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Electronic Supplementary Information (ESI) for

Thermoregulated phase-transfer iridium nanoparticle catalyst: highly selective hydrogenation of C=O bond for α, β-unsaturated aldehydes while C=C bond for α, β-unsaturated ketones

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Experimental Details

Materials and analyses

Iridium (III) chloride ($IrCl_3$, 99.9%, metals basis) was purchased from Alfa Aesar. 1-Pentanol was purchased from Kermel. Cinnamaldehyde (CAL) and other substrates were supplied from Alfa Aesar. All these chemical agents were analytical reagents**.** Thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ (n = 22) was prepared according to the method reported in the literature.[1] The TEM images were taken with a Philips Tecnai G^2 20 TEM at an accelerating voltage of 200 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of metal elements were carried out on Optima 2000DV (Perkin Elmer, USA). Gas chromatography analyses were performed on a Tianmei 7890 GC equipped with a 50 m OV-101 column and an FID detector. GC-MS measurement was performed on a HP 6890 GC/5973 MSD instrument.

Preparation of the iridium nanoparticle catalyst

4 mL of aqueous solution of $IrCl_3$ (6.7×10^{-6} mol), 7.82 mg of thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ (6.7×10^{-6} mol), 4 mL of 1-pentanol were added in a 75 mL teflon-lined standard stainless-steel autoclave and stirred under hydrogen (4 MPa) at 90 °C for 6 h. Then the reactor was cooled to room temperature and depressurized. The color of the aqueous phase changed from light green to brown, indicating the formation of iridium nanoparticles (Ir-NPs) (see Fig. S3).

The reversible phase transfer

The fresh Ir-NPs solution (4 mL) and 1-pentanol (4 mL) were added into a 20 mL Schlenk tube, and then stirred and heated in a 70 ℃ thermostatic oil bath for several minutes under a nitrogen atmosphere. Soon we would observe the Ir-NPs transfer from aqueous to 1-pentanol. After that, the Schlenk tube was cooled to room temperature for enough time, and the Ir-NPs could transfer from 1-pentanol phase to aqueous phase (see Fig. S4).

The chemoselective hydrogenation of cinnamaldehyde

The chemoselective hydrogenation of cinnamaldehyde was carried out in a 75 mL teflon-lined standard stain-steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all experiments. The autoclave was charged with the as-prepared Ir-NPs, water, 1-pentanol, cinnamaldehyde and *n*-decane (as internal standard) and flushed 5 times with 1 MPa H_2. The reactor was pressurized with H_2 up to the required pressure and held at the scheduled temperature for a fixed length of time. Then, the reactor was cooled to room temperature and depressurized. The upper 1-pentanol phase was carefully removed from the lower aqueous phase by syringe and immediately analyzed by GC and GC-MS.

Supplementary Figure

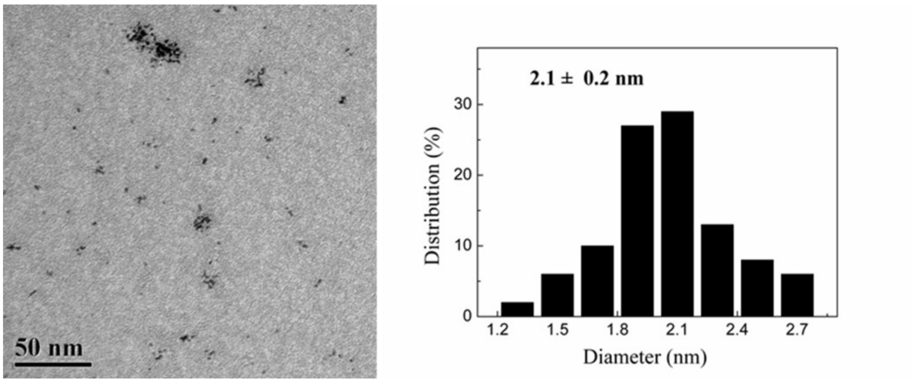

Fig. S1. TEM micrograph and particle size histogram of the Ir-NPs after three cycles

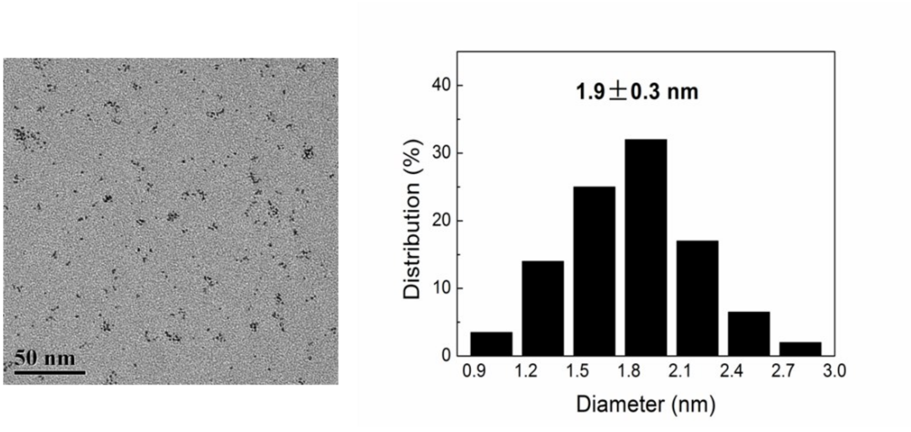

Fig. S2. TEM micrograph and particle size histogram of thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$-stabilized Ir-NPs (Freshly prepared)

Fig. S3. Photograph for the as-prepared Ir-NPs in the aqueous (the lower)/1-pentanol (the upper) biphasic system

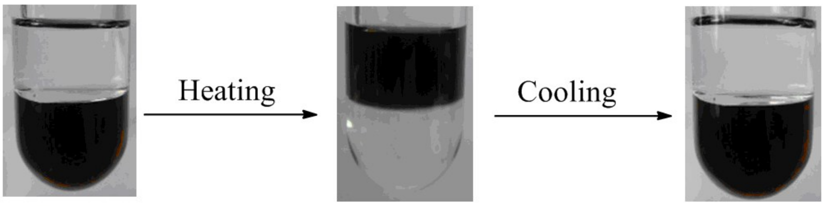

Fig. S4. Phase-transfer photographs for the freshly prepared Ir-NPs in the aqueous (the lower)/1-pentanol (the upper) biphasic system

Table S1 Evaluation of Ir leaching in the reusability experiments

Cycle number	1	2	3	4	5	6	7
Ir leaching (wt. %)	6.5	2.1	1.4	1.1	0.6	0.4	0.5

Table S2 The reusability of the as-prepared Ir-NPs for the chemoselective hydrogenation of CAL.[a]

Entry	Time (min)	Conversion (%)[b]	Selectivity (%)[b,c]
1	30	74	>99
2	30	74	>99
3	40	76	>99
4	90	78	99
5	150	77	99
6	230	73	98
7	390	76	98

[a] Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 6.7×10^{-3} mmol Ir-NPs ($Ph_2P(CH_2CH_2O)_{22}CH_3$/Ir = 1 (molar ratio)), CAL/Ir = 100 (molar ratio), 50 mg of *n*-decane as internal standard, T = 70 ℃, 1 MPa H_2. [b] Determined by GC and GC-MS. [c] Selectivity for cinnamyl alcohol and the main by-product was 3-phenyl-1-propanol.

Supplementary References:

1 M. Solinas, J, Jiang, O.Stelzer and W. A. Leitner, *Angew. Chem., Int. Ed.,* 2005, **44**, 2291-2295.