Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Surface Modification of Pt Nanoparticles with Another Metal Boosting Alkaline Hydrogen Oxidation Reaction

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Experimental

Materials

Pt/C (TEC10E50E, Pt loading: 46.7 wt%) and Pt-Ru/C (TEC61E54, metal loading (Pt+Ru): 52.6 wt%, Pt/Ru mole ratio: 0.67) were purchased from Tanaka Kikinzoku Kogyo. The other chemicals were obtained from Kishida Chemical Co., Ltd.

Catalyst preparation

Various metal-modified Pt/C samples were prepared by conventional impregnation. Commercial Pt/C (200 mg) and 0.040 mmol metal-modifying precursor were dissolved in a mixed solvent comprising 50 mL each of pure water and isopropanol. The solvent was evaporated, and the residue was dried at 353 K for 10 hours. The resulting black powder was heated at 573 K under H_2 flow at 100 mL min^{-1} for 30 min. The modifying metal loading was adjusted to 7.7 at%$_{\mathrm{metal}}$. The precursors used in this study are as follows: $(NH_4)_2[TiO(C_2O_4)_2]\cdot nH_2O$, NH_4VO_3, $Cr(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$, $NH_4[NbO(C_2O_4)2H_2O]\cdot nH_2O$, $(NH_4)6Mo_7O_{24}\cdot 4H_2O$, $Ru(NO_3)_3$, $Rh(NO_3)_3$, $Pd(NO_3)_2$, $AgNO_3$.

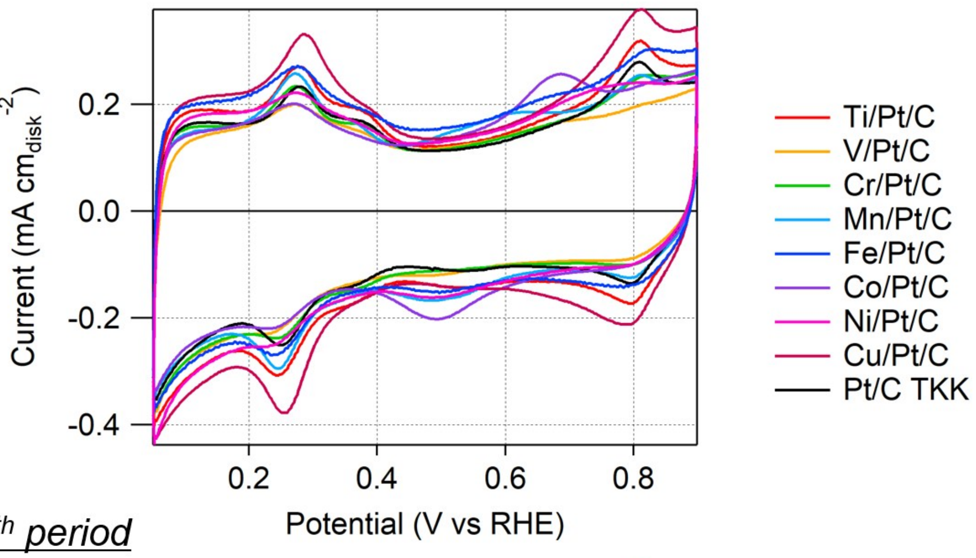
Physical Characterization

Scanning transmission electron microscopy (STEM) and EDS mapping were conducted on a JEM-2100F (JEOL) instrument operated at 200 kV. X-ray diffraction was performed using an FR-E microfocus high-intensity X-ray generator and a Rigaku R-AXIS-VII diffractometer. A 0.5 mm pinhole was used to collimate the X-ray beam of Cu-Kα radiation.

Electrochemical measurement

Electrochemical measurements were conducted on a rotating disk electrode (RDE) setup with a potentiostat (HZ-5000, Hokuto Denko Corp.). The catalyst ink was placed on a polished disk electrode (HR2-D1-GC-5, 5 mm in diameter, 0.196 cm^2) at 10 μg$_{\mathrm{metal}}$ cm$_{\mathrm{disk}}^{-2}$. The HOR was performed using a three-electrode cell with a Pt wire as the counter electrode and a RHE (Miclab Co., Ltd.) as the reference electrode. NaOH solution (0.1 M) in the cell was bubbled with N_2 (100 mL min^{-1}) for 0.5 h. After bubbling with H_2 (100 mL min^{-1}) for 0.5 h, linear sweep voltammograms (LSVs) for the HOR were recorded at 25°C at a RDE rotation rate of 2,500 rpm in the potential range from −0.05 to 0.9 V vs. RHE (anodic scan) at a scan rate of 10 mV s^{-1}. Cyclic voltammetry (CV) for the catalysts was performed in a N_2-purged 0.1 M NaOH solution at 25°C from 0.05 to 0.9 V vs. RHE at 50 mV s^{-1}.

4th period



5th period

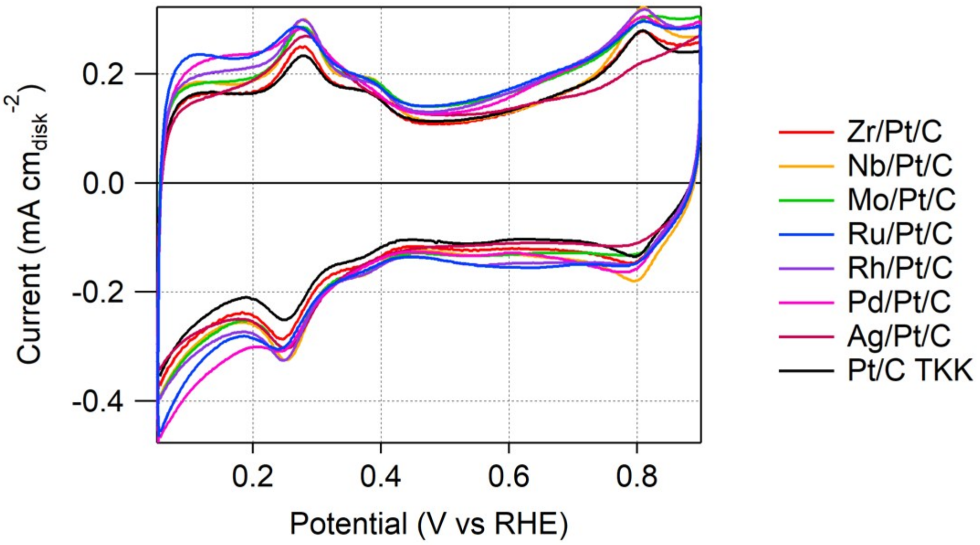


Fig. S1 CVs of M/Pt/C (M: fifteen metals in groups 4–11 of the fourth and fifth periods in the periodic table, omitting Tc) recorded in 0.1 M aqueous NaOH saturated with N_2. Catalyst amount: 10 μg_{Pt} cm disk^{-2}; sweep rate: 50 mV s^{-1}; reference electrode: RHE.

Table S1. Electrochemically active surface area (ECSA) of M/Pt/C evaluated from the H_{UPD} charge, assuming a specific charge of 210 μC cm_{Pt}^{-2}.

Catalyst	ECSA (m^2/g)
Ti/Pt/C	41.4
V/Pt/C	39.7
Cr/Pt/C	34.5
Mn/Pt/C	24.6
Fe/Pt/C	31.3
Co/Pt/C	25.2
Ni/Pt/C	30.3
Cu/Pt/C	50.9
Zr/Pt/C	39.2
Nb/Pt/C	34.9
Mo/Pt/C	32.1
Ru/Pt/C	44.0
Rh/Pt/C	41.6
Pd/Pt/C	52.2
Ag/Pt/C	41.9
Pt/C (TKK)	39.5 ± 4.0 [a]

[a] Each data contains 10% error estimated by repeating experiments using Pt/C for three times.

In Table S1, several catalysts (Cu, Ru, and Pd/Pt/C) showed larger ECSA than Pt/C. The larger values can be explained by H_{UPD} on the modifying metals and/or charge derived from reduction of modifying metals. We used the ECSA in Table S1 to calculate the SA, since it is difficult to eliminate their contribution. It should also be noted that the deviation of Cu/Pt/C from the line in Fig. 5 can be explained by the over estimation of ECSA by the reduction of Cu species.

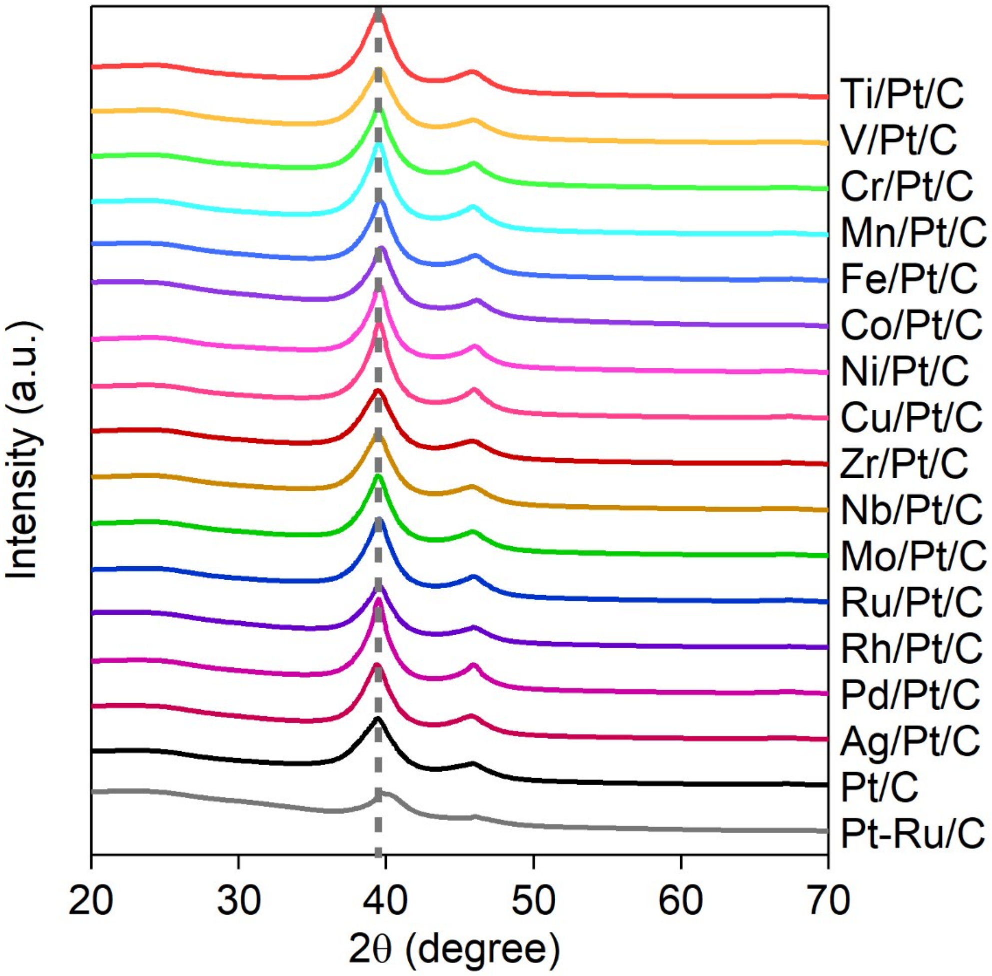


Fig. S2 XRD of M/Pt/C along with unmodified Pt/C and Pt-Ru/C as references. Co/Pt/C showed slight peak shift suggesting formation of Co-Pt alloy. The other modifying metals might form alloy with Pt on surface, although the alloy phases were not clearly observed on the XRD of the other M/Pt/C catalysts.

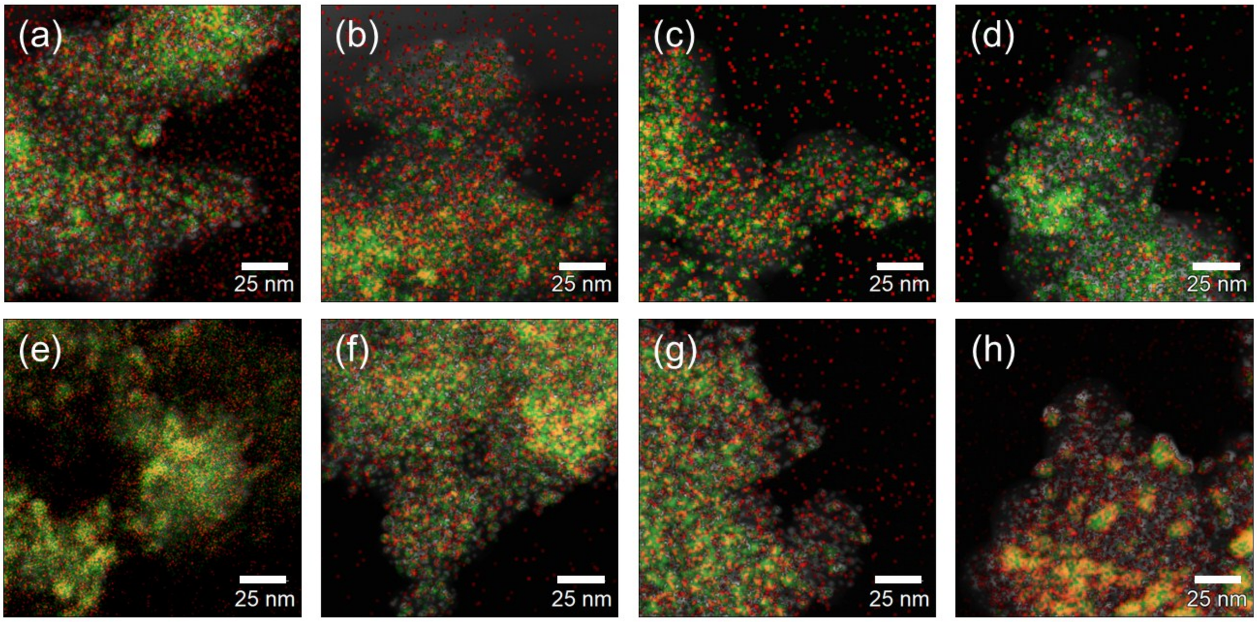


Fig. S3 Overlays of STEM and EDS maps of (a) Mn, (b) Ni, (c) Cu, (d) Mo, (e) Ru, (f) Rh, (g) Pd, and (h) Ag modified Pt/C. Green: Pt, red: modifying metals (M), yellow: Pt+M.

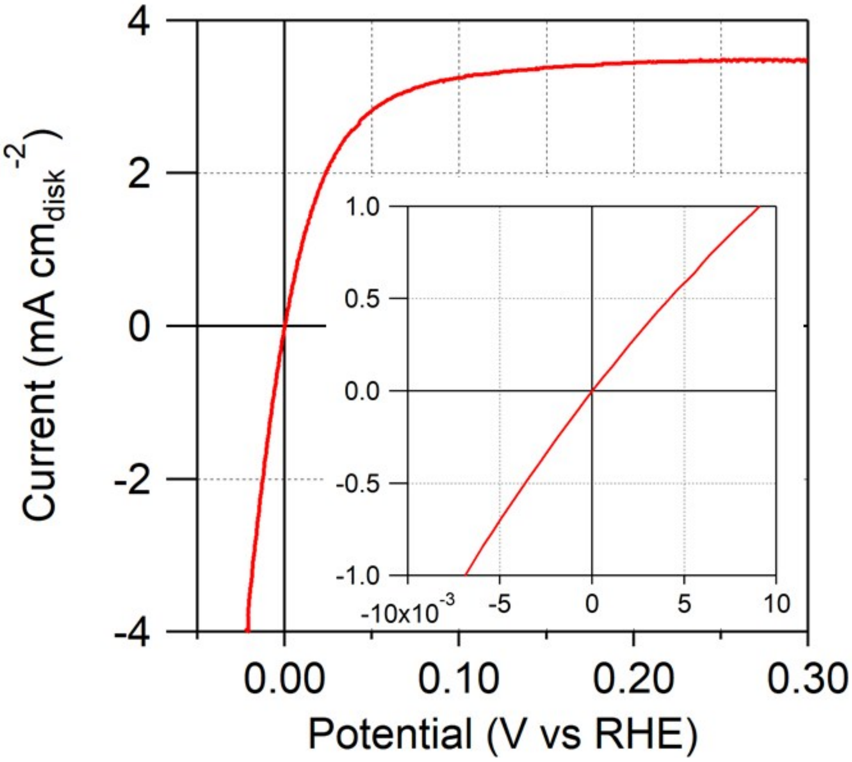


Fig. S4 LSV of Pt-Ru/C (TEC61E54) obtained in 0.1 M aqueous NaOH saturated with H_2 after IR correction. Catalyst amount: 10 μg_{Pt+Ru} cm_{disk}^{-2}; sweep rate (anodic): 10 mV s^{-1}; reference electrode: RHE; rotation rate: 2,500 rpm; temp.: 25°C. The MA was 0.16 A mg_{Pt+Ru}^{-1}.

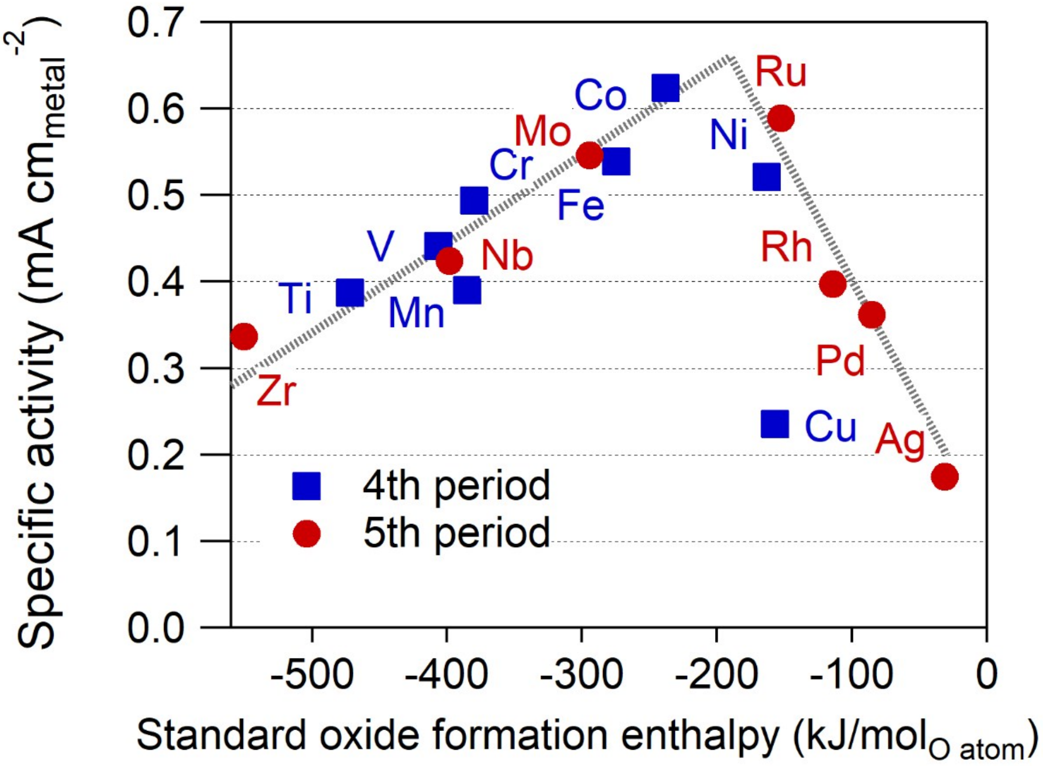


Fig. S5 Plot of the SA of M/Pt/C against the standard oxide formation enthalpy of M (CRC Handbook 2009).