Acceptor-free Alcohol Dehydrogenation by Recyclable Ruthenium Catalyst

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Supporting Information

Synthesis of ruthenium catalyst 1: RuCl₃·xH₂O (Precious Metals Online: 52 mg, 0.25 mmol), (*sec*-BuO)₃Al (2.5 g, 10 mmol) and ethanol (1.2 mL, 20 mmol) were added into 25 mL round bottom flask equipped with condenser. After the mixture was stirred at 100 °C for 1 h to give black suspension, water (2.0 mL) was added quickly. The reaction mixture was stirred further for 30 min at 100 °C. The resulting black solid was filtered, washed with acetone, and dried in the air at room temperature to give **1** as grey powder (0.74 g; 2.5 wt % of Ru).

Dehydrogenation of 1-phenylethanol: In a 50 mL flask equipped with a grease-free high vacuum stopcock and connected to a bubbler, **1** (121 mg, 3.0 mol % Ru) and 1-phenylethanol (122 mg, 1.00 mmol) were mixed with dry toluene (5 mL) under argon atmosphere. The reaction mixture was heated at 80 °C for 10 h. The catalyst was filtered and washed with acetone. Solvent was removed from the filtrate under reduced pressure to give analytically pure acetophenone (120 mg, >99%).

Recycling of 1: A suspension of **1** (121 mg, 3.0 mol % Ru) and 1-phenylethanol (122 mg, 1.00 mmol) in toluene (5 mL) was stirred at 80 °C for 10 h in a flask equipped with a grease-free high vacuum stopcock and connected with bubbler under Ar. After the reaction, **1** was recovered by filtration and was reused after washing with acetone and drying in the air at room temperature.

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Characterization of 1: The catalyst **1** was characterized by transmission electron microscopy (TEM). A distinct fibrous morphology is shown in the TEM images (Figure 1 and 2). The catalyst **1** was also characterized by energy dispersive X-ray spectrometer (EDX) and X-ray photoelectron spectroscopy (XPS). EDX showed the presence of Ru (Figure 3), but Cl was not detected. The XPS data for **1** was collected on an ESCALab250 spectrometer operating at 15 kV and 20 mA at a pressure of about 5×10^{-10} mbar with $\text{Al}_{K\alpha}$ radiations as the excitation source ($h\nu = 1486$ eV). Figure 4 shows the Ru 3d spectrum of **1**. Although the Ru 3d signal is obscured by the C 1s signal of a carbon contaminant, the spectrum shows a doublet for two chemically different Ru entities with peak binding energies of 279.7 eV (Ru 3d_{5/2}) and 284.0 eV (Ru 3d_{3/2}), which confirms the presence of Ru(0) in catalyst **1**. Meanwhile, the peak at 281.2 eV suggests the presence of a Ru-O component, which probably results from oxidation of the ruthenium during preparing **1**. The specific surface area of **1** was determined to be 424.7 m²/g by the N₂ BET method at 77 K.

Figure 1. Low resolution TEM image of **1**.

Figure 2. High resolution TEM images of **1**.

Figure 1. EDX analysis of **1**.

Figure 2. XPS spectra of **1**.