Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ru Atom-modified Covalent Triazine Framework as a Robust Electrocatalyst for Selective Alcohol Oxidation in Aqueous Electrolytes

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Contents

Experimental Section

(1) Catalyst synthesis

CTF was prepared by basically the same method as described in our previous report.[1] Briefly, a mixture of $ZnCl_2$ (4 g, Wako), 2,6-dicyanopyridine (400 mg, Sigma-Aldrich) and Ketchen Black EC600JD (400 mg, Lion Corp.) was vacuum-sealed in a Pyrex glass tube and then heated at 400 °C for 21 h. The resulting black powder was washed with ultra-pure water (UPW), tetrahydrofuran (Wako) and 1 M HCl (Wako), and was then modified with Ru atoms by stirring for 4 h at 100 °C in 0.92 mM $RuCl_3 \cdot nH_2O$ ethanol solution. The resulting Ru-CTF catalyst was washed with UPW to remove unbound Ru atoms. Carbon-supported RuO_2[2] and $Ru(tptz)Cl_3$[3] (tptz=2,4,6-Tris(2-pyridyl)-s-triazine) were synthesized as reference catalysts following reported methods.

(2) Electrochemical characterizations

All electrochemical experiments were performed using a three-electrode system at room temperature. A titanium wire and Ag/AgCl/KCl (sat.) were used as the counter and reference electrodes, respectively. All potentials were calibrated with respect to a reversible hydrogen electrode (RHE). All solutions were deaerated by purging with argon prior to performing measurements. OER activities were evaluated in a 0.1 M $HClO_4$ electrolyte solution (pH 1), and alcohol oxidation activities were evaluated by adding benzyl alcohol (BnOH) to a final concentration of 14 mM. For the quantitative analysis of OER, ^{18}O-labeled water ($H_2{}^{18}O$; Taiyo Nippon Sanso Corp.) was added to a final concentration of 1% to reduce the effect of oxygen contamination from the air. Catalytic ink was prepared by dispersing 1.9 mg Ru-CTF in 250 μL ethanol and 0.25 μL Nafion solution (5 wt %; Sigma-Aldrich) using a homogenizer and was then added dropwise onto a glassy carbon electrode. RuO_2 and $Ru(tptz)Cl_3$ were loaded on the electrode in the same manner by dispersing 0.55 mg RuO_2 and 1 mg $Ru(tptz)Cl_3$ with 7.6 mg Ketjen Black in 500 μL ethanol and 0.5 μL Nafion solution, respectively. The weight of Ru in the loaded catalysts was controlled to be ~0.05 $\mu g/cm^2$. A double-chamber electrochemical cell, in which the two chambers were separated by a Nafion membrane, was used for long-term electrolysis to estimate faradaic efficiencies (FEs). Reaction products in the gas and liquid phases after long-term electrolysis were quantitatively analyzed by gas chromatography mass spectrometry (GC−MS; GCMS-QP2010 Plus, Shimadzu, Japan) and liquid chromatography (LC-UV; ELITE LaChrom, L-2455, L-2130, Hitachi, Japan), respectively.

(3) Physical characterizations

X-ray absorption fine structure (XAFS) measurements were conducted by a transmission method using the hard X-ray beam line BL01B01 of SPring-8, Japan and transmitted X-rays were detected using a double-crystal Si (111) monochromator. X-ray photoelectron spectra (Axis Ultra, Kratos

Analytical Co.) were measured with monochromatic Al Kα X-rays of hν = 1486.6 eV. Thermogravimetric analyses (TGA-50, Shimadzu) were performed to evaluate the thermal stabilities of the prepared catalysts.

Supporting Figures

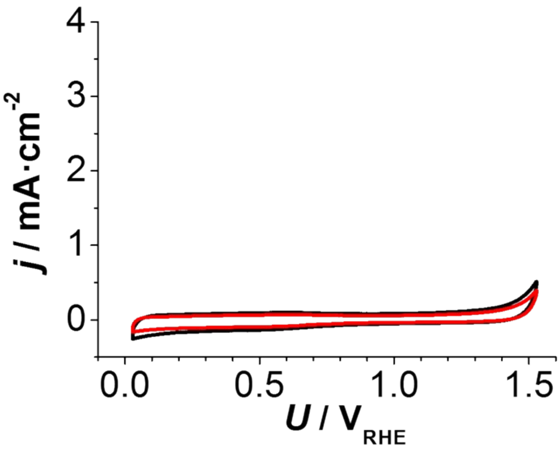

Figure S1. j vs U curves for CTF in 0.1 M $HClO_4$ solution (pH 1) supplemented with BnOH (red line) and without BnOH (black line). Scan rate, 10 mV s^{-1}. Rotational speed, 1500 rpm.

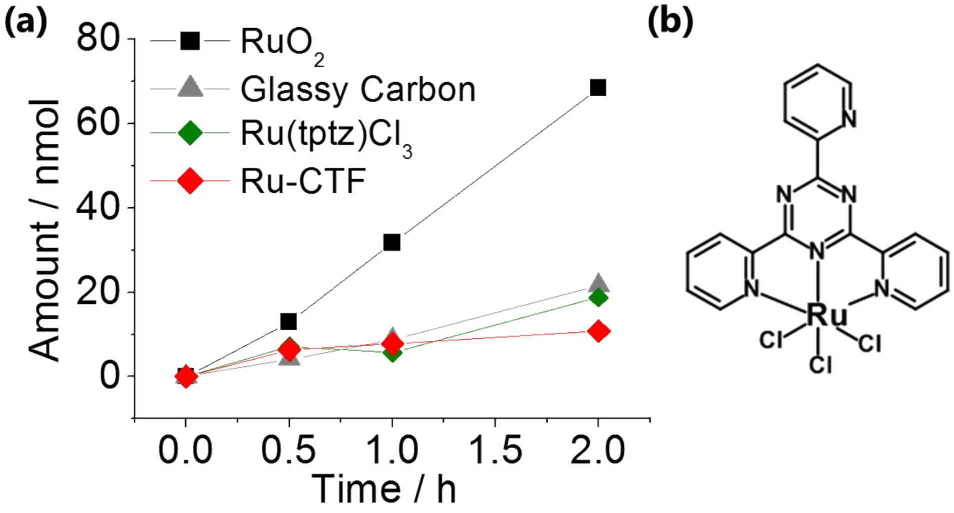

Figure S2. (a) Time course of evolved $^{16}O^{18}O$ by Ru-CTF (red line), RuO_2 (black line), Ru(tptz)Cl_3 (green line) and glassy carbon (grey line). Conditions: 0.1 M $HClO_4$ (pH 1), 1% $H_2{}^{18}O$, and 1.5 V. (b) Structure of Ru(tptz)Cl_3.

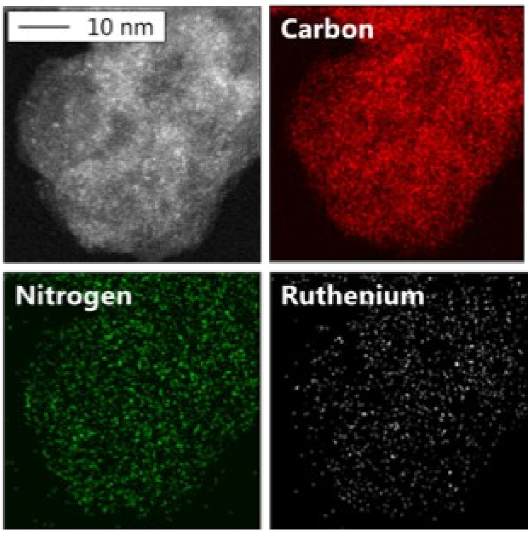

Figure S3. HR-TEM image of Ru-CTF and the corresponding EDX mappings for C, N, and Ru atoms. Scale bar =10 nm.

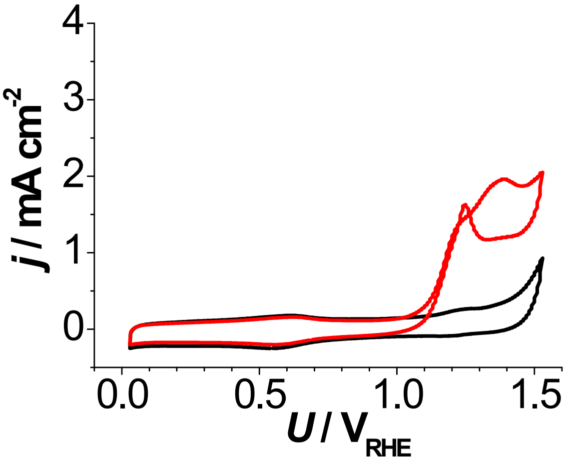

Figure S4. *j* vs *U* curves for Ru(tptz)Cl_3 in 0.1 M $HClO_4$ solution (pH 1) supplemented with BnOH (red line) and without BnOH (black line). Scan rate, 10 mV s^{-1}. Rotational speed, 1500 rpm.

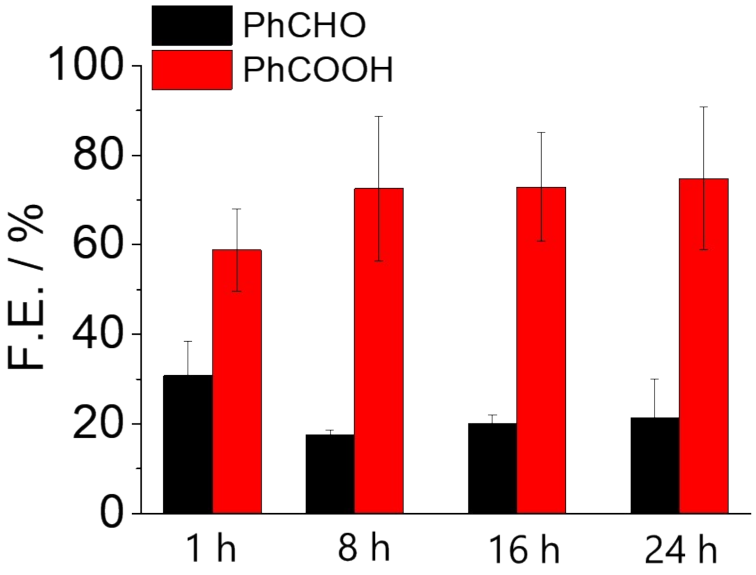

Figure S5. Faradaic efficiencies of PhCHO and PhCOOH with Ru-CTF for each electrolysis period (1 h, 8 h, 16 h and 24h).

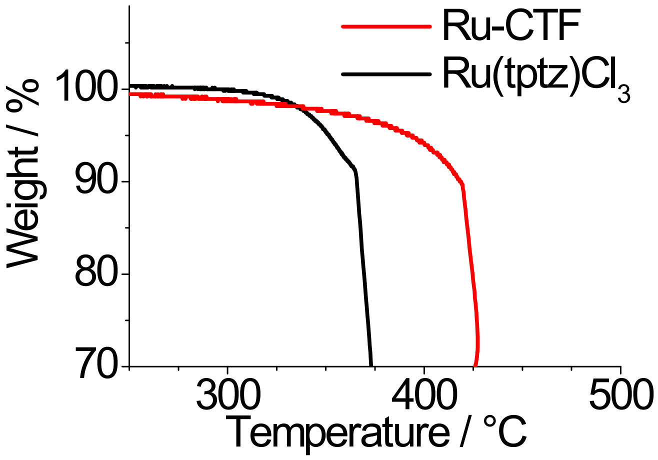

Figure S6. TGA under air for Ru-CTF (red, without carbon particles) and Ru(tptz)Cl_3 (black).

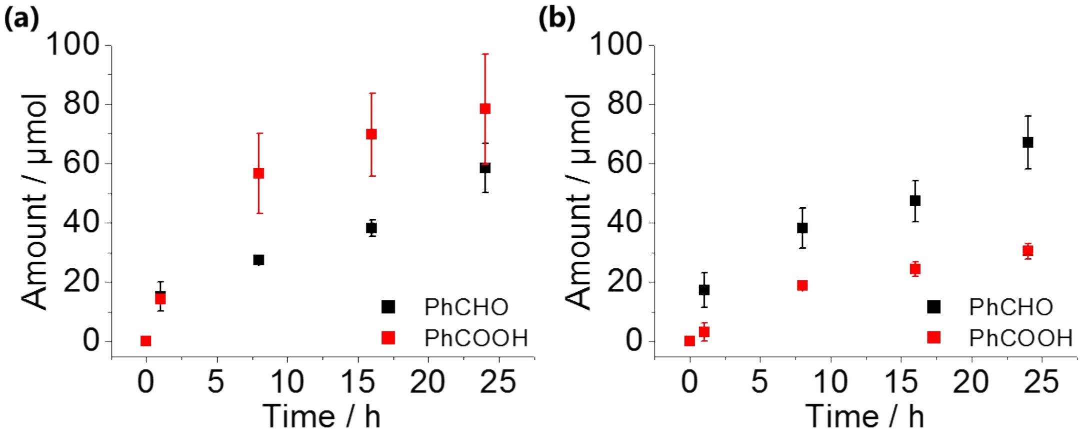

Figure S7. Time course of the PhCHO (black) and PhCOOH (red) generation during the long-term electrolysis with (a) Ru-CTF and (b) Ru(tptz)Cl$_3$.

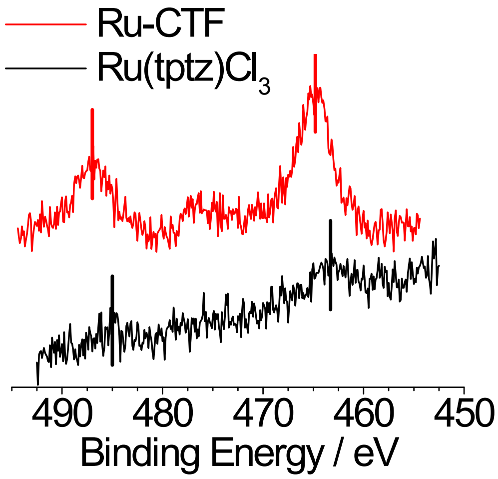

Figure S8. Ru-3p XPS spectra for Ru-CTF (red) and Ru(tptz)Cl_3 (black).

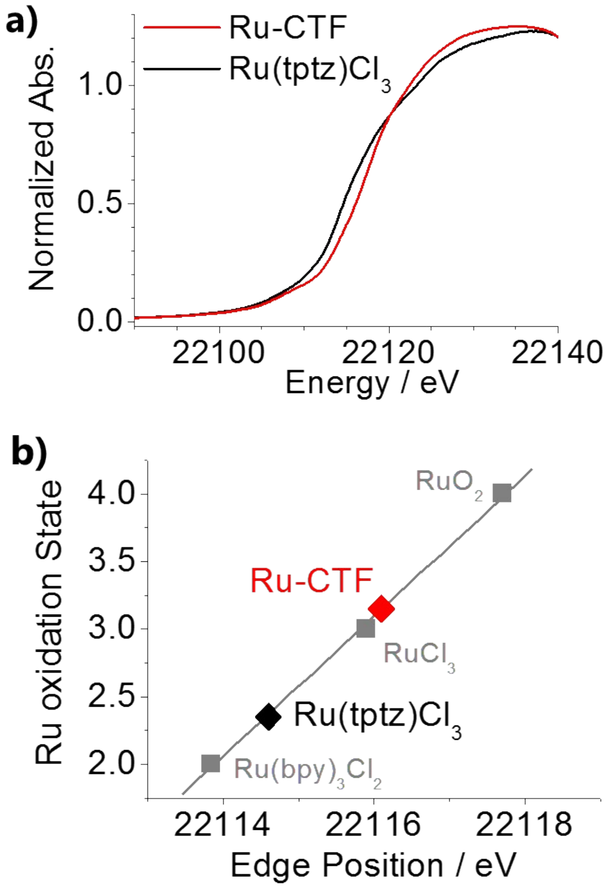

Figure S9. (a) Normalized Ru K-edge XANES spectra of Ru-CTF (red) and Ru(tptz)Cl$_3$ (black). (b) Plot of the edge position (defined as the energy at which absorption = 0.5[4]) as a function of oxidation state with a linear fit of reference compounds. The plot was used to estimate the Ru oxidation state of Ru-CTF (red) and Ru(tptz)Cl$_3$ (black).

[1] K. Kamiya, R. Kamai, K. Hashimoto, S. Nakanishi, *Nat. Commun.* **2014**, *5*, 1–6.

[2] J. Cheng, H. Zhang, H. Ma, H. Zhong, Y. Zou, *Electrochim. Acta* **2010**, *55*, 1855–1861.

[3] M. I. J. Polson, E. A. Medlycott, G. S. Hanan, L. Mikelsons, N. J. Taylor, M. Watanabe, Y. Tanaka, F. Loiseau, R. Passalacqua, S. Campagna, *Chem. - A Eur. J.* **2004**, *10*, 3640–3648.

[4] C. I. Hiley, M. R. Lees, J. M. Fisher, D. Thompsett, S. Agrestini, R. I. Smith, R. I. Walton, *Angew. Chemie - Int. Ed.* **2014**, *53*, 4423–4427.