**Electronic Supplementary Information (ESI) for**

**Thermoregulated phase-separable rhodium nanoparticle catalyst for selective hydrogenation of α,β-unsaturated aldehydes and ketones**

Xiuru Xue, Mingming Niu, Yicheng Xu, Yanhua Wang*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China.

* Corresponding author: *E-mail: yhuawang@dlut.edu.cn; Fax: +86 411 84986033; Tel.: +86 411 84986033.

1. **Materials and analyses**

RhCl₃·3H₂O, cinnamaldehyde, crotonaldehyde, benzylideneacetone and 2-cyclohexen-1-one were purchased from Alfa Aesar. Polyethylene glycol monomethylether 1000 (MPEG-1000) was from Aladdin. Tetraoctyl ammonium bromide (TOAB) and other solvents, such as, toluene, n-heptane and cyclohexane, were purchased from Kermel. Unless otherwise noted, all chemicals were analytical reagents without further purification. Ionic liquid IL_{PEG} (n = 22) was synthesized according to the method reported in the literature.¹ UV-vis measurement was performed on a UV/VIS spectrophotometer. TEM and HRTEM images were carried out by using a Tecnai G² 20 S-TWIN (120 kV) instrument. XRD patterns were acquired on a Panalytical X’Pert Pro MPD diffractometer with Cu Kα radiation (0.15406 nm) at 40 kV and 40 mA. XPS analysis was performed on a Thermo VG ESCALAB 250 Microprobe instrument using Al Kα radiation as the X-ray source. The binding energy of the element was calibrated using a C 1s photoelectron peak at 284.6 eV. GC analyses were performed on Tianmei 7890 GC instrument equipped with an 50 m × 0.25 mm OV-101 column and an FID detector. GC-MS test was performed on a HP6890 GC/5973 MSD instrument with a 30 m × 0.25 mm HP-5MS column (He as a carrier gas). ICP-AES was recorded on Optima 2000 DV (detection limit is 5 μg/L).

2. **Preparation of the TPS-Rh_{nano} catalyst**

RhCl₃·3H₂O (0.68 mg, 2.60 × 10⁻³ mmol) and IL_{PEG} (n = 22, 0.3 g, 0.26 mmol) were added in a 75 mL stainless-steel autoclave and stirred under hydrogen pressure (4 MPa) at 70 °C for 2 h. Then the autoclave was cooled to room temperature and depressurized. The color of the mixture changed from pale yellow to black, indicating the formation of the TPS-Rh_{nano} catalyst.

3. **Selective hydrogenation of α,β-unsaturated aldehydes and ketones**
In a typical experiment, the autoclave was charged with the above-prepared TPS-Rh\textsubscript{nano} catalyst, toluene (3.5 g), \textit{n}-heptane (0.7 g), cyclohexane (0.2 g) and a certain amount of substrate. Then the reactor was replaced three times with 2 MPa H\textsubscript{2} and pressurized with H\textsubscript{2} up to the required pressure at a designated temperature for an appointed time. After reaction, the reactor was cooled to room temperature and depressurized. The upper product phase was analyzed by GC and GC-MS.

5. Supporting figures

\textbf{Fig. S1} XRD of TPS-Rh\textsubscript{nano} catalyst before and after the catalytic reactions

\textbf{Fig. S2} XPS of TPS-Rh\textsubscript{nano} catalyst before and after the catalytic reactions
Fig. S3  GC chromatogram for the model reaction
Fig. S4  GC-MS spectra for the model reaction

5. References