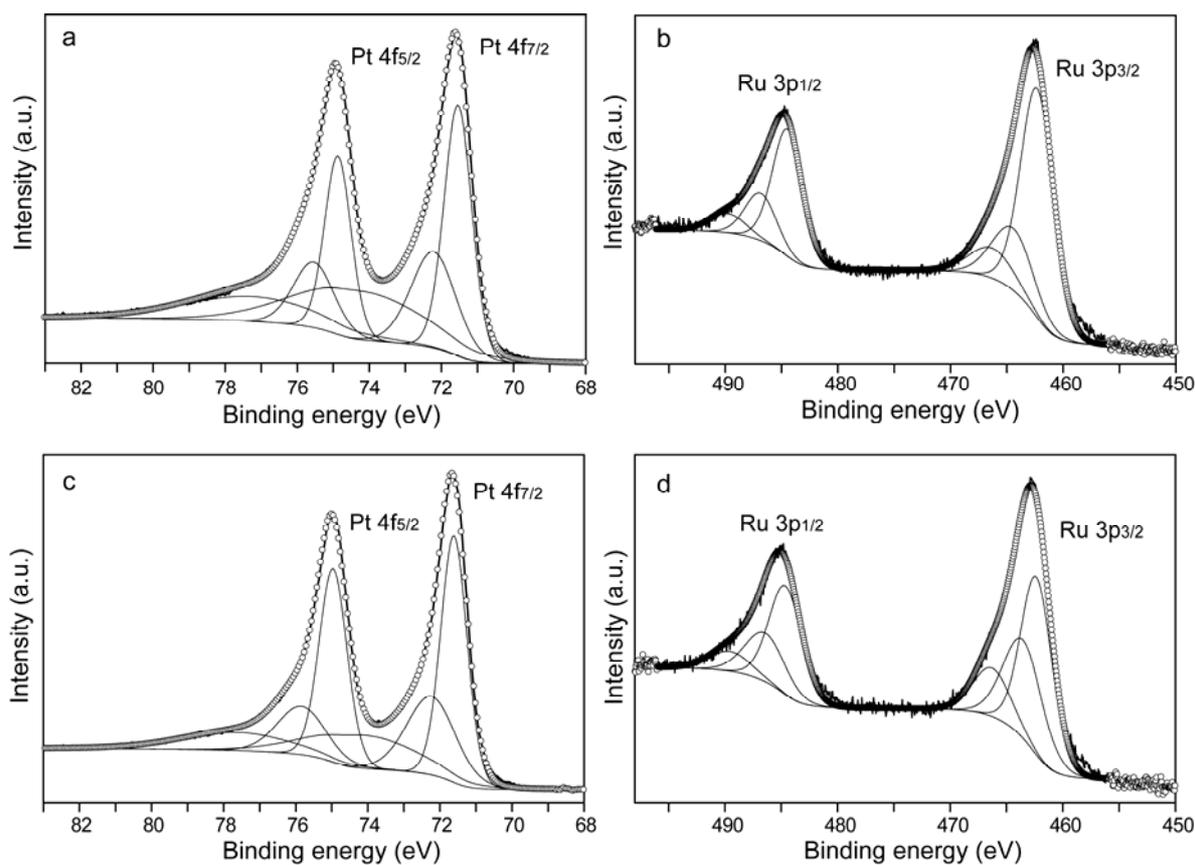
INDEX:

S-1. Supplementary data of XPS analysis

Fig. S1 Survey-scan XPS spectra of the Pt–Ru/C catalysts prepared by glyoxylate reduction. (a) **G20**, (b) **G60**. The survey-scan spectra show no peak of Cl 3p core levels at 198 eV, which indicates no remaining Cl⁻ from the precursor salts.

Fig. S2 XPS core-level spectra for the Pt 4f and Ru 3p regions of the 60-wt.% Pt–Ru catalysts supported on Vulcan XC-72R. (a) Pt 4f and (b) Ru 3p regional spectra of **G60**. (c) Pt 4f and (d) Ru 3p regional spectra of **N60**. Bold line: raw spectra, thin line: component peaks, open circle: the synthetic spectra of the component peaks.

Table S1 Average binding energies (BE) of the component peaks obtained from the Pt 4f and Ru 3p XPS spectra of the Pt–Ru/C catalysts prepared by using glyoxylate reduction and NaBH$_4$ reduction

| Atom	Orbital/spin	BE (eV)				Assignment
		G20	**N20**	**G60**	**N60**	
Pt	4f7/2	71.6±0.1	71.6±0.0	71.5±0.0	71.5±0.1	Pt(0)
	4f5/2	74.9±0.1	75.0±0.0	74.9±0.1	74.9±0.1	
	4f7/2	72.3±0.2	72.3±0.1	72.2±0.1	72.3±0.2	Pt(II)
	4f5/2	75.8±0.3	75.6±0.1	75.6±0.3	75.6±0.2	
	4f7/2	73.9±0.3	74.5±0.3	74.1±0.5	74.5±0.5	Pt(IV)
	4f5/2	77.0±0.6	77.4±0.5	76.9±0.1	77.5±0.2	
Ru	3p3/2	462.2±0.1	462.3±0.1	462.2±0.1	462.3±0.1	Ru(0)
	3p1/2	484.5±0.2	484.5±0.1	484.4±0.1	484.5±0.1	
	3p3/2	464.2±0.3	463.9±0.1	463.9±0.4	463.7±0.2	Ru(IV)
	3p1/2	486.7±0.2	486.6±0.4	486.7±0.2	486.2±0.3	
	3p3/2	466.5±0.7	466.2±0.6	466.2±0.1	466.6±0.3	Ru(IV) (hydrate)
	3p1/2	489.5±0.4	489.7±0.5	489.5±0.3	489.1±0.4	

Population for calculation: four samples in each catalyst

S-2. Supplementary data for the electrochemical characterization of the catalysts

Fig. S3 shows the CV curves obtained in 0.5 mol L^{-1} H_2SO_4 aqueous solutions without methanol. The CV curves were recorded at the 20th sweep in the potential range from −0.15 up to 0.54 V (vs Ag/AgCl) in order to prevent Ru dissolution. All the current data were normalized to current densities (mA mg^{-1}) by the metal amounts loaded to the working electrode. In Pt–Ru electrodes, the CV curve shows no simple potential-dependent distinction of hydrogen adsorption/desorption and double-layer regions due to the overlapping of ruthenium-hydroxide formation/reduction with the hydrogen and double-layer regions.[1] Therefore, the electrochemically active surface area of Pt–Ru catalysts cannot simply be evaluated from the overlapping hydrogen region of about −0.15–0.15 V. For this reason, we avoided estimating the active surface area. The underpotential deposition of atomic hydrogen is a structure-sensitive catalytic process for the lattice planes of Pt crystals.[2] Therefore, hydrogen adsorption/desorption ability would be influenced by the crystal structure of the Pt–Ru nanoparticles. As shown in Table 1 (see Article), however, there is no large difference between the lattice parameters of **G20** and **N20** due to the similar incorporation of Ru into fcc Pt crystals. It is therefore considered that the CV response at the overlapping hydrogen region (−0.15–0.15 V vs Ag/AgCl) would be more influenced by the structural and morphological factors of the nanoparticles and the prominent difference of surface composition, rather than crystallographic factors. The **G20** catalyst showed much higher current densities at the lower potential region of −0.15–0.07 V than at 0.07–0.3 V. As is well known, Ru does not contribute to the development of hydrogen adsorption/desorption peaks.[3] Therefore, the more developing peak at −0.15–0.07 V is attributed to the high Pt(0)/Ru ratio of **G20**. As for **G60**, **N20** and **N60**, the relative proportions of the current densities at 0.07–0.3 V to those at −0.15–0.07 V are larger than that of **G20**. This results from their high Ru/Pt(0) ratios, which increase the formation/reduction of ruthenium hydroxide species. The higher anodic and cathodic current densities for **G20** in the whole potential range reflect the structural and morphological advantages of the Pt–Ru nanoparticles. The high particle dispersion achieved in the **G20** catalyst would increase the exposed active sites, resulting in the increase of the current densities.

References

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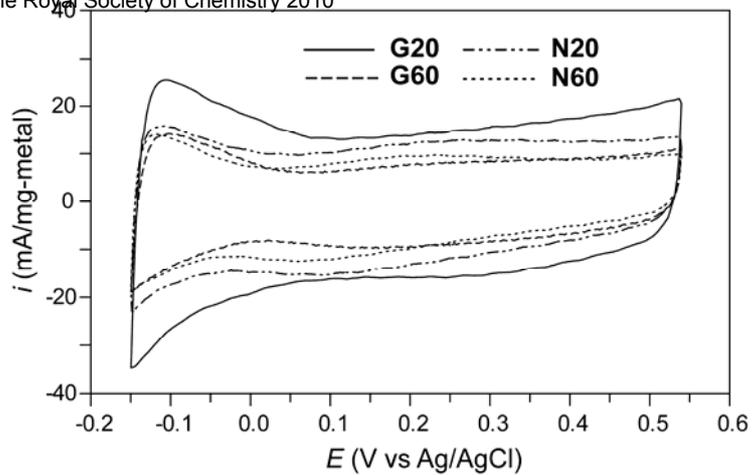
Fig. S3 Cyclic voltammograms obtained in 0.5 mol L^{-1} H$_2$SO$_4$ solutions for the Pt–Ru/C catalysts prepared by glyoxylate reduction and NaBH$_4$ reduction. The data were recorded at room temperature with the sweep rate of 50 mV s^{-1}. All the CV curves show the 20th cycle data in the potential sweep of −0.15–0.54 V vs Ag/AgCl.