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Electronic Supplementary Information (ESI) for:

Fe_2O_3 Supported Pt Single Atom Catalysts for the Selective Hydrogenation of Cinnamaldehyde

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Experimental Section

Chemicals and Materials

Iron oxide (Fe_2O_3, 99.9%) was purchased from Shanghai Yaotian New Material Technology Co. Ltd. Tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$), Tetraamminepalladium (II) nitrate ($Pd(NH_3)_4(NO_3)_2$), Ammonium tetrachloroaurate (III) hydrate ($(NH_4)AuCl_4 \cdot xH_2O$), cinnamaldehyde (CAL), cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), hydrocinnamyl alcohol (HCOL), methanol, ethanol, isopropanol, tridecane and ethyl acetate were purchased from Shanghai Aladdin Biochemistry Technology Co. Ltd, China. All chemical and materials were used as received without any further purification. Deionized water was used throughout this work.

Catalysts Preparation

Typically, about 30 mL volume of agate balls was added to an agate chamber (100 mL), and then 2.0 g of Fe_2O_3 and 7.9 mg of $Pt(NH_3)_4(NO_3)_2$ were also added into the chamber. The ball milling process was operated under the condition of 500 rpm for 24 h at atmospheric pressure and room temperature. After milling, the balls were removed from the milled material, and the obtained powder was put into muffle furnace and heated at 400 °C for 5 h with a heating rate of 2 °C/min. After calcination, Pt_1/Fe_2O_3 was prepared. Other Fe_2O_3 supported atomically dispersed catalysts (e.g., Au and Pd) were synthesized with the similar method. For comparison, PtO_x NPs/Fe_2O_3 was prepared by incipient-wetness impregnation method with the same Pt loading of Pt_1/Fe_2O_3. Specifically, the specific maximum water absorption of Fe_2O_3 was tested to be ~ 0.6 mL/g. 7.9 mg of $Pt(NH_3)_4(NO_3)_2$ was dissolved in 1.2 mL of deionized water. The solution was then poured onto 2 g of Fe_2O_3. The samples were oscillated at 25 °C for 1 h and dried at 120 °C overnight. The obtained powder was put into muffle furnace and heated at 400 °C in air atmosphere for 5 h with a heating rate of 2 °C/min. After calcination, PtO_x NPs/Fe_2O_3 was prepared.

Catalysts Characterization

The loading levels of noble metal were detected by inductively coupled plasma optical emission spectrometer (ICP-OES) on a PerkinElmer OPTIMA 8000DV. The powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advanced Diffractometer with Cu Kα radiation over a scan rate of 5 °/min from 10 to 90 °(2θ). X-ray photoemission spectroscopy (XPS) measurements were performed at an ESCALAB250 X-ray photoelectron spectrometer with carbon as internal standard (C1s = 284.6 eV). The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted on a FEI Tecnai G2 F30 operated at 300 kV. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) and energy dispersion spectrum (EDS) images were recorded on a JEM-ARM200F field emission transmission microscopy operated at 200 kV. X-ray absorption spectroscopy (XAS) measurements for the Pt L-edge were carried out in BL14W beamline with transmission mode at the Shanghai Synchrotron Radiation Facility. PtO_2 and Pt foil were used as reference samples and measured in transmission mode. the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data reduction and analysis were processed by Athena software. The wavelets transform (WT) was produced by Matlab software. H_2-D_2 exchange experiments were carried out in a continuous-flow fixed-bed quartz reactor with inner diameter of 7 mm at atmospheric pressure. About 50 mg powers of catalysts were held at the center of the reactor with quartz-wool plugs. The flow rates of 5% H_2/N_2 purging of the sample tube in all studies were kept at 20 mL/min. After the temperature stabilizing at 80 °C, the sample was dosed with D_2. HD (m/z = 3) signal was collected by online mass spectrometry (Hiden Analytical HPR-20 QIC benchtop Gas Analysis System). FI-IR spectra were collected on Nicolet iS20 spectrometer.

Catalytic Reaction

Selective hydrogenation of CAL was performed in a 10 mL stainless-steel autoclave reactor. In a typical procedure, 0.2 mmol of CAL, 10 mg of Pt_1/Fe_2O_3 catalysts, 2 mL of H_2O and tridecane (as an internal standard) were loaded into the reactor. The air in the reactor was purged out with pure H_2 for more than five times at room temperature. The reaction was carried out at 80 °C under 2 MPa H_2 pressure for 4 h. After the reaction, ice water was used to cool down the reactor to stop the reaction immediately. The organic products were extract thoroughly by ethyl acetate. All the products were analyzed by gas chromatograph (Shimadzu GC-2010 Plus) equipped with an InertCap Pure-WAX capillary column (30 m length, 0.25 mm diameter) and a flame ionization detector (FID). The structure of generated products was confirmed by a Shimadzu GC-MS. For the recycling reactions, the used catalyst was recovered by centrifugation, washed with ethanol and water for several times, and then dried at 333 K for overnight in a vacuum oven. In each run, the Pt_1/Fe_2O_3 catalyst was used directly without any pre-reduction treatment. The amount of substrate is identical to above experiment. The carbon balance has been checked to be higher than 95% for each reaction.

The conversion and selectivity were calculated as:

$$\text{CAL conversion }(\%) = \frac{\text{moles of CAL consumed}}{\text{moles of CAL before reaction}} \times 100\% \qquad (1)$$

$$\text{Product selectivity }(\%) = \frac{\text{moles of product}}{\text{moles of CAL consumed}} \times 100\% \qquad (2)$$

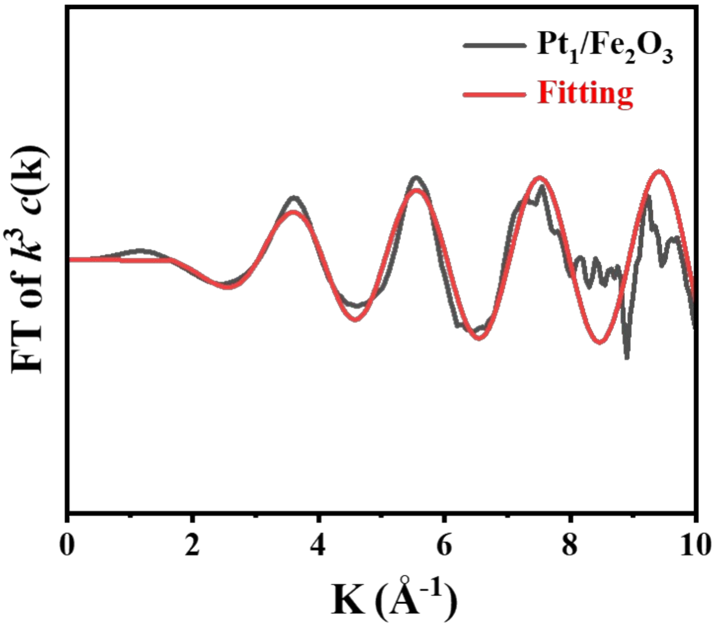

Fig. S1 The corresponding Pt L-edge EXAFS fitting curve of Pt_1/Fe_2O_3.

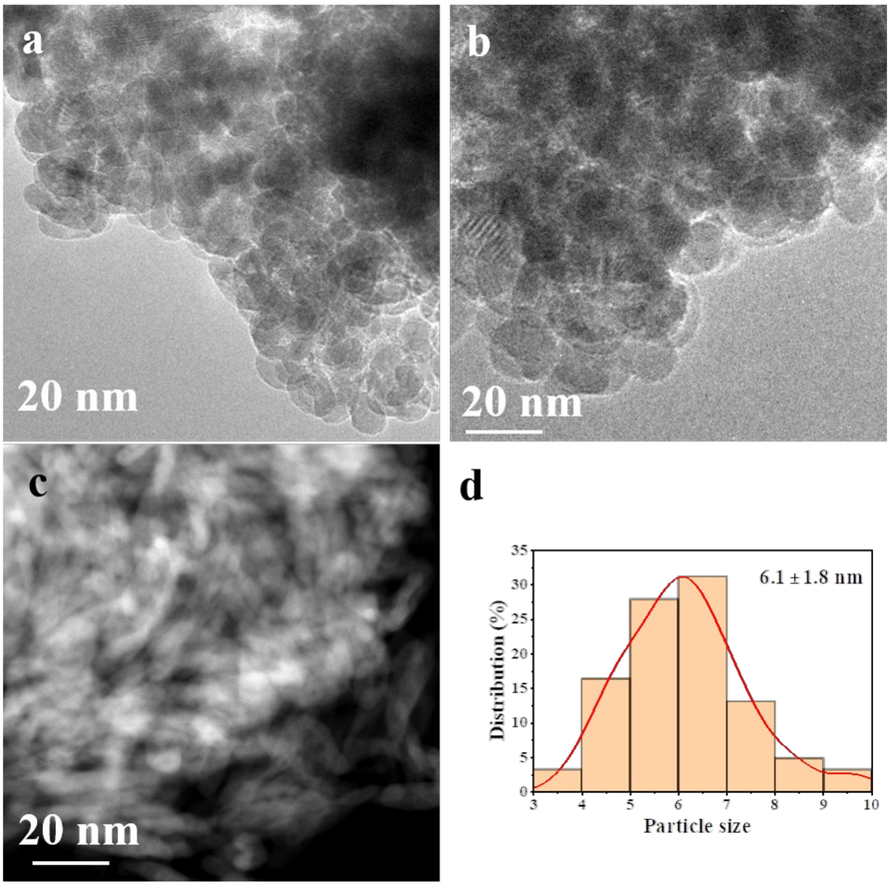

Fig. S2 (a) TEM image of Pd_1/Fe_2O_3. (b) TEM image of Au_1/Fe_2O_3. (c) STEM image and the (d) nanoparticles' size distribution of PtO_x NPs/Fe_2O_3.

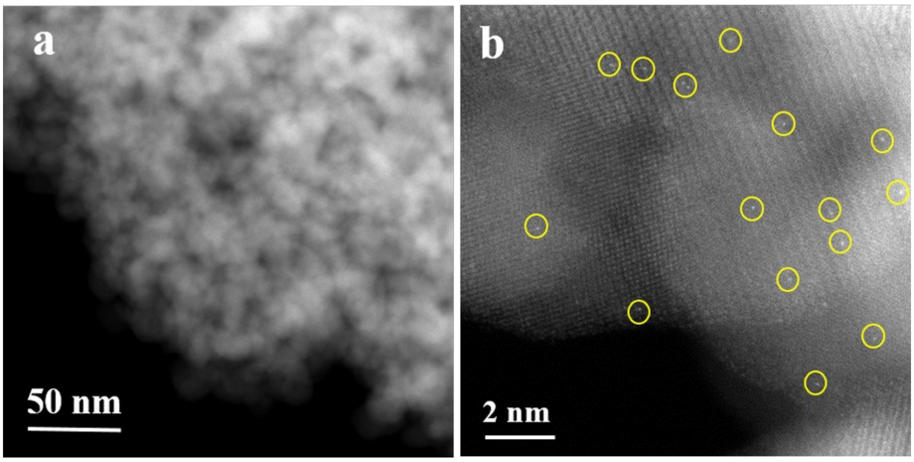

Fig. S3 (a) STEM, (b) AC HAADF-STEM of the spent Pt_1/Fe_2O_3 catalyst.

Table S1. Noble metal loadings of various catalysts.

Samples	Noble metal loading (wt.%)
Pt_1/Fe_2O_3	0.19
Pd_1/Fe_2O_3	0.19
Au_1/Fe_2O_3	0.19
PtO_x NPs/Fe_2O_3	0.19
Pt_1/Fe_2O_3-spent	0.18

Table S2. Structure parameters of EXAFS for Pt_1/Fe_2O_3

Sample	Scattering path	CN[a]	R (Å)[b]	σ^2 ($\times10^{-3}$ Å^2)[c]	E_0 (eV)[d]
Pt_1/Fe_2O_3	Pt-O	3.99±0.88	2.01±0.03	2.11±5.03	9.79±2.20

[a] CN is the coordination number; [b]R is bond distance; [c]σ^2 is Debye-waller factors; [d]E_0 is the inner potential correction. R–factor: 0.00295.