Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Facile Synthesis of Carbon-Supported PdAu Nanonetworks for Cinnamaldehyde Hydrogenation

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Experimental Section

Chemicals and Materials

CAL, HCAL, COL, and HCOL were obtained from Adamasbeta (Shanghai) Chemical Reagent Co., Ltd. Ortho-xylene was sourced from Anneji (Shanghai) Pharmaceutical Chemical Co., Ltd. Anhydrous ethanol, sodium borohydride, tetrahydrofuran, and tetrachloroauric acid were procured from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Sodium tetrachloropalladate and conductive carbon black were acquired from Merck Chemical Technology (Shanghai) Co., Ltd. and Cabot Corporation, respectively. Commercial palladium carbon (10% w/w) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Preparation of PdAu NWs supported on carbon

In the typical preparation method of PdAu NWs@C, 10 mg of carbon black was dispersed in 10 mL anhydrous ethanol in a 100 mL beaker with the assistance of sonication. 2 mL of fresh $NaBH_4$ solution (containing 3.2 mg $NaBH_4$) was added subsequently. Five minutes later, the mixture of 412 μL Na_2PdCl_4 (0.02 M) and 340 μL $HAuCl_4$ (0.024 M) was rapidly injected into the above solution. And the mixture was reacted for another 5 min. Magnetic stirring was maintained throughout the preparation process except for the ultrasonic process. The precipitates were collected by centrifugation and then washed with water and ethanol in sequence. The obtained catalyst was denoted as PdAu NWs@C. For comparison, $PdAu_3$ NWs@C and Pd_3Au NWs@C were prepared using the same method as mentioned above, with only a change in the amount of Na_2PdCl_4 and $HAuCl_4$ used.

Cinnamaldehyde hydrogenation reaction

PdAu NWs@C (2.5 mg), CAL (255 μL), o-xylene (internal standard substance, 20 μL), and a magnetic rotor were added to THF (10 mL), and the mixture was placed in a stainless steel high-pressure vessel. Then, high-purity hydrogen gas was introduced into the mentioned high-pressure vessel above, which was ventilated three times. The reaction was carried out at 25 ^{o}C and 2 MPa H_2 for 5 hours, with stirring accompanying the entire reaction process. After hydrogen removal, the product is filtered and sampled for gas chromatography composition analysis.

PdAu-NWs@C (2.5 mg), CAL (255 μL), o-xylene (internal standard, 20 μL), and a magnetic rotor were added to 10 mL of THF and placed in a stainless steel high-pressure vessel. High-purity hydrogen gas was then introduced into the vessel, which was purged three times. The reaction occurred at 25°C and 2 MPa H_2 for 5 hours, with continuous stirring. After hydrogen was removed, the product was filtered and analyzed by gas chromatography for composition.

Characterization

GC-FID analysis was conducted using a Linghua instrument GC9890ES gas chromatograph, with o-xylene as the internal standard. The conditions were: 0.50 μL injection volume, 0.03 MPa pre-column pressure, 0.30 MPa gas phase loading pressure, 0.1 MPa hydrogen pressure, 0.15 MPa air pressure, 260°C injection temperature, 280°C detection temperature, and 180°C column temperature. The chromatographic column used was an OV-1701, 30 m x 0.32 mm x 0.50 μm. Under these conditions, o-xylene, cinnamaldehyde, phenylpropanol, and cinnamyl alcohol were analyzed. The retention times were: o-xylene at 4.2 minutes, phenylpropanol at 7.7 minutes, cinnamaldehyde at 11.2 minutes, and cinnamyl alcohol at 12.3 minutes.

[Conv. (CAL), %] denotes the conversion rate of the substrate, [Select. (HCAL), %] indicates the selectivity for saturated aldehydes, [Select. (COL), %] shows the selectivity for unsaturated alcohols, and [Select. (HCOL), %] represents the selectivity for saturated alcohols. In the formula, m stands for the mass of the substance being measured; mi refers to the mass of the internal standard substance; A signifies the peak area of the test substance; Ai denotes the peak area of the internal standard substance; f represents the relative correction factor; mo indicates the mass of the analyte in the original solution; m(HCAL), m(COL), and m(HCOL) denote the masses of hydrocinnamaldehyde, cinnamyl alcohol, and hydrocinnamyl alcohol measured after the reaction; mx represents one of the three products to be tested for selectivity.

$$\frac{m}{m_i} = f\frac{A}{A_i} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

(1)

$$Conv.(CAL) = \frac{m_o - m}{m_o} \times 100\% \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$Selec.(x) = \frac{m_x}{m_{(HCAL)} + m_{(COL)} + m_{(HCOL)}} \times 100\% \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

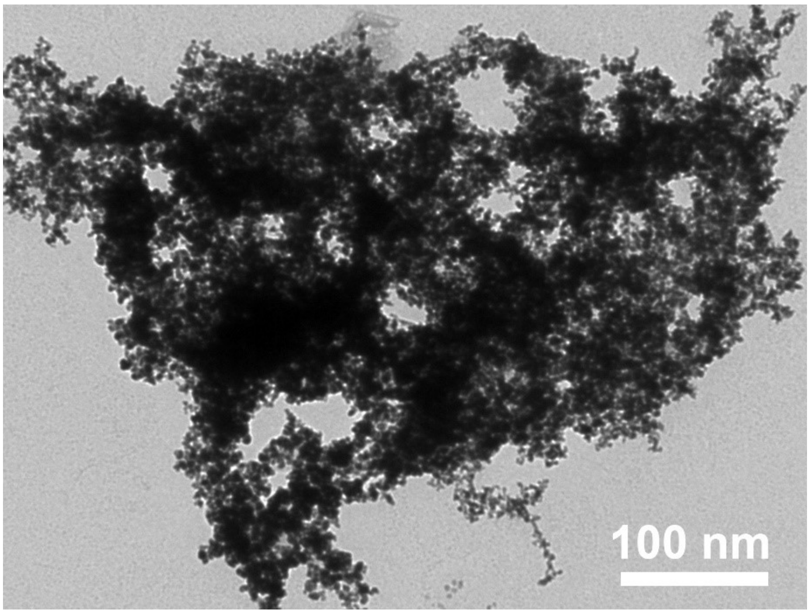

Figure S1 Morphology of PdAu NPs without carbon black

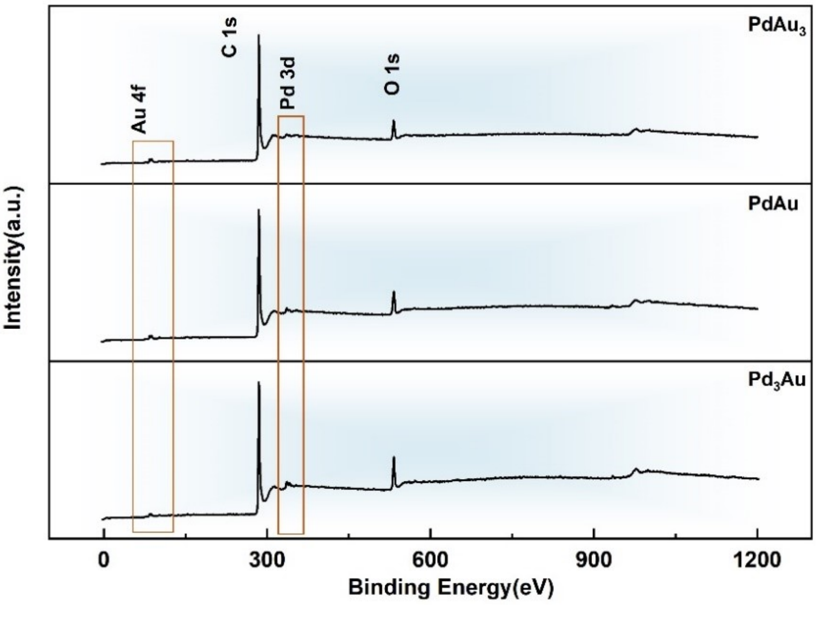

Fig.S2 XPS survey spectra of PdAu NWs@C

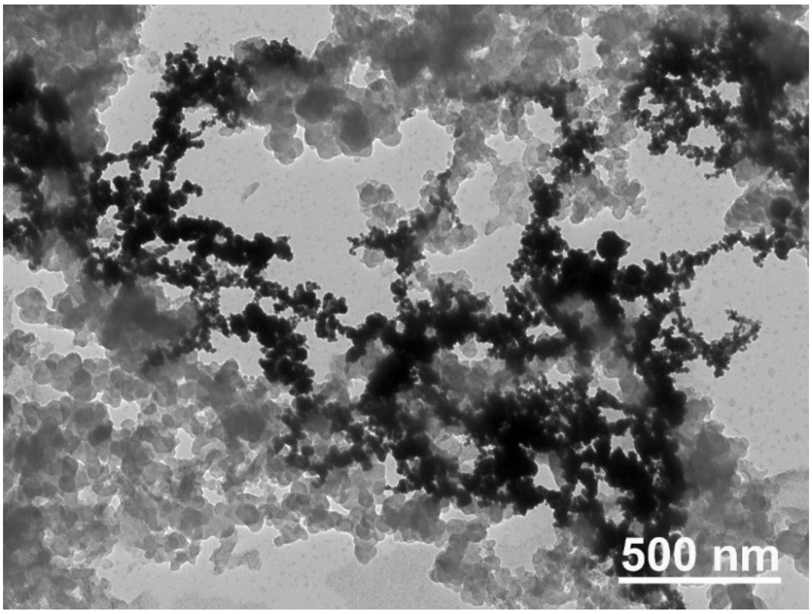

Fig.S3 Morphology of the catalyst after cyclic reaction

Table S1 Comparison of the catalytic performance of supported catalysts for cinnamaldehyde hydrogenation.

Catalysts	Time (h)	Pressure (MPa)	Temperature (°C)	Conversion (%)	Selectivity (%, HCAL)	References
PdAu NWs@C	5	2	25	98.0	92.7	This work
$Ni_{12}P_5/SiO_2$	6	3	100	81.7	92.2	[1]
30 wt% Ni@OCNT	16	1.3	120	96	93	[2]
0.2 % Pd-1.2 % Ni/SBA-15	2	1.2	80	96.3	87.8	[3]
Au_6-Pd_1/SN	3	0.1	25	99.8	91.0	[4]
Pd0.5Au0.5 NPs	24	0.5	50	86	96	[5]
PdIr/SiC	2	0.3	25	70	91.2	[6]
4-Pd@ZrO_2	9	1	120	100	86	[7]
Pd/MCM-41	2	1	110	61.2	84.5	[8]
Pd@SG-ZSM-5	2	1	150	58.3	73.3	[9]

References

[1] H. Wang, Y. Shu, M. Zheng, T. Zhang, Selective Hydrogenation of Cinnamaldehyde to Hydrocinnamaldehyde over SiO_2 Supported Nickel Phosphide Catalysts, Catal. Lett. 124(3) (2008) 219-225.

[2] K.N. Patil, P. Manikanta, P. M. Srinivasappa, A.H. Jadhav, B.M. Nagaraja, Exploring the confined space and active sites of Ni@OCNTs catalyst for chemoselective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde, Journal of Environmental Chemical Engineering 10(5) (2022) 108208.

[3] S. Han, Y. Liu, J. Li, R. Li, F. Yuan, Y. Zhu, Improvement Effect of Ni to Pd-Ni/SBA-15 Catalyst for Selective Hydrogenation of Cinnamaldehyde to Hydrocinnamaldehyde, Catalysts 8(5) (2018) 200.

[4] H. Wang, Y. Shi, Z. Wang, Y. Song, M. Shen, B. Guo, L. Wu, Selective hydrogenation of cinnamaldehyde to

hydrocinnamaldehyde over Au-Pd/ultrathin SnNb2O6 nanosheets under visible light, J. Catal. 396 (2021) 374-386.

[5] J. Pinto, A. Weilhard, L.T. Norman, R.W. Lodge, D.M. Rogers, A. Gual, I. Cano, A.N. Khlobystov, P. Licence, J. Alves Fernandes, Unravelling synergistic effects in bi-metallic catalysts: deceleration of palladium–gold nanoparticle coarsening in the hydrogenation of cinnamaldehyde, Catal. Sci. Technol. 13(14) (2023) 4082-4091.

[6] P. Li, Y. Wang, Y. Wang, G. Jin, X.-Y. Guo, X. Tong, Silicon Carbide Supported Palladium-Iridium Bimetallic Catalysts for Efficient Selective Hydrogenation of Cinnamaldehyde, Chin. J. Chem. 38(4) (2020) 367-371.

[7] K.N. Patil, D. Prasad, J.T. Bhanushali, B. Kakade, A.H. Jadhav, B.M. Nagaraja, Chemoselective hydrogenation of cinnamaldehyde over a tailored oxygen-vacancy-rich Pd@ZrO_2 catalyst, New J. Chem. 45(12) (2021) 5659-5681.

[8] R. Li, W. Yao, Y. Jin, W. Jia, X. Chen, J. Chen, J. Zheng, Y. Hu, D. Han, J. Zhao, Selective hydrogenation of the C=C bond in cinnamaldehyde over an ultra-small Pd-Ag alloy catalyst, Chem. Eng. J. 351 (2018) 995-1005.

[9] L. Alfilfil, J. Ran, C. Chen, X. Dong, J. Wang, Y. Han, Highly dispersed Pd nanoparticles confined in ZSM-5 zeolite crystals for selective hydrogenation of cinnamaldehyde, Microporous Mesoporous Mater. 330 (2022) 111566.