

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

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, cinnamaldehyde, crotonaldehyde, benzylideneacetone and 2-cyclohexen-1-one were purchased from Alfa Aesar. Polyethylene glycol monomethylether 1000 (MPEG-1000) was from Aladdin. Tetrabutyl 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 K α radiation (0.15406 nm) at 40 kV and 40 mA. XPS analysis was performed on a Thermo VG ESCALAB 250 Microprobe instrument using Al K α 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 \times 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 \times 0.25 mm HP-5MS column (He as a carrier gas). ICP-AES was recorded on Optima 2000 DV (detection limit is 5 $\mu\text{g/L}$).

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

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (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_{nano} catalyst, toluene (3.5 g), *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 H₂ and pressurized with H₂ 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

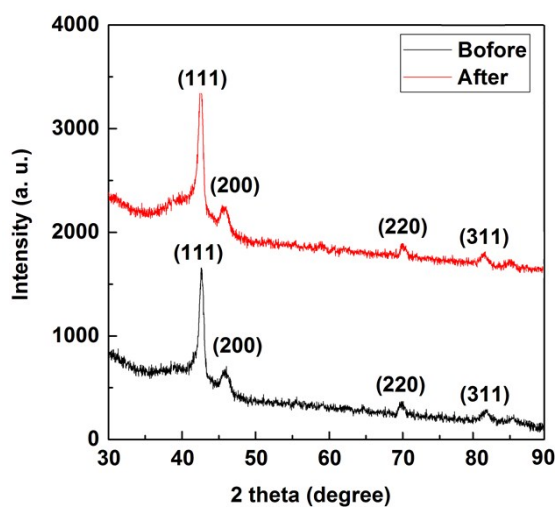


Fig. S1 XRD of TPS-Rh_{nano} catalyst before and after the catalytic reactions

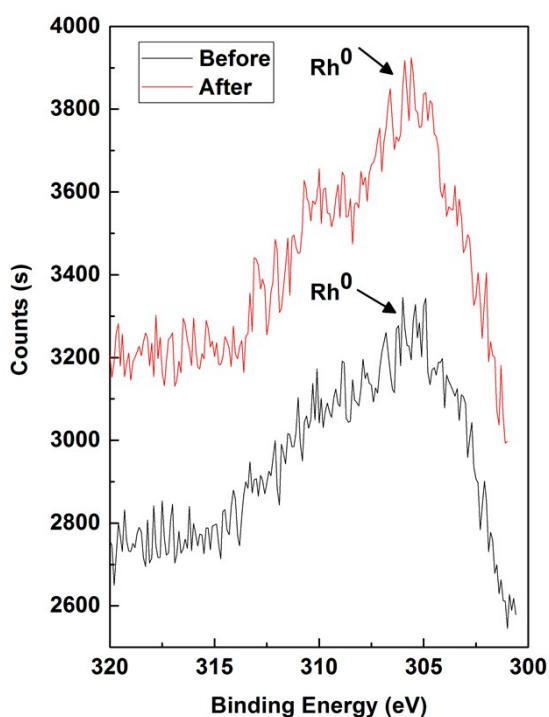


Fig. S2 XPS of TPS-Rh_{nano} catalyst before and after the catalytic reactions

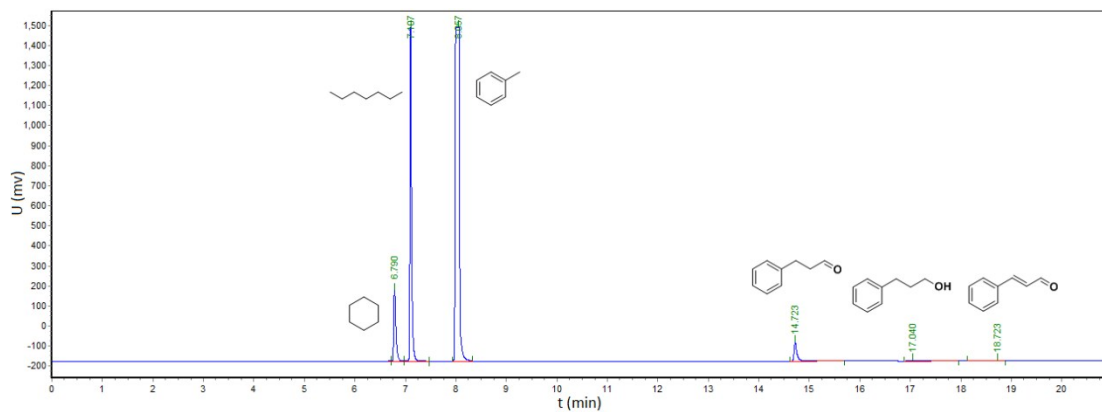
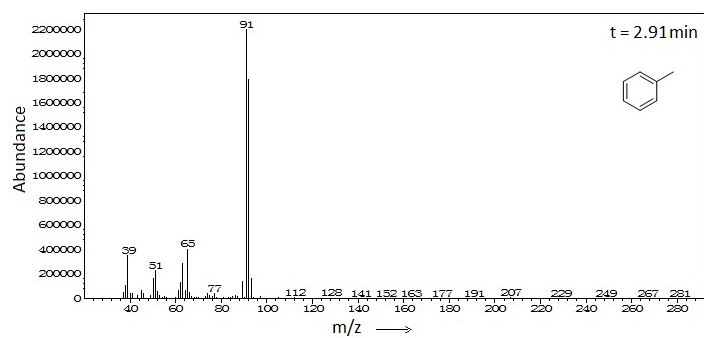
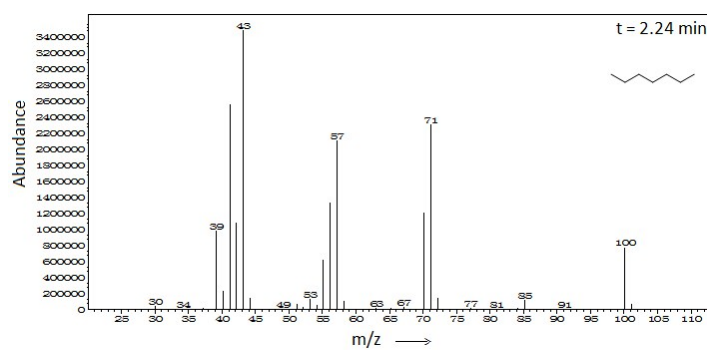
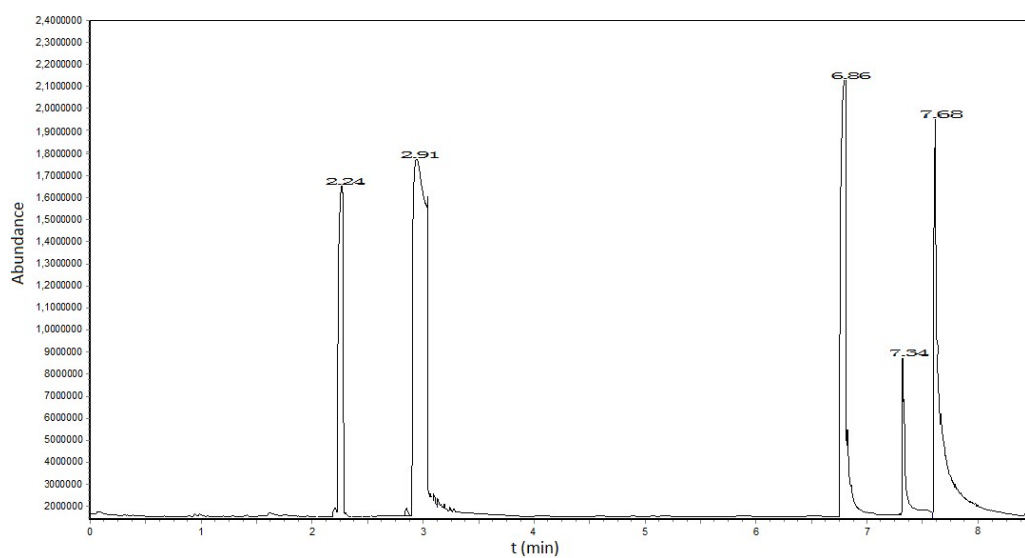


Fig. S3 GC chromatogram for the model reaction



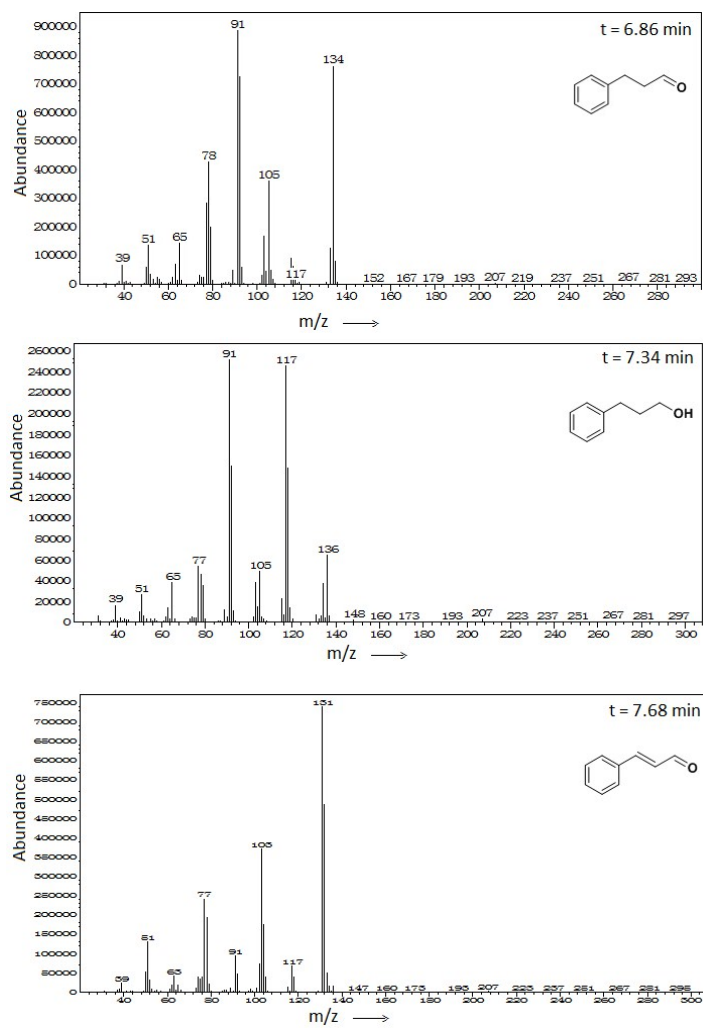


Fig. S4 GC-MS spectra for the model reaction

5. References

- 1 B. Tan, J. Jiang, Y. Wang, L. Wei, D. Chen, Z. Jin, *Appl. Organometal. Chem.*, 2008, **22**, 620.