

## Electronic Supplementary Information

### Experimental section:

A series of ferric hydroxide or oxide supported Au catalysts were prepared by co-precipitation. Dilute aqueous solutions of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  ( $0.1 \text{ g ml}^{-1}$ ) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $1 \text{ mol l}^{-1}$ ) were mixed uniformly, then added drop-wise into aqueous  $\text{Na}_2\text{CO}_3$  solution ( $1 \text{ mol l}^{-1}$ ) with vigorous stirring at room temperature, and the pH of the finally resulted solution was controlled to *ca.* 8.5. After stirring and aging for 3 hours respectively, the resulting precipitate was filtrated and washed with distilled water, followed by dried at  $50 \text{ }^\circ\text{C}$  for 6 hours. Then, the resulted precipitate was treated at  $200 \text{ }^\circ\text{C}$  for 5 h (denoted as  $\text{Au/Fe}(\text{OH})_x$ ), and at  $500 \text{ }^\circ\text{C}$  for 4 h (denoted as  $\text{Au/Fe}_2\text{O}_3$ ) respectively.  $\text{Pd/Fe}(\text{OH})_x$  and  $\text{Pt/Fe}(\text{OH})_x$  as well as blank  $\text{Fe}(\text{OH})_x$  were prepared in the same manner. 4.4 wt%  $\text{Au/Fe}_2\text{O}_3$  bought from World Gold Council (denoted as  $\text{Au/Fe}_2\text{O}_3\text{-W}$ ) was also employed. All reagents used in this procedure are analytical grade and were used without further purification.

Catalytic experiments of chemoselective hydrogenation of aromatic nitro compounds were carried out in a 90 ml autoclave equipped with magnetic stirring. In hydrogenation process under  $\text{CO/H}_2\text{O}$  conditions, 0.05g catalyst, 7.5 mmol substrate (15 mmol for *p*-nitro acetophenone), 7 ml 2-ethoxyethanol (12 ml for 4-Bromonitrobenzene), 3 ml (4 ml for 4-Bromonitrobenzene)  $\text{H}_2\text{O}$  and 0.5-1.5 MPa CO were successively charged into the reactor. Then, each autoclave was heated to the required temperature ( $100\text{-}120 \text{ }^\circ\text{C}$ ) and carried out for 1.5-6h.

Qualitative analyses were conducted with a HP 6890/5973 GC-MS with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted with a Agilent 6820 GC equipped with a FID detector.

After reaction gas analyses were carried out with Angilent 1790T gas chromatograph with a molecular sieve 5 A plot column and HP 6890/5973 GC-MS for identification of  $\text{H}_2$  and  $\text{CO}_2$  respectively.

### Characterizations:

Au, Pd and Pt loadings in the catalysts were measured by a 3520 ICP AES instrument of ARL Co. USA. BET surface areas were obtained by physisorption of  $\text{N}_2$  at  $-196 \text{ }^\circ\text{C}$  on a Micromeritics ASAP 2010. Before measurement, samples were outgassed to 0.1 Pa at  $200 \text{ }^\circ\text{C}$  for 2h. The surface composition of the catalysts was examined by XPS (VG ESCALAB 210) with contaminated C as internal standard ( $\text{C}_{1s}=284.6 \text{ eV}$ ). The surface composition of the samples was determined from the peak areas of the corresponding lines using origin fitting. X-ray diffraction was performed with a Siemens D/max-RB powder X-ray Diffractometer. Diffraction patterns were recorded with  $\text{Cu } K\alpha$  radiation (30 mA, 40 kV) and a position-sensitive detector using a step size of  $0.017^\circ$  and a scan step time of 29.845 s. High-resolution scanning transmission electron microscopy (STEM) in high angle annular dark field (HAADF) mode was performed using a JEOL 2010F microscope operating at 200 kV. The powder of catalysts was suspended in ethanol with an ultrasonic dispersion for 5-10 minutes and then the resulted solution was dropped on a carbon film of copper grid.

Table S1 Basic physicochemical properties of the supported Au, Pd and Pt catalysts

Catalysts	Noble metal loading (wt %)	BET surface area (m <sup>2</sup> /g)	Mean pore diameter (Å)	B.E. of Au <sub>4f7/2</sub> , Pd <sub>3d5/2</sub> or Pt <sub>4f7/2</sub> (eV)	Area ratio of Au <sup>+</sup> /Au, Pd <sup>2+</sup> /Pd or Pt <sup>4+</sup> /Pt <sup>2+</sup>
Au/Fe(OH) <sub>x</sub>	1.5	201.8	27.9	83.6, 86.0	0.07
Au/Fe <sub>2</sub> O <sub>3</sub>	1.6	42.4	85.2	83.6	--
Au/Fe <sub>2</sub> O <sub>3</sub> -W	4.4	39.0	109.1	83.6	--
Pd/Fe(OH) <sub>x</sub>	2.8	226.6	26.9	337.7	--
Pt/Fe(OH) <sub>x</sub>	2.2	212.7	29.3	72.6, 74.7	1.8

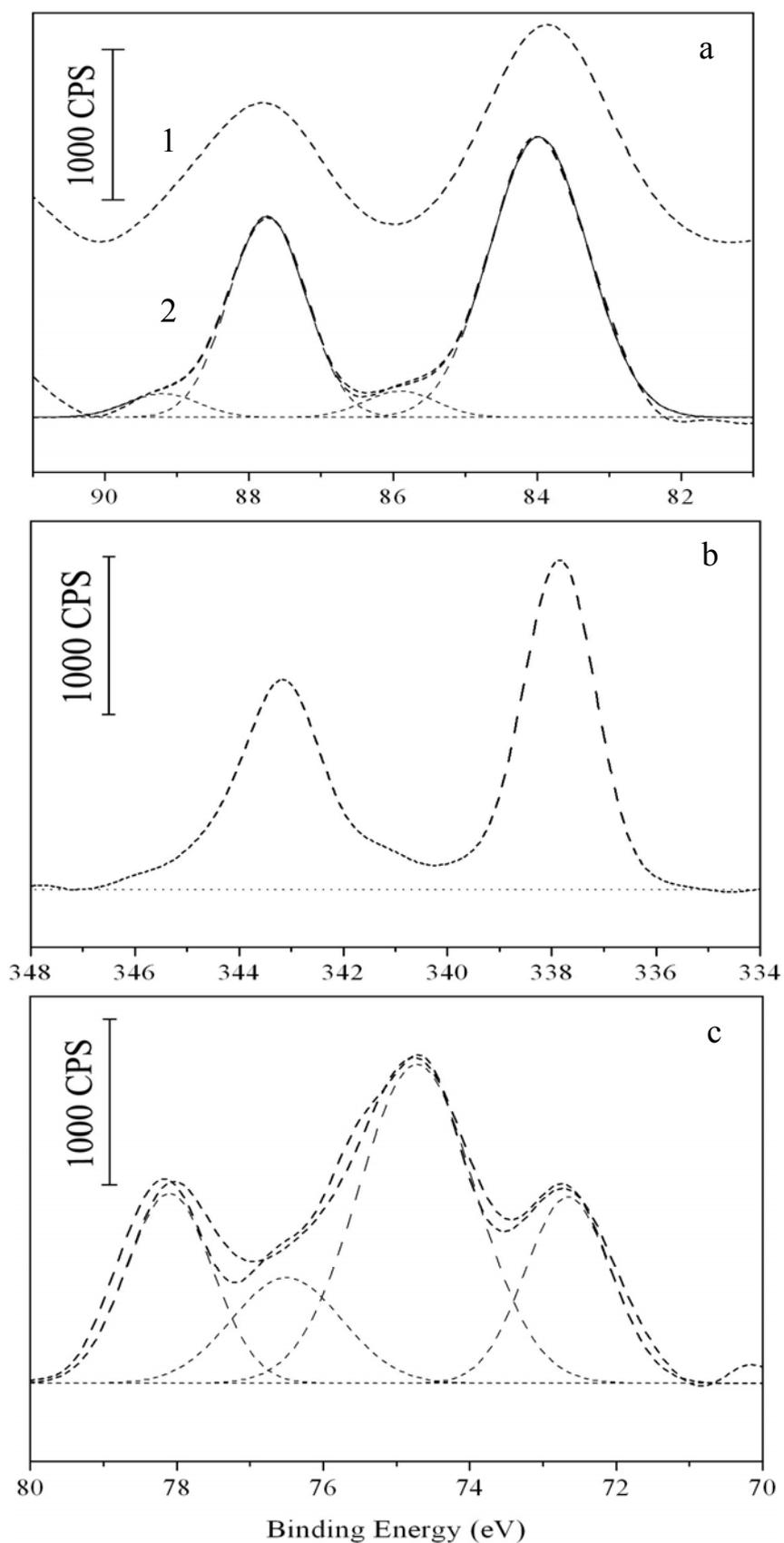


Fig. S1. XPS spectra of supported Au, Pd and Pt catalysts: a (1) 1.5 wt% Au/Fe(OH)<sub>x</sub>, a (2) 1.6 wt% Au/Fe<sub>2</sub>O<sub>3</sub>, b 2.8 wt% Pd/Fe(OH)<sub>x</sub>, c 2.2 wt% Pt/Fe(OH)<sub>x</sub>

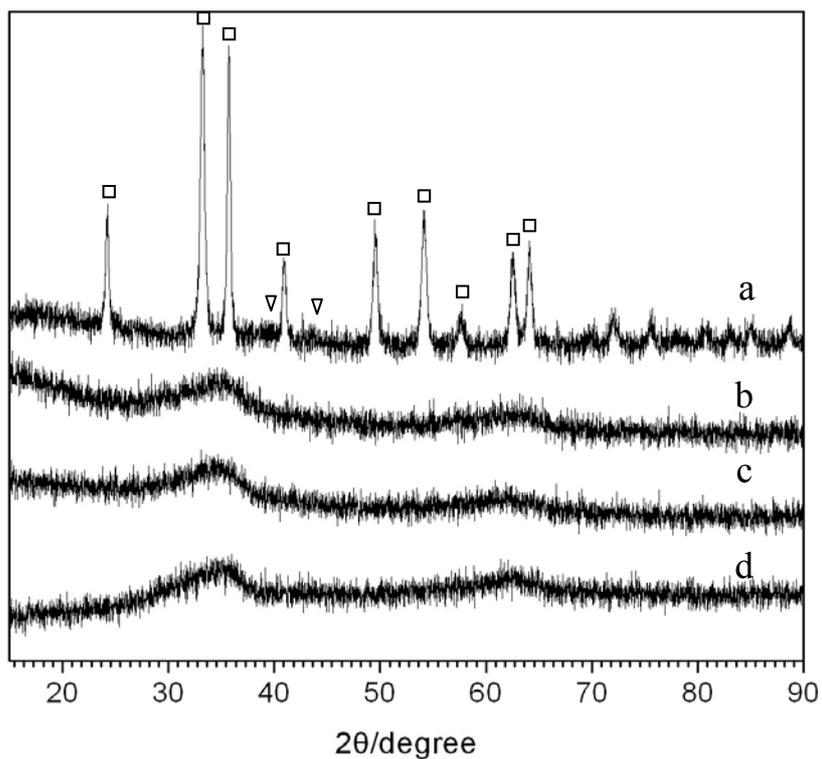


Fig. S2. X-ray diffraction patterns for supported Au, Pd and Pt catalysts: a 1.6 wt% Au/Fe<sub>2</sub>O<sub>3</sub> b 1.5 wt% Au/Fe(OH)<sub>x</sub>, c 2.8 wt% Pd/Fe(OH)<sub>x</sub>, d 2.2 wt% Pt/Fe(OH)<sub>x</sub>. (□) hematite, (▽) metallic gold.

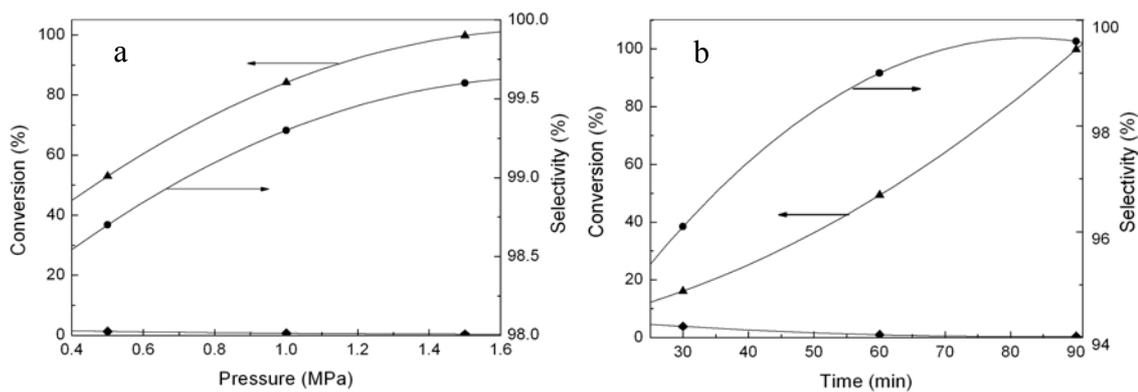


Fig. S3 Kinetic curves for reduction of *p*-nitro acetophenone under different CO pressure (a) and with different reaction time (b). (▲) conversion; (●) Selectivity; (□), Percentage of byproduct.