Supplementary Information

Hierarchically Structured Porous Organic Polymer Microspheres with Built-in Fe₃O₄ Supraparticles: Construction of Dual-Level Pores for Pt-

Catalyzed Enantioselective Hydrogenation

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Figure S1. SEM images of Fe₃O₄ supraparticles (a), Fe₃O₄@PS microspheres (b), and a series of Fe₃O₄@POP microspheres synthesized with varying the ratios of VBC and DVB (w/w): 70/30 for Fe₃O₄@POP-1 (c), 60/40 for Fe₃O₄@POP-2 (d), 50/50 for Fe₃O₄@POP-3 (e), and 40/60 for Fe₃O₄@POP-4 (f). Insets are the corresponding TEM images with a magnified view.



Figure S2. TEM images of the Pt-loaded Fe_3O_4 @POP composite microspheres prepared by using the various reductants including: (a) NaBH₄, (b) NH₂-NH₂, (c) HCHO, and (d) ethanol.



Figure S3. TEM images of the Pt composite catalysts supported by the Fe₃O₄@POP-1 (a), Fe₃O₄@POP-2 (b), Fe₃O₄@POP-3 (c), and Fe₃O₄@POP-4 (d) microspheres, respectively. The scale bars are 500 nm.

Table S1. The catalytic performance on the hydrogenation of ethyl pyruvate with the $Fe_3O_4@POP-3$ supported Pt catalysts prepared with the different reducing agents.^a The detailed gas chromatograms are shown in Figure S4.

Entry	Reductant	Conversion / %	<i>e.e.</i> /%
1	H_2	16.5	9.2
2	НСНО	99.8	32.8
3	ethanol	99.8	41.7
4	NH ₂ NH ₂	35.1	5.5
5	NaBH ₄	99.7	57.9

^a Pt catalyst: 0.006 mmol; solvent: toluene, 10 mL; reaction time: 20 h; molar ratio of substrate/Pt: 125/1; molar ratio of Pt/CD: 6/1; H₂ pressure: 20 bar.

Table S2. The catalytic performance on the hydrogenation of ethyl pyruvate with the catalysts containing the various contents of Pt nanoparticles.^a The detailed gas chromatograms are shown in Figure S5.

Entry	Catalyst	Conversion /%	ee /%
1	Fe ₃ O ₄ @POP-3-Pt (5 wt%)	80.5	35.2
2	Fe ₃ O ₄ @POP-3-Pt (10 wt%)	99.8	80.7
3	Fe ₃ O ₄ @POP-3-Pt (20 wt%)	99.6	53.3
4	Fe ₃ O ₄ @POP-3-Pt (40 wt%)	99.7	57.9

^a Pt catalyst: 0.006 mmol; solvent: toluene, 10 mL; reaction time: 20 h; molar ratio of substrate/Pt: 125/1; molar ratio of Pt/CD: 6/1; H₂ pressure: 20 bar; reductant: NaBH₄. The Pt contents were determined by the ICP-AES.



Figure S4. GC spectra of the catalysates. The three peaks in each spectrum correspond to the compouds in turn, ethyl pyruvate, (R)-ethyl lactate and (S)-ethyl lactate. Thus the conversion and *e.e.* value for each catalysis reaction could be obtained and were summarized in Table S1.



Figure S5. GC spectra of the catalysates. The three peaks in each spectrum correspond to the compouds in turn, ethyl pyruvate, (R)-ethyl lactate and (S)-ethyl lactate. Thus the conversion and *e.e.* value for each catalysis reaction could be obtained and were summarized in Table S2.

Entry	H ₂ pressure /bar	Conversion /%	<i>e.e.</i> /%
1	1	30.1	35.4
2	10	89.5	55.9
3	20	99.8	80.7
4	30	99.7	63.2
5	40	99.9	54.3

Table S3. The effect of H_2 pressure on the hydrogenation of ethyl pyruvate with the Fe₃O₄@POP-3 supported Pt catalysts (10 wt%).^a

^a Pt catalyst: 0.006 mmol; solvent: toluene, 10 mL; reaction time: 20 h; molar ratio of substrate/Pt: 125/1; molar ratio of Pt/CD: 6/1; reductant: NaBH₄.