Palladium Nanoparticles Supported on Ionic Liquid Modified, Magnetic Nanobeads – Recyclable, High-Capacity Catalysts for Alkene Hydrogenation

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1. Materials and methods

Carbon coated cobalt nanomagnets (Co/C, 20.5 m\(^2\)/g, mean particle size \(\approx 25\) nm) were purchased from Turbobeads Llc, Switzerland. Prior to use, they were washed in a concentrated HCl / water mixture (1:1) 5 times for 24 h. Acid residuals were removed by washing with millipore water (5x) and the particles were dried at 50°C in a vacuum oven.\(^1\) All other commercially available compounds were used as received.

The magnetic nanobeads were dispersed using an ultrasound bath (Sonorex RK 255 H-R, Bandelin) and recovered with the aid of a neodymium based magnet (15 x 30 mm). They were characterized by IR-ATR spectroscopy (Biorad Excalibur FTS 3000), elemental microanalysis (LECO CHN-900), transmission electron microscopy (CM30 ST-Philips, LaB\(_6\)cathode, operated at 300 kV point resolution \(\sim 4\) Å), x-ray powder diffraction, and inductively coupled plasma optical emission spectrometry (Spectro Analytical Instruments ICP Modula EOP).

Poly(benzylchloride)styrene coated cobalt nanoparticles \(^5\)\(^2\) and benzyl-alcohol functionalized cobalt nanoparticles \(^7\)\(^3\) were prepared on the gram scale following previously reported procedures.

Pd\(_2\)(dba)\(_3\)·CHCl\(_3\) was purchased (Sigma-Aldrich) and used as received. As determined by the procedure reported by Ananikov et al.\(^4\), the ratio of Pd\(_2\)(dba)\(_3\):dba was 1:0.46, which reflects that 68% of the Pd content is present as Pd\(_2\)(dba)\(_3\), while 32% of the Pd content are already present as Pd nanoparticles.

A solution of Na\(_2\)PdCl\(_4\) in water (conc. 1 mg Pd per mL) was freshly prepared by mixing PdCl\(_2\) (1 eq.) with NaCl (2 eq.) in H\(_2\)O using an ultrasound bath for 30 min.

NMR spectra were recorded with a Bruker AV 300 spectrometer with CHCl\(_3\) as standard. Chemical shifts (\(\delta\)) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The signals in the spectra are described as d (doublet), t (triplet), and m (multiplet).

Gas chromatography was recorded on Fisons Instruments GC8000 equipped with a capillary (30 m x 250 µm x 0.25 µm) and flame ionization detector.

2. Nomenclature of the nanobeads

The nomenclature of the nanobeads is as follows:

- **Co/C** carbon coated cobalt nanoparticles
- **PS-IL@Co/C** poly(benzyl-methyl imidazolium chloride)styrene functionalized carbon coated cobalt nanoparticles
- **Bz-IL@Co/C** benzyl-methyl imidazolium chloride functionalized carbon coated cobalt nanoparticles
- **Spacer-IL@Co/C** benzamidopropyl-butyl-imidazolium bromide functionalized carbon coated cobalt nanoparticles
- **IL@Co/C** PS-IL@Co/C, Bz-IL@Co/C, and Spacer-IL@Co/C
- **Pd@PS-IL@Co/C** Pd NPs deposited on PS-IL@Co/C
- **Pd@Bz-IL@Co/C** Pd NPs deposited on Bz-IL@Co/C
Pd@Spacer-IL@Co/C  Pd NPs deposited on Spacer-IL@Co/C
Pd@IL@Co/C  Pd NPs deposited on IL@Co/C

3.  GC data

All products are literature-known and all spectroscopic data matched with those reported in the literature.

**1,2-Diphenylethane**\(^5\)

1,2-Diphenylethane was prepared from trans-stilbene (360.5 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 20 °C/min, 300 °C; \(t_R\) = dodecane (3.54 min), 1,2-diphenylethane (7.66 min), trans-stilbene (9.37 min).

**Ethylbenzene**\(^6\)

Ethylbenzene was prepared from styrene (228.9 μL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 20 °C/min, 240 °C; \(t_R\) = ethylbenzene (4.29 min), styrene (4.65 min), dodecane (8.30 min).

**Ethane-1,1-diyldibenzene**\(^5\)

Ethane-1,1-diyldibenzene was prepared from ethane-1,1-diyldibenzene (283.0 μL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 16 °C/min, 300 °C; \(t_R\) = dodecane (3.49 min), ethane-1,1-diyldibenzene (6.26 min), ethene-1,1-diyldibenzene (6.47 min).

**Isobutylbenzene**\(^7\)

Isobutylbenzene was prepared from (2-methylprop-1-en-1-yl)benzene (293.5 μL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 24 °C/min, 300 °C; \(t_R\) = isobutylbenzene (6.01 min), (2-methylprop-1-en-1-yl)benzene (6.72 min), dodecane (7.80 min).

**1-Chloro-4-ethylbenzene**\(^6\)

1-Chloro-4-ethylbenzene was prepared from 1-chloro-4-vinylbenzene (274.6 μL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (5 min), 25 °C/min, 300 °C; \(t_R\) = 1-chloro-4-ethylbenzene (4.51 min), 1-chloro-4-vinylbenzene (4.88 min), dodecane (7.12 min).
1-Ethyl-4-methoxybenzene[6]

1-Ethyl-4-methoxybenzene was prepared from 1-methoxy-4-vinylbenzene (269.2 μL, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (5 min), 25 °C/min, 300 °C; \( t_R \) = 1-methoxy-4-vinylbenzene (4.90 min), 1-ethyl-4-methoxybenzene (5.64 min), dodecane (7.14 min).

1,3-Diphenylpropan-1-one[5]

1,3-Diphenylpropan-1-one was prepared from chalcone (416.5 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 140 °C (3 min), 16 °C/min, 300 °C; \( t_R \) = dodecane (3.52 min), 1,3-diphenylpropan-1-one (9.19 min), chalcone (10.22 min). The selective hydrogenation of the C=C double bond was proved by \( ^1H \) NMR and \( ^{13}C \) NMR: \( ^1H \) NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.98 \) (d, \( J = 7.4 \) Hz, 2H), 7.57 (t, \( J = 7.3 \) Hz, 1H), 7.47 (t, \( J = 7.5 \) Hz, 2H), 7.41 – 7.14 (m, 5H), 3.32 (t, \( J = 7.6 \) Hz, 2H), 3.09 (t, \( J = 7.6 \) Hz, 2H); \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)): \( \delta = 199.3, 141.3, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2. \)

Methyl-3-phenylpropanoate[5]

Methyl-3-phenylpropanoate was prepared from methyl cinnamate (324.4 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 100 °C (3 min), 20 °C/min, 300 °C; \( t_R \) = dodecane (5.95 min), methyl-3-phenylpropanoate (6.47 min), methyl cinnamate (7.43 min).

Bicyclo[2.2.1]heptanes[8]

Bicyclo[2.2.1]heptane was prepared from norbornene (188.3 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 60 °C (3 min), 30 °C/min, 300 °C; \( t_R \) = norbornene (2.53 min), bicyclo[2.2.1]heptane (2.87 min), dodecane (7.27 min).

4-Methoxyaniline[9]

4-Methoxyaniline was prepared from 1-methoxy-4-nitrobenzene (306.3 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 70 °C (3 min), 13 °C/min, 200 °C; \( t_R \) = 4-methoxyaniline (8.81 min), dodecane (9.01 min), 1-methoxy-4-nitrobenzene (10.92 min).
4-Chloraniline was prepared from 1-chloro-4-nitrobenzene (315.1 mg, 2 mmol) according to the general procedure. The progress of the reaction was monitored by GC analysis: 50 °C (3 min), 5 °C/min, 170 °C; $t_r = 4$-chloroaniline (15.73 min), 1-chloro-4-nitrobenzene (16.64 min), dodecane (16.91 min).

4. Preparation of samples for ICP-OES analysis

General procedure for the preparation of Pd samples to determine the Pd amount on Pd@Co/C catalysts

5.0 mg Pd@Co/C were heated in 3.2 mL aqua regia for 30 min. Upon cooling, the mixture was diluted with H$_2$O (millipore grade) and after collecting the particles with an external magnet the solution was filtrated in a 10 mL measuring flask. After washing the particles for three times with H$_2$O with subsequent filtration the measuring flask was filled to 10 mL. The Pd concentration was then determined by ICP-OES analysis.

General procedure for the preparation of Pd and Co samples to determine the Pd and Co amount in hydrogenated products

250.0 mg 1,2-Diphenylethane was heated in 3.2 mL aqua regia for 30 min. Upon cooling, the mixture was diluted with H$_2$O (millipore grade) and filtrated in a 10 mL measuring flask. After washing the vial for three times with H$_2$O with subsequent filtration the measuring flask was filled to 10 mL. The Pd and Co concentration was then determined by ICP-OES analysis.

5. IR spectra

Figure S1. Example for following the reaction progress of the nanoparticle synthesis by IR spectroscopy. IR spectra of PS-Cl@Co/C 5 and PS-IL@Co/C 6 are shown.
6. TEM pictures

![TEM pictures](image)

**Figure S2.** Transmission electron microscopy (TEM) pictures of A) Pd@PS-IL@Co/C 2b (24 wt%), B) Pd@Bz-IL@Co/C 3b (31 wt%), C) Pd@Spacer-IL@Co/C 4b (34 wt%), and D) Pd@Spacer-IL@Co/C 4b (34 wt%) after 12 cycles. Carbon coated cobalt nanoparticles have a diameter of 20-100 nm, while the Pd-NPs on the surface of the carbon coated cobalt nanoparticles have a diameter of 5-15 nm.

7. XRD measurements

![XRD spectrum](image)

**Figure S3.** X-ray diffraction spectrum of Pd@Spacer-IL@Co/C 4b with a palladium content of 34 wt%. The characteristic peaks for Co and Pd are detected.
8. NMR spectra
9. References