# Electronic supplementary information

### NH<sub>2</sub>-MIL-125(Ti)-derived porous cages of titanium oxides supported

# Pt-Co alloys for chemoselective hydrogenation reactions

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#### **Experimental Procedures**

#### **Characterization Methods**

Microstructural and morphological characterizations of samples were carried out on a Tecnai F30 transmission electron microscopy (TEM), and a scanning electron microscopy (SEM, HITACHI UHR FE-SEM SU8220). The thickness of samples was measured on an atomic force microscopy (AFM, Park Systems XE-70) with noncontact mode. X-ray diffraction (XRD) was carried out in a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. Surface elemental composition and chemical state of samples were analyzed by X-ray photoelectron spectroscopy (XPS) on Thermo ESCALAB 250Xi with Al-  $K\alpha$  radiation (hv = 1486.6 eV). Brunauer-Emmett-Teller (BET) surface area analysis and porosity measurement in the relative pressure range  $P/P_0 = 0-1.0$  were performed at 77K on an automated adsorption analyzer (Micromeritics Tristar II Plus). Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet 6700 spectrometer. Raman spectroscopy was conducted on a Jobin Yvon LabRAM HR Evolution Raman spectrometer. Hydrogenation products

were analyzed using a gas chromatography-mass spectrometer (GC-MS, Agilent 7890A/5795C).

# Materials

All chemical reagents were used as received. 2-aminoterephthalic acid was purchased from Alfa-Aesar, and other chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

#### **Fabrication of Composite Catalysts**

Synthesis of  $NH_2$ -MIL-125(Ti) ( $Ti_8O_8(OH)_4(bdc$ - $NH_2)_6$ ).  $NH_2$ -MIL-125(Ti) polyhedral nanocrystals were prepared by a modified solvothermal synthetic route<sup>1</sup>. In a typical procedure, a solution (10 mL) containing titanium(IV) isopropoxide (0.177 mL, 0.6 mmol) and 2-aminoterephthalic acid (217 mg, 1.2 mmol) in a mixing solvents of dry DMF and anhydrous CH<sub>3</sub>OH (1:1, v/v) was prepared. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 150 °C for 15 h in an oven with a digital programmable controller. Afterwards, the mixture was cooled to room temperature, and a yellow powder was recovered by centrifugation. The collected powder was washed with DMF to remove the residual organic ligand, and with anhydrous CH<sub>3</sub>OH to exchange DMF. Finally, NH<sub>2</sub>-MIL-125(NH<sub>2</sub>) was dried under vacuum at 100 °C overnight.

Synthesis of Porous Cages of Titanium Oxides (PCT).  $NH_2$ -MIL-125( $NH_2$ ) (10 mg) was dispersed into anhydrous  $C_2H_5OH$  (5 mL) by sonication. Afterwards, the mixture

was added L-alanine (47.5 mg, 0.533 mmol) and then transferred to a 25 mL Teflonlined autoclave with heating at 176 °C for 24 h in an oven. The white precipitate was collected by centrifugation, washed thrice with anhydrous  $C_2H_5OH$ , and dried under vacuum at 80 °C overnight.

The synthetic experiments were performed under the identical otherwise conditions when using glycine, L-lysine and DL-serine to replace L-alanine, respectively. The molar amounts of these amino acids used were 0.533 mmol.

Synthesis of Pt NPs Loaded Porous Cages of Titanium Oxides (Pt/PCT). NH<sub>2</sub>-MIL-125(NH<sub>2</sub>) (10 mg) were dispersed into anhydrous C<sub>2</sub>H<sub>5</sub>OH (5 mL) by sonication, and L-alanine (47.5mg, 0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.8 mg, 3.5 µmol) were added in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 12 h in an oven. The dark gray precipitate was collected by centrifugation, washed thrice with anhydrous C<sub>2</sub>H<sub>5</sub>OH, and dried under vacuum at 80 °C overnight. The product was defined as Pt/PCT\_1.

Pt NPs loaded porous cages of titanium oxides were also prepared at 165 °C under the otherwise identical condition, and the as-made product was defined as Pt/PCT\_2. *Synthesis of Pt-Co NPs Loaded Porous Cages of Titanium Oxides (Pt-Co/PCT)*. NH<sub>2</sub>-MIL-125(NH<sub>2</sub>) (10 mg) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.9 mg, 10 µmol) were added to anhydrous C<sub>2</sub>H<sub>5</sub>OH (5 mL), and after sonication to form a homogeneous suspension, L-alanine (47.5 mg, 0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.8mg, 3.5 µmol) were introduced in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 24 h in an oven. The dark gray precipitate was collected by

centrifugation, washed thrice with anhydrous C<sub>2</sub>H<sub>5</sub>OH, and dried under vacuum at 80 °C overnight.

Synthesis of PtFe NPs Loaded Porous Cages of Titanium Oxides (PtFe/PCT). NH<sub>2</sub>-MIL-125(NH<sub>2</sub>) (10 mg) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (4.0 mg, 10 µmol) were added to anhydrous C<sub>2</sub>H<sub>5</sub>OH (5 mL), and after sonication, L-alanine (47.5 mg, 0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.8mg, 3.5 µmol) were introduced in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 24 h in an oven. The dark gray precipitate was collected by centrifugation, washed thrice with anhydrous C<sub>2</sub>H<sub>5</sub>OH, and dried under vacuum at 80 °C overnight.

Synthesis of Pt-Co NPs Loaded P25 (Pt-Co/P25). P25 (10 mg) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.9 mg, 10  $\mu$ mol) were added to anhydrous C<sub>2</sub>H<sub>5</sub>OH (5 mL), and after sonication, L-alanine (47.5 mg, 0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.8 mg, 3.5  $\mu$ mol) were introduced in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 24 h in an oven. The dark gray precipitate was collected by centrifugation, washed thrice with anhydrous C<sub>2</sub>H<sub>5</sub>OH, and dried under vacuum at 80 °C overnight.

Synthesis of Pt-Co Loaded on TiO<sub>2</sub> (Pt-Co/TiO<sub>2</sub>). Anatase TiO<sub>2</sub> was prepared by a modified synthetic route.<sup>2</sup> The as-synthesized NH<sub>2</sub>-MIL-125(Ti) (~100 mg) was heated to 380 °C with an elevated temperature rate of 5 °C min<sup>-1</sup> and kept at the temperature for 5 h under air atmosphere. Upon naturally cooling down to room temperature, the white powder of anatase TiO<sub>2</sub> was collected.

TiO<sub>2</sub> (10 mg) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.9 mg, 10  $\mu$ mol) were added to 5 mL anhydrous C<sub>2</sub>H<sub>5</sub>OH, and after sonication, L-alanine (47.5 mg, 0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.8 mg, 3.5  $\mu$ mol) were introduced in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 24 h in an oven. The dark gray precipitate was collected by centrifugation, washed thrice with anhydrous C<sub>2</sub>H<sub>5</sub>OH, and dried under vacuum at 80 °C overnight.

*Synthesis of MIL-125(Ti)*. MIL-125(Ti) was obtained according to a reported method.<sup>3</sup> Terephthalic acid (250 mg, 1.5 mmol) and titanium isoproproxide (0.3 mL, 1 mmol) were added into a mixed solvent of dry DMF (4.5 mL) and anhydrous CH<sub>3</sub>OH (0.5 mL). The resultant mixture was gently stirred for 5 minutes prior to transferring to a 25 mL Teflon-lined autoclave and heated at 150 °C for 15 h in an oven. Afterwards, the mixture was cooled to room temperature.

#### Catalytic Hydrogenation of α,β-Unsaturated Aldehydes.

Hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes (equation 1) was carried out in a stainlesssteel reaction vessel (50 mL) with a glass vial (10 mL). A mixture containing catalyst (10 mg), ethanol (6 mL) and substrate (0.4 mmol) was added to the glass vial and encapsulated into the reaction vessel. After flushing with H<sub>2</sub> inside the vessel to remove air, the vessel was purged with H<sub>2</sub> up to the desired pressure. The vessel was kept at the desired temperature with gentle stirring for a certain reaction time. The solution was purified with a filter, and diluted with ethanol before being subjected to gas chromatographic analysis with a mass spectrometer.



# References

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- Wang Z., Li X., Xu H., et al. Porous anatase TiO<sub>2</sub> constructed from a metal-organic framework for advanced lithium-ion battery anodes. *J. Mater. Chem. A* 2014, 2, 12571-12575.
- 3. Dan-Hardi M., Serre C., Frot T., et al. A New Photoactive Crystalline Highly Porous Titanium(IV) Dicarboxylate. *J. Am. Chem. Soc.* 2009, **131**, 10857-10859.



Fig. S1. (a) TEM and (b) SEM images of  $NH_2$ -MIL-125(Ti); (c) corresponding XRD pattern of the sample. All scale bars are 100 nm.



Fig. S2. XRD pattern of PCT prepared by the L-alanine assistant route.



**Fig. S3.** (a) TEM and (b) AFM images of PCT revealing the assembled structures with sheets in thickness range of 10-30 nm; (c) the height cross-sectional profiles of sheets labelled in the AFM image.



**Fig. S4.** TEM images of samples prepared by the L-alanine assistant route under different conditions. (a) 200 °C and (b) introducing additional water (50  $\mu$ L); (c) corresponding XRD patterns of both samples.



Fig. S5. Raman spectra of PCT and Pt-Co/PCT.



Fig. S6. High-resolution XPS spectra of Ti 2p. (a) PCT and (b) Pt-Co/PCT.



**Fig. S7.** N<sub>2</sub> physisorption isotherms at 77 K and pore size distribution of (a, c) PCT and (b, d) Pt-Co/PCT, respectively.



**Fig. S8.** Time-dependent experiments performed to study the possible growth mechanism for the formation of PCT. TEM images of intermediates captured at (a) 1 h, (b) 2 h, (c) 4 h, and (d) 8 h.



Fig. S9. TEM image of sample prepared from  $NH_2$ -MIL-125(Ti) in ethanol without adding any amino acid molecules.



**Fig. S10.** TEM images of (a) MIL-125 and (b) sample prepared by an L-alanine assisted synthetic route for transformation of MIL-125.



Fig. S11. XRD pattern of Pt-Co/PCT.



Fig. S12. TEM image of Pt-Co/PCT showing dispersive Pt-Co NPs and their aggregates.



Fig. S13. HRTEM image of Pt-Co NPs in the Pt-Co/PCT sample.



**Fig. S14.** TEM images and XRD patterns of samples prepared at 176 °C for 24 h with different molar ratio of  $H_2PtCl_6$  to  $Co(NO_3)_2$  by adjusting the amount of  $Co(NO_3)_2$ . (a, d) 3.5 µmol and 3.5 µmol, (b, e) 3.5 µmol and 10 µmol, and (c, f) 3.5 µmol and 20 µmol, respectively.



Fig. S15. (a, b) TEM images with different magnifications, (c) SEM image and (d) XRD pattern of PtFe/PCT prepared by introducing 3.5  $\mu$ mol H<sub>2</sub>PtCl<sub>6</sub> and 10  $\mu$ mol Fe(NO<sub>3</sub>)<sub>3</sub> to the synthetic system.



**Fig. S16.** (a) TEM, (b) SEM, and (c) HRTEM images of Pt/PCT\_1 and (d) corresponding XRD pattern. The inset of (c) is a FFT pattern of the HRTEM image.



**Fig. S17.** Pt/PCT\_2 composites prepared at 165 °C for 12 h: (a) TEM and (b) SEM images and (c) corresponding XRD pattern.



**Fig. S18.** TEM image of sample prepared from the synthetic system of NH<sub>2</sub>-MIL-125(Ti) (10 mg),  $Co(NO_3)_2$  (10 µmol),  $H_2PtCl_6$  (3.5 µmol), and L-alanine (0.533 mmol) at 165 °C for 24 h.



**Fig. S19.** Time-dependent experiments performed to study the possible growth mechanism for the formation of Pt-Co/PCT. TEM images of intermediates captured at (a) 1 h, (b) 2 h, (c) 4 h, and (d) 8 h.



**Fig. S20.** (a) TEM and (b) HRTEM images and (c) XRD pattern of Pt-Co/PCT after six successive catalytic cycles.



**Fig. S21.** SEM and TEM images and XRD patterns of Pt-Co alloys loaded (a, b, c)  $TiO_2$  and (d, e, f) P25, respectively. They were defined as Pt-Co/TiO<sub>2</sub> and Pt-Co/P25, respectively.



**Fig. S22.** XRD patterns of samples prepared while using (1) cobalt layered double hydroxides, (2)  $SiO_2$ , and (3) SBA-15 as supports via the L-alanine assistant route.

These supports (10 mg) and Co(NO<sub>3</sub>)<sub>2</sub> (10  $\mu$ mol) were added to anhydrous C<sub>2</sub>H<sub>5</sub>OH (5 mL), and after sonication, L-alanine (0.533 mmol) and H<sub>2</sub>PtCl<sub>6</sub> (3.5  $\mu$ mol) were introduced in turn. The resultant mixture was transferred to a 25 mL Teflon-lined autoclave and heated at 176 °C for 24 h in an oven.

Cobalt layered double hydroxides were prepared by mixing  $Co(NO_3)_2$  and 2-methylimidazole in methanol and heated at 100 °C for 4 h.



Fig. S23. FTIR spectra of CAL/Pt-Co/PCT, CAL/Pt/PCT\_1 and CAL.

CAL/Pt-Co/PCT (or CAL/Pt/PCT\_1) was prepared by adding CAL and Pt-Co/PCT (or Pt/PCT\_1) into ethanol and stirring for 24 h at room temperature.



**Fig. S24.** Schematic of the possible catalytic CAL process for selective hydrogenation of carbonyl groups by Pt-Co/PCT.

# Appendix 1



**Fig. S25.** Hydrogenation of cinnamaldehyde over different catalysts under 0.2 MPa  $H_2$  at 80 °C for 3 h by GC-MS analysis. (a) Pt-Co/PCT, (b) Pt/PCT\_1, (c) PtFe/PCT, (d) Pt<sub>3</sub>Co/PCT, (e) Pt-Co/TiO<sub>2</sub>, (f) Pt-Co/P25, and (g) Pt/PCT\_2.



**Fig. S26.** Time-dependent hydrogenation of cinnamaldehyde over Pt-Co/PCT under 0.2 MPa  $H_2$  at 80 °C by GC analysis. (a) 0.5, (b) 1, (c) 3, (d) 6, (e) 12, and (f) 24 h.



**Fig. S27.** Recyclability tests of Pt-Co/PCT for catalytic hydrogenation of cinnamaldehyde under 0.2 MPa H<sub>2</sub> at 80 °C for 3 h by GC analysis. (a)  $1^{st}$ ; (b)  $2^{nd}$ ; (c)  $3^{rd}$ ; (d)  $4^{th}$ ; (e)  $5^{th}$  and (f)  $6^{th}$  use of Pt-Co/PCT.



Fig. S28. Hydrogenation of different substrates over Pt-Co/PCT under 0.2 MPa  $H_2$  at 80 °C for 3 h by GC analysis. (a) furfural; (b) 3-methyl-2-butenal and (c) 4-methoxycinnamaldehyde.