Electronic Supplementary Information

Pd-MCM-48: A novel recyclable heterogeneous catalyst for chemoand regioselective hydrogenation of olefins and coupling reactions

Subhash Banerjee*, Vagulejan Balasanthiran, Ranjit T. Koodali* and Grigoriy A. Sereda*

414 E. Clark Street, Department of Chemistry, The University of South Dakota, Vermillion, SD 57069 USA

Synthesis of Pd(0) Nanoparticles

Pd(0) nanoparticles were synthesized according to the published procedure by the reduction of Na₂PdCl₄ with NaBH₄ in the presence of tetra-*n*-octylammoniumbromide (TOAB) as a capping and stabilizing agent. Briefly, a 9.6 mL portion of a 47 mM aqueous solution of Na₂PdCl₄ (yellow color) was mixed with 40 mL of a 50 mM solution of TOAB dissolved in toluene and stirred at 300 rpm for 15 minutes. A red–brown color organic solution and the colorless aqueous phase were observed due to the complete transfer of Na₂PdCl₄ to the organic phase. The colorless aqueous phase was separated and the toluene phase was dried over Na₂SO₄. Then, 11.4 mL of a freshly prepared 0.5 (M) NaBH₄ aqueous solution was added drop by drop for a period of two hours under vigorous stirring. The mixture was stirred overnight, and subsequently washed with 40 mL of a 0.1 M H₂SO₄ aqueous solution, 40 mL of a 0.1 M NaOH aqueous solution, and 40 mL of water. Finally the organosol was dried over anhydrous Na₂SO₄.

Transfer of Pd(0) nanoparticles to the aqueous phase

The aqueous 0.1 M 4-dimethylaminopyridine (DMAP) solution (10 mL) used as a phase transfer agent was prepared by dissolving 0.1 g of DMAP in 10 mL of deionized water. Next, this solution was added to 40 mL of the as-synthesized Pd nanoparticles solution in toluene. The mixture was stirred for 2 h to complete transfer of the Pd nanoparticles to the aqueous phase.

Characterization of Catalyst 1:



Figure 1 Nitrogen adsorption-desorption isotherm of catalyst 1 (0.6 wt %).



Figure 2 Pore size distribution of catalyst **1** (calculated from the Barrett-Joynder-Halenda equation using desorption isotherm) confirmed the pore size distribution is narrow and sizes around 2.5 nm.

Textural properties of Pd-MCM-48 (catalyst 1) have been presented below:

Sample Name	Multipoint BET	Pore volume	Desorption	Amount of Pd
	(m^2g^{-1})	(ccg^{-1})	pore diameter	(%) (AAS study)
			(nm)	
Pd-MCM-48 (0.6 wt	1800	0.94	2.5	0.6
%)				

CO-Pulse (Chemisorption) studies of catalyst 1:

Sample Name	Pd dispersion (%)	Surface area/g of metal (m^2g^{-1})
Pd-MCM-48 (0.6 wt %)	22	95.3

Synthesis of Catalyst 2:

The catalyst **2** was synthesized by depositing a Pd-salt on the pre-prepared MCM-48. First MCM-48 was synthesized using the following procedure. In a typical synthesis, 50 mL deionized water, 25 mL ethanol, 1.2 g (3.3 mmol) of CTAB, 6 mL of aq. NH₃ (0.09 mol) and 1.8 mL (8 mmol) of TEOS were sequentially added to a 125 mL polypropylene bottle and stirred for 4 h at a stir rate of 300 rpm. The molar composition of the initial siliceous gel is 0.41 CTAB: 11 aq. NH₃: 1.0 TEOS: 53 Ethanol: 344 H₂O. After 4 h, the material was washed extensively with deionized water, and dried overnight at 100 °C. The dried material was finely ground with a mortar and pestle and calcined at 550 °C (ramp rate of 3 °C per minute) for 6 h in an alumina crucible to remove the surfactant molecules. Next, the appropriate amount of Na₂PdCl₄, 15 ml ethanol and 5 ml water were stirred for 2 h. The material was again dried overnight at 100 °C finely ground with a mortar and pestle and calcined at 550 °C (ramp rate of 3 °C per minute) for

6 h in an alumina crucible to remove the surfactant molecules. The calcined Pd-MCM-48 may contain Pd in the +2 oxidation state. Hence they were reduced in hydrogen flow (20 mL/ min) at 300 ^oC for 2 h in a tubular furnace.

Scanned copy of ¹H NMR spectra of all products and ¹³C NMR spectra of selected products:



















¹³C NMR: Scheme 2, Product A



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¹H NMR: Scheme 2, Product **B**







































Reusability of the catalyst 1 for the hydrogenation of cinnamic acid:

The reusability of the catalyst **1** was checked for the hydrogenation of cinnamic acid as model reaction. The catalyst was reused up to ten times without loss of its activity. The powder XRD studies indicate that the cubic phase of MCM-48 was remained unchanged even after the 8th run. The activity of the catalyst was checked up to 10th cycle and the results are presented in the Table below:

Entry	Time (min.)	Conversion (%) ^a
1	30	100
2	30	100
3	30	100
4	45	100
5	45	100
6	60	100
7	60	98
8	60	90
9	60	85
10	90	80

Table 6 (a): Reusability of catalyst 1 for the hydrogenation of cinnamic acid

^aConversion was determined by the analysis of ¹H NMR spectra.

Table 6 (b): Reuse of catalyst 1 for the Heck reaction of iodobenzene with n-butyl acrylate

Entry	Time (h)	Conversion (%) ^a
1	5	98
2	5	95
3	6	80
4	6	70

^aConversion was determined by the analysis of ¹H NMR spectra.