
Supporting Information

Supported Pd-Au bimetallic nanoparticles as efficient catalyst for hydrodeoxygenation of vanillin with formic acid at room temperature

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1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. The scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold. The transmission electron microscopy (TEM) images were taken using a Philips Tecnai 12 microscope operating at 120 kV. TEM samples were prepared by dispersed in methanol and placed on a carbon film covered copper grid. High resolution transmission electron microscopy (HRTEM) was performed on a FEI Tecnai G2 F20 S-TWIN. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer, using an Al K α X-ray source (1486.6 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. The crystal structures of the synthesized catalysts were recorded by a D8 ADVANCED X-ray diffractometer (XRD), employing a range from 5 ° to 80 °. The H₂-TPD data were obtained on a Micromeritics AutoChem II S3 2920 instrument. Products were analyzed by gas chromatography (GC) on an Agilent 7890A gas chromatograph with flame ionization detection, equipped with HP-5 capillary columns, and gas chromatography-mass spectroscopy (GC-MS) with a Thermo Scientific Trace 1300 GC/MS instrument equipped with TR-5MS columns.

2. Catalysts Preparation

The g-C₃N₄ support was synthesized according to a former report.¹ The pyrolysis of melamine was carried out in a tubular furnace under air. The sample was heated from room temperature to 500 °C at a heating rate of 5 °C min⁻¹ and kept at this temperature for 2 h. After cooling to room temperature, g-C₃N₄ was obtained.

MIL-101(Fe) was synthesized in the following steps. Typically, 1350.0 mg (5.0 mmol) of FeCl₃·6H₂O were dissolved in 15.0 mL of DMF, and then the solution was mixed with a solution of 500.0 mg (3 mmol) of terephthalic acid in 15.0 mL of DMF. The mixed solution was stirred thoroughly for 30 min and transferred to a Teflon-lined autoclave and treated in an oven for 24 h at 110 °C. The resulting solid was then separated by centrifugation, washed with DMF and subsequently with methanol to remove un-reacted ligands. The product was dried under vacuum at 50 °C for 12 h.

Catalysts were prepared by impregnation-reduction method, and in the typical preparing

procedure of PdAu/g-C₃N₄, 500 mg of g-C₃N₄ was dispersed in 50 mL of deionized water, then 3 mL of Na₂PdCl₄ solution (5 mg Pd per mL), 64 mg AuCl₃ solution (15 mg Au) and 150 mg L-lysine were added. The mixture was then vigorously stirred for 30 min under argon atmosphere. After that, NaBH₄ solution (60 mg dissolved in 10 mL deionized water) was added drop by drop in an ice bath, the mixture was further stirred for 1 h. And then 15 mL acetone was added into the mixture, the catalyst was further aged for 24 h without stirring. Finally, the catalyst was collected by centrifugation, washed with deionized water three times and dried under vacuum at 50 °C for 12 h. Other catalysts used in this work were prepared in the same way except that metal precursors and catalyst support are different.

3. Catalytic HDO of vanillin

In a typical reaction procedure, 0.5 mmol of vanillin and corresponding catalyst were placed in a sealed tube, then 2 mL of deionized water and 200 μL 88 wt% FA aqueous solution were added. After the vanillin was dissolved, 6 mL of EA was added, and the mixture was stirred at room temperature for 1 h. After reaction, the mixture was extracted with EA, and the catalyst could be separated by filter, dried under vacuum and reused. The products were analyzed by GC and GC-MS, and then isolated by column chromatography in isolated yields. In this work, all the experiments were carried out in triplicate.

4. Catalytic performance in recent studies

Table S1 Catalytic performance in recent studies on the HDO of vanillin with formic acid as the hydrogen source

| Catalyst | Temperature (°C) | Time (h) | Atmosphere | Yield (%) | Ref. |
|---------------------------------------|------------------|----------|---------------------------|-----------|-----------|
| Pd/TiO ₂ @NC | 150 | 4 | 0.5 MPa of N ₂ | 99 | 2 |
| Ag-Pd@g-C ₃ N ₄ | 40 W bulb | 4 | - | 99 | 3 |
| Pd/NMC | 150 | 3 | 0.5 MPa of N ₂ | 99 | 4 |
| Au-Pt/CeO ₂ | 150 | 4.5 | 1.5 MPa of N ₂ | 99 | 5 |
| Co@NC-700 | 180 | 4 | 0.5 MPa of N ₂ | 96 | 6 |
| Co@NG-6 | 160 | 6 | - | 99 | 7 |
| Pd@HPC-DCD | 140 | 12 | 0.5 MPa of N ₂ | 100 | 8 |
| PdAu/g-C ₃ N ₄ | Room temperature | 1 | Atmosphere air | 99 | This work |

5. ICP-MS results of the catalysts

Table S2. ICP-MS analysis of prepared catalysts

| Catalyst | Element | Metal Content (mg/kg) |
|---------------------------------------------------|---------|-----------------------|
| PdAu/g-C ₃ N ₄ | Pd | 15818 |
| | Au | 14426 |
| Pd/g-C ₃ N ₄ | Pd | 15167 |
| Au/g-C ₃ N ₄ | Au | 15321 |
| PdNi/g-C ₃ N ₄ | Pd | 14213 |
| | Ni | 15502 |
| PdCu/g-C ₃ N ₄ | Pd | 16718 |
| | Cu | 13507 |
| RuAu/g-C ₃ N ₄ | Ru | 14024 |
| | Au | 13827 |
| PdAu/Al ₂ O ₃ | Pd | 13287 |
| | Au | 13131 |
| PdAu/SiO ₂ | Pd | 16385 |
| | Au | 14805 |
| PdAu/AC | Pd | 14715 |
| | Au | 13601 |
| PdAu/MIL-101(Fe) | Pd | 19239 |
| | Au | 15188 |
| PdAu/g-C ₃ N ₄ ^a | Pd | 14949 |
| | Au | 13744 |

^a Catalyst after 5 runs.

6. XPS spectra of catalysts

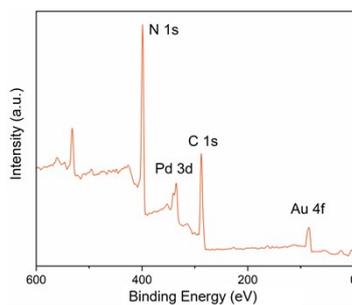


Fig. S1 XPS survey spectra of PdAu/g-C₃N₄.

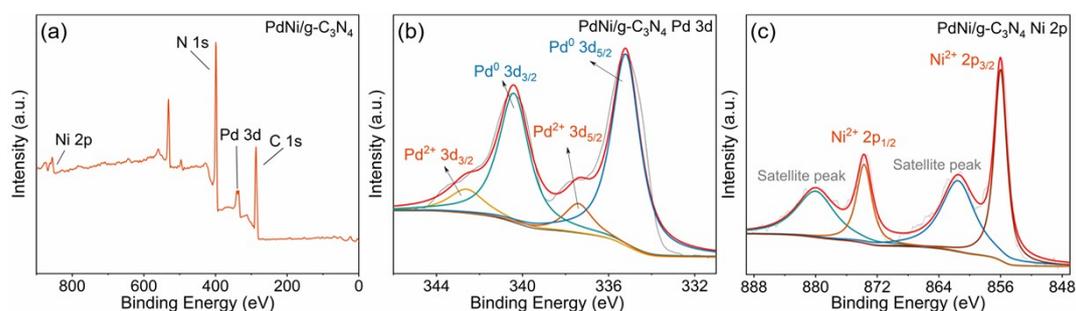


Fig. S2 XPS spectra of PdNi/g-C₃N₄ (a) survey, (b) Pd 3d region, (c) Ni 2p region.

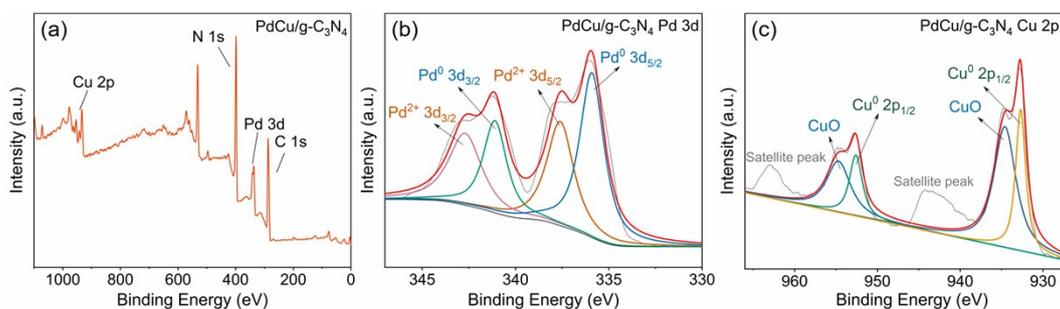


Fig. S3 XPS spectra of PdCu/g-C₃N₄ (a) survey, (b) Pd 3d region, (c) Cu 2p region.

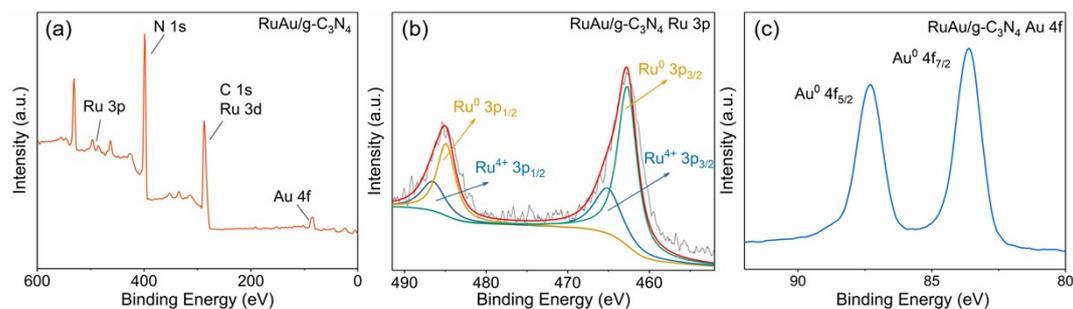


Fig. S4 XPS spectra of RuAu/g-C₃N₄ (a) survey, (b) Ru 3p region, (c) Au 4f region.

7. Time-course monitoring of c_{FA}

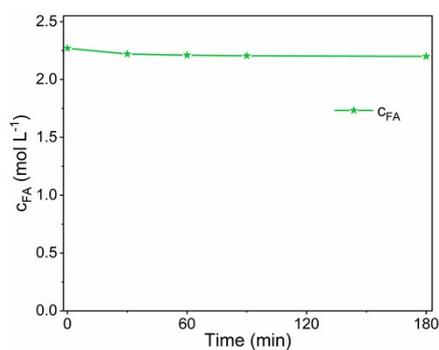


Fig. S5 Time-course monitoring of c_{FA} in reaction system without PdAu/g-C₃N₄.

8. Results of the experiments with vanillin alcohol

Table S3. Hydrogenolysis of vanillin alcohol with FA^a

| | | |
|-------|--------------------------------------|--------------------|
| | | |
| Entry | Catalyst | Yield ^b |
| 1 | None | No reaction |
| 2 | g-C ₃ N ₄ | No reaction |
| 3 | PdAu/g-C ₃ N ₄ | 99 |
| 4 | Pd/g-C ₃ N ₄ | 99 |
| 5 | Au/g-C ₃ N ₄ | 21 |

^a Reaction conditions: vanillin alcohol (0.5 mmol), 2 mL H₂O and 6 mL EA, 25 mg catalyst, 200 μ L 88 wt% FA aqueous solution, room temperature, air atmosphere, 1 h. ^b Yields of MMP were determined by GC with hexadecane as an internal standard.

9. TEM image of recovered PdAu/g-C₃N₄

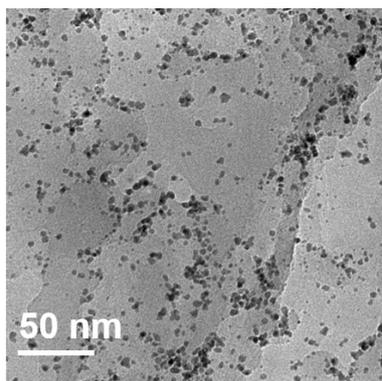


Fig. S6 TEM image of PdAu/g-C₃N₄ after 5 runs.

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