Electronic Supplementary Information

Optimizing the activity of Pd based catalysts towards room-temperature formic acid decomposition by Au alloying

Zihao Xing, Zilong Guo, Xiangyu Chen, Peng Zhang and Wensheng Yang* State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130022, China.

Experiment Section

Catalyst Preparation

The carbon-supported PdAu alloyed catalysts were synthesized by a modified coprecipitation method as follows. First of all, moderate Vulcan XC-72 carbon powder was ultrasonically dispersed in 300 mL of water and stirred sufficiently ink. Next, the precursor solution is made of 100 mL solution containing H_2PdCl_4 (5 mg_{Pd}) and HAuCl_4 (x which is given from 1 to 5 mg_{Au}) which were configured and adjusted by 1 M fresh NaOH solution to pH 4.0. Then, 5 times molar sodium citrate solution than the total amount of Pd and Au atomic molar were adding to the 300 mL initial solution and stirred for 30 min. 100 mL fresh prepared NaBH₄ solution with the same molar of sodium citrate were to be ready to drop to into the carbon carrier suspension system in sequence. Later, the precursor solution was quickly dropped into the above suspension.

The mixture was stirred overnight. Finally, the catalysts was filtered and washed with the ultrapure water and then dried in vacuum at 60 °C overnight. The different composition of mixture was labeled Pd_{0.90}Au_{0.10}, Pd_{0.82}Au_{0.18}, Pd_{0.75}Au_{0.25}, Pd_{0.69}Au_{0.31} and Pd_{0.64}Au_{0.36} according to the feeding Au atomic fraction. For comparison, the monometallic catalysts of Pd/C and Au/C with a metal loading of 5 wt.% were also prepared separately using the same method.

Physical characterization

The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) graphs were obtained using a Philips TECNAI G2 microscopy with an acceleration voltage of 200 kV. Samples were dispersed in ethanol and dropped onto a holey carbon support grid for observation. X-ray diffraction (XRD) measurement was performed by a Bruker D8 Advance with CuK α 1 (=1.5405 Å) as a radiation source, these measurements were carried out with a scanning speed of 2-degree min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed using ESCALAB 250 spectrometer with MgK α source (1254.6 eV).

The reaction device for formic acid decomposition

The formic acid decomposition experiment was carried out by the following instrument.



Scheme S1. The reaction device for formic acid decomposition.

Typically, the catalyst (20 mg) was placed in a round flask, before the addition of the solution (2 mL of solution containing 1.1 M HCOOH and 0.8M HCOONa), high purified N₂ was used to remove air for 10 min. The system was kept at 303 K when the reaction was carrying on, and the volume of gas was calculated by the following formula, in which the V_R , P, P⁰ means the volume of the reformed gas, the recorded pressure and the standard atmosphere, respectively. The constant 683.5 is the total volume for whole reaction device.

$$V_R = \frac{683.5P}{P^0}$$

CO-stripping experiment

CO-stripping experiment was performed by an EG&G mode 273 potentiostat/galvanostat and a three-electrode test cell. A glass carbon electrode, a Pt foil and a saturated calomel electrode (SCE) were used as the work, counter and reference electrodes, respectively. Typically, 5 mg catalyst was dispersed in a mixture solution (950 mL ethanol and 50 mL 5% Nafion solution), and 10 mL of the dispersion was dropped on a φ 5 glass carbon electrode. Cyclic voltammetry experiment was performed in 0.5 M H₂SO₄ solution to clean the electrode surface at a scan rate of 20 mV/s from - 0.2 V to 0.8 V (vs SCE). CO adsorption was performed in 0.5 M H₂SO₄ solution at a voltage of 0.1V for 30 min when CO gas was flowed continuously. Before the CV and after the CO adsorption, high purified N₂ was flowed 30 min to remove the air and CO of solution. CO-stripping was performed in 0.5M H₂SO₄ solution at a scan rate of 20 mV/s from -0.2 V to 1.0 V (vs SCE), which was used to detect the number of the surface Pd atoms. The electrochemically active surface area (ECSA) was calculated by the following formula :

$$ECSA = \frac{Q(\mu A \bullet mV)}{V (mV/S) \times m_{Pd} (g) \times 420(\mu C/cm^2)}$$

In which Q is the integrated CO stripping area during the electro-adsorption of CO on Pt, V is the scan rate and m_{Pd} is the mass of feeding Pd. The value, 420 μ C cm⁻², is the coulombic charge needed to strip a CO monolayer.

The method for the calculation of TOF

Turnover frequency (TOF) was calculated by the following formula

$$TOF = \frac{n_{reactant}}{n_{Pd} \cdot t}$$

$$n_{reactant} = 0.5 V_R / V_m = \frac{342p}{p^0 V_m}$$
$$n_{Pd} = n_{co} = \frac{Q}{N_A \cdot v \cdot 2e^{-1}}$$

in which $n_{reactant}$ and n_{Pd} mean the mole number of reaction and active sites, respectively. V_m means the molar volume of gas at 303 K, t represents the whole reaction time (The time value for accounting for TOF is 1 min, the volume of gas released is 40, 71, 81, 111, 145 and 125 mL for ordinal sample) and Q is calculated by the integration of the area of CO desorption which was obtained from CO-stripping. N_A is the Avogadro constant and v is the scan rate constant (20 mV/s). The method for the calculation of lattice strain

Given the nature of the alloyed particles, the lattice strain of Pd is most relevant for surface catalysis. To estimate the lattice parameter \mathbf{a} in the particle, we take the pure Pd/C with lattice parameter \mathbf{a}_0 and PdAu alloy with lattice parameter a. Using the XRD-derived nanoparticle compositions and lattice-parameter, it is given by as followed.

Lattice strain = $(a_0 - a)/a$

The lattice parameter (a) is conculcated by the Vegard's law. Vegard's law is the empirical heuristic that the lattice parameter of a solid solution of two constituents is approximately equal to a rule of mixtures of the two constituents' lattice parameters at the same temperature.

$$a = \frac{\sqrt{2\lambda}}{\sin\theta}$$

In this equation. λ =0.154056 nm (wavelength of Cu radiation).



Figure S1. Size distribution from TEM images of (a) Pd (b) $Pd_{0.90}Au_{0.10}$ (c) $Pd_{0.82}Au_{0.18}$ (d) $Pd_{0.75}Au_{0.25}$ (e) $Pd_{0.69}Au_{0.31}$ (f) $Pd_{0.64}Au_{0.36}$. To derive the size distribution curve, at least 100 particles in the TEM images were measured.



Figure S2. TEM images and size distribution of the Au/C sample. At least 100 particles in the TEM images were measured to derive the size distribution curve.



Figure S3. Volume of the gas generated from the room-temperature (30 °C) FAD over the Au/C sample. No gas was detectable during the 10 min reaction, meaning the neglectable activity of the Au/C sample towards the reaction.



Figure S4. CO_{ad} stripping voltammograms and CVs of Pd/C, Au/C and PdAu/C catalysts in 0.5 M H_2SO_4 solution with a scan rate of 20 mV/s⁻¹. The CO stripping area was integrated and the surface area was calculated assuming coulombic charge required to strip a CO monolayer is 420 μ C cm⁻².



Figure S5. The electrochemically active surface area (ECSA) of Pd/C and PdAu/C catalysts derived from hydrogen underpotential deposition and CO stripping experiments. ECSA of the Pd/C catalyst was derived to be 323 m²/g and these of the PdAu/C catalysts with the Au ratio of 0.10, 0.18, 0.25, 0.31 and 0.36 were 308, 288, 253, 268 and 280 m²/g respectively. The Pd/C sample exhibited the highest ECSA, attributed to its relatively small average size as shown in Fig. S1.



Figure S6. XPS spectra of the catalysts in the regions of (a) Pd 3d, (b) Au 4f and (c) O 1s. The Pd 3d core-level spectra could be fitted into four symmetric peaks corresponding to Pd (0) $(3d_{5/2})$ and $(3d_{3/2})$ and Pd (\mathbb{I}) $(3d_{5/2})$ and $(3d_{3/2})$. The Au 4f spectra show a couple of distinct peaks corresponding to Au $4f_{7/2}$ and $4f_{5/2}$. The O 1s could be fitted into two peaks corresponding to the lattice and adsorbed oxygen species (see Fig. S7 for more details). These results indicate the high capability of Pd and the very low capability of Au towards dissociative adsorption of O₂.



Figure S7. (a) Variations in binding energies of Pd (\mathbf{I}) 3d_{3/2}, Pd (0) 3d_{3/2}, Pd (\mathbf{I}) 3d_{5/2} and Pd (0) 3d_{5/2} with the Au atomic fraction used in the syntheses. The banding energy of Pd (II) 3d_{3/2} shifted from 342.24 to 342.20, 341.90, 341.82 and 341.78 eV and that of Pd (0) shifted from 341.33, 341.21, 341.05, 340.89 and 340.88 eV as the Au fraction increased from 0.10 to 0.18, 0.25, 0.31 and 0.36. In the same trend, the banding energy of Pd (\mathbf{I}) 3d_{5/2} shifted from 336.86 to 336.78, 336,64, 336.42 and 336.40 eV and that of Pd (0) shifted from 335.96 to 335.88, 335.82, 335.62 and 335.60 eV as the Au fraction increased from 0.10 to 0.18 in binding energies of Au 4f_{5/2} and Au 4f_{7/2} with the Au atomic fraction used in the syntheses. The banding energy of Au 4f_{5/2} shifted from 87.61 to 87.74, 87.81, 87.82 and 87.82 eV and that of Au 4f_{7/2} shifted from 84.02 to 84.05, 87.09, 87.10 and 87.10 eV as the Au fraction increased from 0.10 to 0.18, 0.25, 0.31 and 0.36.



Figure S8. Variation in lattice O relative content (LOC) on surface of the catalysts with the Au atomic fraction used in the syntheses. The LOC value increased from 0.51 to 0.53, 0.54 and 0.62 with increasing the Au fraction from 0.10 to 0.18, 0.25 and 0.31, and decreased to 0.55 with further increasing the Au fraction to 0.36. The existence of lattice oxygen suggested the formation of PdO species on surface of the alloyed catalysts.



Figure S9. Comparison of the variations in relative contents (RC) of Pd (II) on the catalyst surface and TOF of the catalysts with the atomic fraction of Au. Both the changes in the RC of Pd (II) and the ratio of Pd (II)/Pd (0) are in consistence with the change in TOF, suggesting the PdO species are the active sites for the room-temperature FAD.



Figure S10. The recyclability of the $Pd_{0.69}Au_{0.31}/C$ catalyst. After each cycle, the catalyst was separated from the reaction system by adequately filtering, washing with distilled water and then dried in vacuum. The catalyst showed only slight change in the catalytic activity after five cycles, suggesting its good recyclability.



Figure S11. (a) TEM image, (b) Size distribution and (c) Pd 3d XPS spectra of the $Pd_{0.69}Au_{0.31}/C$ catalyst before the catalytic run. (d) TEM image, (e) Size distribution and (f) Pd 3d XPS spectra of the $Pd_{0.69}Au_{0.31}/C$ catalyst after the catalytic run. The results showed that there was no obvious aggregation of the nanoparticles after the reaction.

Catalyst	TOF/	Reactant	Reference	
	h-1		in main text	
Pd _{0.69} Au _{0.31} /C	6634	1.1 M FA + 0.8 M SF	This work	
Pd/C	1539			
B-Doped Pd	1184	1.1 M FA + 0.8 M SF	4	
Ag@Pd	192	1 M FA	5	
Pd clusters@Slicate-1 Zeolite	856	6.0 M FA + 6.0 M SF	8	
Pd ₆₀ Au ₄₀ /ZrSBA	1185	0.2 M FA	10	
Pd-PdO/C	3172	1.1 M FA + 0.8 M SF	12	

Table S1. Comparison of room-temperature TOF of the $Pd_{0.69}Au_{0.31}/C$ catalyst with the Pd-based catalysts reported in literatures.

Table S2. The percentages and ratios of the evolved gas generated with the $Pd_{0.69}Au_{0.31}/C$ catalyst.

Catalysts	${ m H}_2/\%$	O_2 / %	$N_2 / \%$	CO ₂ / %	H ₂ : CO ₂	N ₂ : O ₂
Pd _{0.69} Au _{0.31} /C	46.91	1.45	6.82	44.82	1.05: 1	4.70: 1