

**Rhodium Nanoparticles Entrapped in Boehmite Nanofibers:
Recyclable Catalyst for Arene Hydrogenation under Mild Conditions**
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General: All Chemicals were purchased from commercial sources and used without further purification. The $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from PMO Pty Ltd (<http://www.precmet.com.au>). The wide-angle XRD pattern was obtained on a MAC Science Co, M18XHF diffractometer with Cu K radiation. The TEM images were taken on a JEOL JEM 2010F (Field Emission Electron Microscope) instrument operated at 200 kV. ^{27}Al MAS NMR spectra were obtained with a Bruker DSX400 spectrometer. The resonance frequency was $\nu_0 = 104.26$ MHz, with a recycling time of 3s and a short pulse time of 1 μs (flip angle $\cong \pi/10$). The spinning frequency was 14 kHz and AlCl_3 ($\delta = 0$ ppm) was taken as a reference.

Synthesis of the Catalyst 1: $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (Rh content: 37.7 w%) (200 mg, 0.732 mmol of Rh), 2-butanol (1.59 g, 21.5 mmol), $\text{Al}(\text{O-}i\text{-sec-Bu})_3$ (4.30 g, 17.5 mmol) were added to a 25 mL round flask equipped with condenser. After being stirred at 100 °C for 3 h to give black suspension, water (1.1 mL) was added dropwise. The reaction mixture was

further stirred at 100 °C for 30 min, then kept at room temperature for the aging. The black solid filtered, washed with acetone and dried at 120 °C oven for 1h to give **1** as dark-gray powder (1.50 g, 5.02 w% of Rh). Rhodium content was analyzed by ICP (Inductively coupled plasma).

We can make the 0.1 ~ 8 w% Rh loaded **1**. There was no activity decrease in high content **1**.

Hydrogenation of anisole at room temperature, 1 atm H₂: To a solution of anisole (54 µL, 0.50 mmol) in hexane (1.0 mL), **1** (10 mg, 1.0 mol%) was added 10 mL round flask, and the reaction mixture was stirred at room temperature for 1 h under a H₂ balloon. The speed of stirring is 550 min⁻¹. The catalyst was filtered then dried in the air for reused. The filtrate was analyzed by gas chromatography with 100 % of hydrogenated product. Turnover frequency defined as moles of H₂ per moles of total metal (not exposed metal) per hour.

Hydrogenation of anisole at 75 °C, 4 atm H₂ (solventless, Sub/Cat = 10000/1):
The anisole (1090 µL, 10.0 mmol), **1** (2.0 mg, 0.01 mol%) was added 15 mL Ace pressure tube, and the reaction mixture was stirred at 75 °C for 30 h under the constant pressure of 4 atm H₂. The speed of stirring is 550 min⁻¹. The catalyst was filtered then

dried in the air for reused. The filtrate was analyzed by gas chromatography with 100 % of hydrogenated product. Turnover frequency defined as moles of H₂ per moles of total metal (not exposed metal) per hour.

When we checked the reaction mixture during the reaction, the partial hydrogenated product (15 %) was detected by gas chromatography and ¹H NMR (After 18 h).

