Journal of Molecular Catalysis A: Chemical 307 (2009) 142–148

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Preparation and catalytic studies of palladium nanoparticles stabilized by dendritic phosphine ligand-functionalized silica

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ARTICLE INFO

Article history:
Received 5 December 2008
Received in revised form 11 March 2009
Accepted 12 March 2009
Available online 25 March 2009

Keywords:
Dendrimer
Heterogeneous catalysis
Hydrogenation
Palladium nanoparticle
Solid support

ABSTRACT

Silica is a prominently utilized heterogeneous metal catalyst support. Functionalization of the silica with poly(ether imine) based dendritic phosphine ligand was conducted, in order to assess the efficacy of the dendritic phosphine in reactions facilitated by a silica supported metal catalyst. The phosphinated poly(ether imine) (PETIM) dendritic ligand was bound covalently to the functionalized silica. For this purpose, the phosphinated dendritic ligand containing an amine at the focal point was synthesized initially. Complexation of the dendritic phosphine functionalized silica with Pd(COD)Cl_2 yielded Pd(II) complex, which was reduced subsequently to Pd(0), by conditioning with EtOH. The Pd metal nanoparticle thus formed was characterized by physical methods, and the spherical nanoparticles were found to have >85% size distribution between 2 nm and 4 nm. The metal nanoparticle was tested as a hydrogenation catalyst of olefins. The catalyst could be recovered and recycled more than 10 times, without a loss in the catalytic efficiency.

1. Introduction

Studies on solid supports present a significant importance in heterogeneous organometallic catalysis [1,2]. Alumina, silica, carbon and MCM types are the most commonly adopted solid supports, in order to impregnate or immobilize metal catalysts. Traditionally, solid supports are known to facilitate the catalyst recovery and recycling. Many developments further have shown that solid supported catalysts mediate reactions resulting in higher selectivities in the products formed. Functionalization of the solid supports with suitable chelating ligands is emerging as a viable strategy to circumvent not only the pertinent metal catalyst deterioration and leaching limitations, but also to stabilize the metal particles and to adjust their catalytic efficiencies. Various types of functionalization of the silica with ligands are reported previously. Few pertinent examples are: (i) phosphino ferrocene [3]; (ii) phosphino phenoxazine [4]; (iii) Schiff-bases from 3-amino propyl silica and pyridine, thiophene, furan, pyrrole and acetophenone derivatives [5–7]; (iv) amino propyl moieties [8]; (v) urea-cross-linked imidazolium derivative [9–11] and (vi) (P, N) ligands constituted with bis-phosphinoamino moiety, diphenylphosphino pyridine moiety and Schiff-base from 3-aminopropyl silica and a diphenylphosphine derivative of phenyl ethanone [12,13]. Each of these ligands, functionalizing the silica, was used to form the palladium metal catalyst. The resulting silica bound catalysts were found to exhibit considerable increases in the catalytic efficiencies and selectivities in chosen reactions, as well as, their recoverabilities and reusabilities. Functionalization of silica with the newly emerged dendritic ligands has been demonstrated in recent years. In a series of pioneering work, Alper and co-workers reported not only the facile synthesis of poly(amido amine) series of dendrimers on the silica support, but also further functionalization of the dendritic moieties with phosphine ligands and palladium metal complexes [14–16]. These dendritic metal complexes on silica support were shown to lead higher product selectivities and recyclabilities. In continuing our work in the area of poly(propyl ether imine) (PETIM) dendrimers [17–22], we tested the functionalization of silica with a phosphinated PETIM dendrimer, followed by the formation of a palladium metal catalyst and studies of the catalytic reactions. In the event, we identify that the functionalization of silica with a phosphinated PETIM dendrimer provides an ability to form smaller size distribution of metal particles and their subsequent profound catalytic efficiencies. Functionalization of the silica support with diphenylphosphinomethyl-derivatized dendritic amine, palladium nanoparticle formation and the catalytic studies are described herein.

2. Experimental

2.1. General

Solvents were dried and distilled according to the literature procedures [23]. The amine functionalized dendrimer **1** [17] and

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doi:10.1016/j.molcata.2009.03.020

$PdCODCl_2$ [24] were synthesized according to known procedures. The olefin substrates were used as received or treated through a short column of activated alumina. In case of phosphine compounds, the experiments were performed under an inert gas atmosphere. FT-IR spectra were recorded as the KBr sample. ^{13}C, ^{29}Si and ^{31}P solid state NMR spectral analyses were performed on a spectrometer operating at 75.4 MHz, 59.6 MHz and 121.4 MHz, respectively. The following abbreviations are used to explain the multiplicities: s, singlet; m, multiplet; band, several overlapping signals; b, broad. Elemental analysis was performed using an automated CHNS analyzer. For ICP-OES analysis, samples were digested in $HCl:HNO_3 = 3:1$ and heated for 1 h, diluted with H_2O and analyzed for Pd content. ICP-OES measurements were performed at 340.98 nm, with Pd standard. XPS was recorded using Al Kα radiation (1486.6 eV). Binding energies were calibrated with respect to C(1s) at 284.5 eV, with a precision of 0.2 eV. For TEM analysis, an acetone dispersion was drop-cast onto a carbon coated copper grid, and TEM observations were performed. Gas chromatographic analyses were performed by flame ionization gas chromatography (FID).

2. To a solution of G1 amine **1** [17] (1.5 g, 2.53 mmol) in H_2O (40 mL), a solution of Boc_2O (0.14 g, 0.63 mmol) in H_2O:THF (2:1, 15 mL) was added dropwise, at room temperature, stirred for 24 h. The reaction mixture was extracted first with Et_2O (2× 30 mL), then separately with CH_2Cl_2 (2× 30 mL) and $CHCl_3$ (2× 30 mL). The combined CH_2Cl_2 and $CHCl_3$ portions were concentrated, diluted with $CHCl_3$ (30 mL), washed with water (10 mL), dried (Na_2SO_4), solvents evaporated *in vacuo* and dried to afford **2**, as an oil. Yield: 0.33 g (75%); FT-IR (neat) ν: 3365, 3297, 2935, 2859, 2801, 1712, 1469, 1367, 1171, 1115; ^1H NMR (300 MHz, $CDCl_3$): δ 5.11 (b s, 1H), 3.50–3.38 (m, 20H), 3.24–3.18 (m, 2H), 2.83–2.79 (m, 6H), 2.49–2.45 (m, 18H), 1.76–1.64 (m, 20H), 1.44 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 156.0, 78.9, 69.2, 69.0, 50.7, 39.6, 38.6, 33.3, 33.1, 33.0, 29.8, 29.6, 28.4, 27.4; HRMS *m*/*z*: 693.5859 $[M+H]^+$; calcd for $C_{35}H_{77}N_6O_7$: 693.5854.

3. A mixture of diphenylphosphine (1.02 g, 5.45 mmol) and paraformaldehyde (0.17 g, 5.32 mmol) in MeOH (10 mL) was heated at 70 °C for 10 min. The reaction mixture was cooled to room temperature and treated with a solution of **2** (0.6 g, 0.87 mmol) in MeOH (10 mL). After 0.5 h, PhMe (20 mL) was added and the solution heated at 65 °C for 0.5 h, and then stirred at room temperature for 12 h. The reaction mixture was concentrated *in vacuo* and hexane (20 mL) was added. The product precipitated, which was collected and dried at 60–65 °C for 10 h, to afford Boc-protected **3**, as a colorless foamy solid. Yield: 1.43 g (88%); FT-IR (neat) ν: 3316, 3053, 2942, 2861, 2803, 1708, 1482, 1437, 1174, 1119, 742, 696; ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.36 (m, 24H) 7.27 (band, 36H), 5.05 (b s, 1H), 3.54 (s, 8H), 3.47–3.38 (m, 12H), 3.26–3.09 (m, 14H), 2.94–2.86 (m, 6H), 2.64 (band, 12H), 1.76–1.54 (m, 20H), 1.42 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 156.0, 138.2, 138.0, 133.1, 132.9, 130.7, 130.6, 78.6, 68.8, 68.7, 68.5, 58.8, 58.7, 52.9, 50.6, 29.8, 28.4, 26.8, 26.5, 26.3–25.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ −28.4; ESI-MS *m*/*z*: 1919.1692 $[M+O+Na]^+$; calcd for $C_{113}H_{142}N_6O_8P_6Na$: 1919.9213.

To a solution of the above Boc-protected **3** (1.2 g, 0.64 mmol) in CH_2Cl_2 (70 mL), TFA (2.8 mL, 38.3 mmol) was added and the solution stirred at room temperature for 4 h. The reaction mixture was washed with saturated aq. $NaHCO_3$ (2× 30 mL), brine (2× 30 mL), the organic portion dried (Na_2SO_4) and concentrated to afford **3**, as a colorless gum. Yield: 1.05 g (92%); FT-IR (neat) ν: 3402, 3052, 2942, 2861, 2803, 1482, 1437, 1174, 1119, 741, 695. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–7.35 (m, 24H), 7.27 (band, 36H), 3.54 (d, *J* = 3 Hz, 8H), 3.48–3.39 (m, 16H), 3.26–3.19 (m, 12H), 2.91 (band, 6H), 2.66 (b, 12H), 1.77–1.59 (m, 20H), 1.61 (band, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 138.1, 137.9, 133.0, 132.8, 130.6, 130.4, 128.3, 128.2, 68.7, 68.3, 58.7, 50.6, 29.5, 26.7, 26.5, 26.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ −28.4.

4. A mixture of silica (3 g, 9.5–11 µm, pore volume 50–76 Å, surface area 475–560 $m^2\,g^{-1}$) and $(MeO)_3Si(CH_2)_3Cl$ (6.5 g, 32.6 mmol) in PhMe (100 mL) was refluxed for 8 h. The solvents were removed *in vacuo* and the residue was admixed again with $(MeO)_3Si(CH_2)_3Cl$ (6.5 g, 32.6 mmol) and PhMe (100 mL) refluxed for 8 h and the solvents removed *in vacuo*. Treatment with $(MeO)_3Si(CH_2)_3Cl$ was repeated once more the reaction mixture was refluxed for 8 h and then solvents removed *in vacuo*. The resulting residue was washed with CH_2Cl_2 (5× 15 mL) and dried at 60 °C for ∼10 h, to afford **4** (3.5 g). ^{13}C NMR: δ 50.7 (OCH_3), 47.7 (CH_2Cl), 27.6 ($CH_2CH_2CH_2$), 8.8 ($SiCH_2$); ^{29}Si NMR: δ −112.3; Anal. found: C 5.55, H 1.78. Loading of methoxychloropropyl group onto silica was estimated to be 1.16 mmol/g of silica, calculated on the basis of elemental analysis.

5. A mixture of **3** (1.0 g, 67.6 mmol) and **4** (1.5 g) in $CHCl_3$ (60 mL) was refluxed for 24 h, solvents were then removed *in vacuo*. The residue was washed with $CHCl_3$ (5× 10 mL), MeOH (3× 10 mL), and dried to afford **5** (1.6 g). FT-IR (KBr): ν 3437, 2948, 1482, 1436, 1100, 804, 742, 696; ^{13}C NMR: δ 128.8 (PPh_2), 68.7 (CH_2O), 51.3 (CH_2N), 27.2 ($CH_2CH_2CH_2$), 9.6 ($SiCH_2$); ^{31}P NMR: δ −28.4; ^{29}Si NMR: δ −112.3; Anal. found: C 7.50, H 1.82, N 2.02. Loading of phosphinated dendritic amine onto silica was 0.24 mmol/g of silica, calculated on the basis of elemental analysis.

5-Pd(II) complex A suspension of **5** (0.74 g) in THF (20 mL) was admixed with $Pd(COD)Cl_2$ (0.17 g, 0.59 mmol) and stirred at room temperature for 24 h. The reaction mixture filtered, washed with THF (6× 10 mL), CH_2Cl_2 (6× 10 mL) and dried for ∼6 h at 50 °C, to afford **5**-Pd(II) complex (0.74 g). ^{13}C NMR: δ 130.2 ($PdCl_2PPh_2$), 68.1 (CH_2O), 51.5 (CH_2N), 26.5 ($CH_2CH_2CH_2$), 9.9 ($SiCH_2$); ^{29}Si NMR: δ −110.6; ^{31}P NMR: δ 13.9. Loading of Pd by ICP-OES analysis: 0.43 mmol/g of silica; XPS: 337.6 eV (Pd $3d_{5/2}$), 342.9 eV (Pd $3d_{3/2}$).

6. A mixture of **5**-Pd(II) complex (0.74 g) and EtOH (100 mL) was refluxed for 24 h, filtered and the residue washed with EtOH (5× 20 mL), dried for 8 h, at 60 °C, to afford the metal nanoparticle-silica composite **6** (0.71 g). ^{13}C NMR: δ 9.2 ($SiCH_2$), 25.4 ($CH_2CH_2CH_2$), 50.5 (CH_2N), 66.6 (CH_2O), 129.9 ($OPPh_2$); ^{29}Si NMR: δ −111.7; ^{31}P NMR: δ 12.9, 29.6. Loading of Pd by ICP-OES: 0.40 mmol/g of silica; XPS: 335.6 eV (Pd $3d_{5/2}$), 340.7 eV (Pd $3d_{3/2}$) and 337.5 eV (Pd $3d_{5/2}$), 342.6 eV (Pd $3d_{3/2}$).

2.2. *General procedure of hydrogenation*

A stainless steel reactor (50 mL) was charged with the olefin substrate (1 mmol), **6** (0.5 mol %) and EtOAc (5 mL). The autoclave was closed and maintained at H_2 (g) pressure of 1 atm. The mixture was stirred at 25 °C and the progress of the reaction was monitored by GC. Upon completion of the reaction, the mixture was centrifuged, the precipitate washed with EtOAc (5× 5 mL), dried at 50 °C, and used again in the recycling experiments.

3. Results and discussion

Functionalization of silica with a first generation phosphinated dendritic amine was desired, as the dendritic amine is pre-formed, requiring a protection and a deprotection step, before its attachment to the solid support. A nucleophilic substitution is a commonly adopted reaction for the functionalization of amines onto silica [25,26]. The phosphinated dendritic amine ligand was prepared according to Scheme 1.

The amine terminated first generation PETIM dendrimer **1** was synthesized by following the reported procedure [17]. The mono-protection of an amine group in **1** was conducted using di-*tert*-butyl dicarbonate (Boc_2O), in water:THF solution for 24 h. The reaction afforded the mono-protected dendrimer **2**, in 75% yield. Double phosphinomethylation of **2** was performed using *in situ* formed PPh_2CH_2OH, which was prepared from $HPPh_2$ and HCHO [27,28], to afford the phosphinated dendron, in 88% yield. The protecting group was removed subsequently to afford **3**, in 92% yield. The IR spectrum of **3** exhibited disappearance of the vibrational peak, corresponding