Supplementary Information for

Platinum Monolayer Electrocatalysts for Anodic Oxidation of Alcohols

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References

Methods

Catalysts Syntheses.

Six single crystals Au(111), Pd(111), Rh(111), Ru(0001), Ir(111), and Pt(111) of 8mm in diameter were obtained from Metal Crystals and Oxides, and the single crystals surfaces were oriented to better than 0.2° . The surfaces were prepared following standard procedures,¹ and then they were mounted in a holder for work in a “hanging meniscus” configuration or into the FTIR cell. Quality of single crystal surfaces were examined by cyclic voltammogram and a Pt monolayer was deposited by displacing an underpotentially deposited Cu monolayer layer on single crystal surfaces (further details in Fig. S1).

Commercial carbon-supported nanoparticle catalysts Pt/C, Au/C and Pd/C were obtained from ETEK. Pd₉Au₁ alloy nanoparticles was synthesized using wet impregnation of XC-72 carbon by Pd and Au chlorides, dried, and reduced using NaBH₄ solution. Pt_{ML} was deposited on Au/C, Pd/C and Pd₉Au₁/C by galvanic displacement of a Cu UPD layer.

Electrochemical Measurements.

All electrochemical measurements were carried out under room temperature. Current density data were reported with surface area normalized in terms of the electrochemical active surface area (ECSA) that was determined by the charge of stripping one Cu UPD monolayer on Pt(111) or Pt_{ML} (assuming $480 \mu\text{C}/\text{cm}^2_{\text{Pt}}$). The potentials given in this paper were referenced to that of the Ag/AgCl electrode.

IRRAS.

In situ IRRAS studies were carried out with a Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. An unpolarized light beam was used. The spectral resolution was set to 8 cm^{-1} and 128 interferograms were together added to each spectrum. Spectra are given in absorbance units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected infrared intensities corresponding to the sample and reference single-beam spectrum, respectively. The reference spectrum was collected at 0.1 V in the same solution (0.5M methanol or ethanol in 0.1M HClO_4). $\text{Pt}_{\text{ML}}/\text{Au}(111)$ electrode was employed in IRRAS study. A ZnSe hemisphere was used as the infrared window.

DFT calculation.

DFT calculations were conducted using DMol3,^{2,3} which utilized the effective core potentials, double-numerical basis set with polarization functions and GGA-PW91 for the exchange and correlation functional.⁴ A global orbital cutoff of $5.5\text{ \AA}$ was used. Brillouin-zone integrations were performed on a grid of $4\times 4\times 1$ Monkhorst-Pack special k-points. The metal surface was modeled by a four-layer slab with a (2×2) unit cell respectively, which was separated by enough vacuum space. The bottom two layers of atoms were fixed in their optimized bulk positions while the other layers were allowed to relax with the adsorbates.

Fig. S1. Preparation of Pt monolayer catalysts: voltammetry curves for the underpotential deposition of Cu on single crystal surfaces in 0.05 M H_2SO_4 with 0.05M CuSO_4 , and for the respective single crystal surface in 0.1M HClO_4 ; sweep rate 10 mV/s. (a) Au(111); (b) Pd(111); (c) Ir(111); (d) Rh(111); (e) Ru(0001).

Fig. S2. Cyclic voltammogram of all catalytic surfaces (viz. Pt(111), Pt_{ML}/Au(111), Pt_{ML}/Pd(111), Pt_{ML}/Ir(111), Pt_{ML}/Rh(111), and Pt_{ML}/Ru(0001)) during MOR (a) and EOR (b) in 0.1M HClO₄ containing 0.5M methanol or 0.5M ethanol with a sweep rate of 10mV/s.

Fig. S3. Cyclic voltammetry curves of a Pt monolayer on a Au(111) surface (Pt_{ML}/Au(111)) obtained by galvanic displacement of the Cu monolayer, a Pt monolayer on a Pd(111) surface (Pt_{ML}/Pd(111)) and a Pt(111) surface. The electrolyte solution is 0.1 M HClO₄ and the sweep rate is 10mV/s.

Table S1. *In Situ* IRRAs spectra band assignments^{5,6}

Wavenumber/cm ⁻¹	Assignment
2343	CO ₂ asymmetric stretching
2090	CO linear bonding
1705	C=O stretching of CH ₃ CHO and CH ₃ COOH in solution
1620-1635	C=O stretching of adsorbed acetaldehyde and acetyl
~1598	H-O-H deformation of adsorbed water
1396-1410	O-C-O stretching of adsorbed acetate
~1350	CH plane bending of adsorbed acetate
1280	C-O stretching of CH ₃ COOH in solution
1368	CH ₃ symmetric deformation and C-H wagging in CH ₃ CHO

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