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High-performance and long-lived Rh nanocatalyst for hydroformylation of styrene

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1. Materials and analyses

RhCl₃•3H₂O (AR) was from Beijing Research Institute of the Chemical Industry. Styrene was purchased from Kermel and was stored in a refrigerator after distilled in vacuum. Cyclohexane was also purchased from Kermel. Syngas (CO/H₂, 99.99%) was from Dalian guangming special gas company. The ionic liquid *N,N*-dimethyl-*N*-(2-(2-methoxyethoxy)ethyl)-2-(2-(2-octyloxyethoxy)ethyl)ammonium methanesulfonate (abbreviated as IL) was synthesized according to the method in the reported literature.¹ 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 analyses were performed on a HP6890 GC/5973 MSD instrument with a 30 m × 0.25 mm HP-5MS column (He as a carrier gas). TEM images were carried out by using a Philips Tecnai G² 20 instrument (200 kV). ICP-AES was recorded on Optima 2000 DV (detection limit is 10 µg/L). FT-IR spectrometer (Nicolet Avatar 360) was conducted by using the KBr disc method.

2. Preparation of the thermoregulated phase-separable Rh nanocatalyst

In a typical experiment, a mixture of IL (5.00 g, 11.2 mmol) and RhCl₃•3H₂O (7.42 mg, 0.028 mmol) was added in a 75 mL standard stainless-steel autoclave. Then the reactor was replaced three times with 2 MPa H₂ and stirred under hydrogen pressure (4 MPa) at 70 °C for 2h. After reaction, the reactor was cooled to room temperature and depressurized. The color of the solution turned from canary yellow into black, indicating the formation of the thermoregulated phase-separable Rh nanocatalyst.

3. Hydroformylation of styrene

In a typical experiment, a mixture of the above thermoregulated phase-separable Rh nanocatalyst (0.06 g, containing 3.39×10^{-4} mmol of Rh), cyclohexane (2.5 g), *n*-decane (0.1 g, as internal standard) and a certain amount of styrene was added in a 75 mL standard stainless-steel autoclave. Then the reactor was replaced three times with 2 MPa H₂ and stirred under the required syngas pressure (CO/H₂ = 1:1, mol/mol) at a designated temperature for an appointed time. After reaction, the reactor was cooled to room temperature and depressurized. The upper product phase was easily separated from the lower catalyst phase and directly analyzed by GC and GC-MS.

4. TEM images of Rh nanocatalyst

The thermoregulated phase-separable Rh nanocatalyst was diluted with ethanol by an ultrasonic

dispersing method. Then, a drop of the solution was placed onto a carbon-coated copper grid and dried at ambient temperature. The TEM images were taken with a Philips Tecnai G² 20 TEM at an accelerating voltage of 200 kV.

5. FT-IR tests

After reaction, 1–2 drops of the thermoregulated phase-separable Rh nanocatalyst were taken onto a dry KBr disc by a clean pipette and been slowly covered by another KBr disc from the side. In this process, it needed to ensure that there has no bubble in the liquid-film. Then the prepared samples were conducted by FT-IR spectrometer at spectrum range of 400–4000 cm⁻¹, scanning times of 32 times, a resolution of 2 cm⁻¹. During the scanning process, it was necessary to avoid the interference of H₂O and CO₂ from the air.

6. Reference

- 1 Y Li., B. Zhao, Y. Wang, J. Jiang, *Sciencepaper Online*, 2009, **3**, 170.