

Supplementary Information

Hydrophobic effect on supported ionic liquid phase Pd nanoparticles hydrogenation catalysts

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Experimental

1. General methods

All syntheses were performed using standard Schlenk techniques under an argon atmosphere. CH₃CN and CH₂Cl₂ were purified by standard procedures.[77] The ILs **B1–B4** were prepared by previously described procedures.[78] Elemental analyses of the organosilicas were carried out on a CHN Perkin Elmer M CHNS/O Analyzer 2400. The N₂ isotherms of the supports, previously degassed at 100°C under vacuum for 3 h, were obtained using Tristar 3020 Micromeritics equipment. The specific surface areas were determined by the BET multipoint method and the average pore size was obtained by the BJH method. Solid-state ¹³C and ²⁹Si NMR measurements for the **sg0–sgB4** supports were taken using a Varian 500 MHz spectrometer. The infrared spectra were obtained on an ABB FTLA 2000 with a resolution of 4 cm⁻¹, with 128 cumulative scans. STEM samples were prepared by the slow evaporation of a drop of each colloidal solution deposited under an argon atmosphere onto a holey carbon-covered copper grid. STEM analyses were performed using an XFEG Cs-corrected FEI Titan 80/300 microscope at INMETRO operated at 200 kV. XRF analyses were performed using a Shimadzu Sequential XRF-1800 spectrometer. GC analyses were run with an Agilent Technologies GC System 6820 with a DB-17 column (oven temperature 40°C). GC-MS analyses were run with a Shimadzu QP50 with a Rtx-5MS column (oven temperature 40°C) employing an ionising voltage of 17 eV.[79] ¹H, ²H, ¹³C NMR, COSY and HSQC analysis of the samples obtained by reduction with deuterium of 1,3-cyclohexadiene catalysed by Pd/**sg0** and Pd/**sgB4** catalysts were performed on a Varian 400 MHz. The deuterium incorporation in the reaction products was quantified by comparing the ¹H NMR obtained spectra with those obtained using a standard sample and by carrying out ²H NMR (relaxation delay 1 to 10 s for both cases).[80, 81] The Pd depth profiles were determined using the RBS (Rutherford Backscattering Spectrometry) technique with a 1.5 MeV He⁺ incident beam provided by the 3 MV Tandemtron accelerator of the IF-UFRGS. The backscattered particles were detected by an Si surface-barrier detector placed at a scattering angle of 165°. The electronic resolution of the system was around 13 keV. The energy to

depth conversion was accomplished by using stopping power values provided by the SRIM code (2013.00 version).[82]

2. Synthesis of the **B1–B4** ILs

1-n-Butylimidazole (6.2 g, 50 mmol) was reacted with 3-chloropropyltrimethoxysilane (9.9 g, 50 mmol) at 90°C under an inert atmosphere for 72 h. The reaction mixture was cooled to room temperature and then washed with dry diethyl ether. After being dried under reduced pressure at 40°C, a slightly yellow viscous liquid 1-n-butyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride (**B1**) was obtained and stored under inert atmosphere for further characterisation and application (yield: 14.5 g, 90%). To a solution of **B1** (3.2 g, 10 mmol) in dry acetonitrile (10 mL), the desired salt AgNO₃ (1.7 g, 9.8 mmol), AgPF₆ (2.5 g, 9.8 mmol) or LiNTf₂ (3.4 g, 12 mmol) was added and the resulting mixture was vigorously stirred at room temperature under inert atmosphere for 24 h. After that, the solution was filtered and washed with dry CH₂Cl₂. After being dried under reduced pressure at 40°C, in each case, a yellow viscous liquid was obtained and stored under an inert atmosphere for their further characterisation and application, thus providing the ILs **B2**, **B3** and **B4**.

B1 IL: ¹H NMR (CD₃CN, 400MHz): δ (ppm) 0.57–0.63 (t, 2H, *J* = 8.49 Hz, SiCH₂CH₂CH₂N), 0.91–0.96 (t, 3H, *J* = 7.32 Hz, NCH₂CH₂CH₂CH₃), 1.25–1.39 (m, 2H, NCH₂CH₂CH₂CH₃), 1.81–1.85 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 3.52 (s, 9H, CH₃OSi), 4.22–4.36 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 7.70 (s, 2H, NCH₂CH₂N), and 10.08 (s, 1H, NCHN). ¹³C NMR (CD₃CN, 400MHz): δ (ppm) 6.2 (SiCH₂CH₂CH₂N), 13.6 (NCH₂CH₂CH₂CH₃), 19.8 (NCH₂CH₂CH₂CH₃), 24.4 (SiCH₂CH₂CH₂N), 32.5 (NCH₂CH₂CH₂CH₃), 49.8 (NCH₂CH₂CH₂CH₃), 50.8 (CH₃OSi), 52.1 (SiCH₂CH₂CH₂N), 123.1 (NCH₂CH₂N), and 137.7 (NCHN). Yield: 14.5 g; 90%.

B2 IL: ¹H NMR (CD₃CN, 400MHz): δ (ppm) 0.57–0.63 (t, 2H, *J* = 8.50 Hz, SiCH₂CH₂CH₂N), 0.92–0.97 (t, 3H, *J* = 7.33 Hz, NCH₂CH₂CH₂CH₃), 1.28–1.40

(m, 2H, NCH₂CH₂CH₂CH₃), 1.80–1.87 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 3.55 (s, 9H, CH₃OSi), 4.17–4.25 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 7.54 (s, 2H, NCH₂CH₂N), and 9.17 (s, 1H, NCHN). ¹³C NMR (CD₃CN, 400MHz): δ (ppm) 6.3 (SiCH₂CH₂CH₂N), 13.7 (NCH₂CH₂CH₂CH₃), 20.0 (NCH₂CH₂CH₂CH₃), 24.1 (SiCH₂CH₂CH₂N), 32.5 (NCH₂CH₂CH₂CH₃), 50.2 (NCH₂CH₂CH₂CH₃), 50.9 (CH₃OSi), 52.5 (SiCH₂CH₂CH₂N), 123.4 (NCH₂CH₂N), and 137.2 (NCHN). Yield: 3.2 g; 95%.

B3 IL. ¹H NMR (CD₃CN, 400MHz): δ (ppm) 0.59–0.64 (t, 2H, J = 8.50 Hz, SiCH₂CH₂CH₂N), 0.96–1.01 (t, 3H, J = 7.31 Hz, NCH₂CH₂CH₂CH₃), 1.29–1.43 (m, 2H, NCH₂CH₂CH₂CH₃), 1.81–1.96 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 3.57 (s, 9H, CH₃OSi), 4.12–4.19 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 7.43 (s, 2H, NCH₂CH₂N), and 8.45 (s, 1H, NCHN). ¹³C NMR (CD₃CN, 400MHz): δ (ppm) 6.3 (SiCH₂CH₂CH₂N), 13.7 (NCH₂CH₂CH₂CH₃), 20.0 (NCH₂CH₂CH₂CH₃), 24.4 (SiCH₂CH₂CH₂N), 32.4 (NCH₂CH₂CH₂CH₃), 50.3 (NCH₂CH₂CH₂CH₃), 51.0 (CH₃OSi), 52.6 (SiCH₂CH₂CH₂N), 123.4 (NCH₂CH₂N), and 136.2 (NCHN). Yield: 4.0 g; 94%.

B4 IL: ¹H NMR (CD₃CN, 400MHz): δ (ppm) 0.59–0.65 (t, 2H, J = 8.49 Hz, SiCH₂CH₂CH₂N), 0.90–0.93 (t, 3H, J = 7.30 Hz, NCH₂CH₂CH₂CH₃), 1.19–1.32 (m, 2H, NCH₂CH₂CH₂CH₃), 1.83–1.95 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 3.62 (s, 9H, CH₃OSi), 4.20–4.35 (m, 4H, SiCH₂CH₂CH₂N, NCH₂CH₂CH₂CH₃), 7.35 (s, 2H, NCH₂CH₂N), and 8.75 (s, 1H, NCHN). ¹³C NMR (CD₃CN, 400MHz): δ (ppm) 6.1 (SiCH₂CH₂CH₂N), 13.8 (NCH₂CH₂CH₂CH₃), 19.8 (NCH₂CH₂CH₂CH₃), 24.5 (SiCH₂CH₂CH₂N), 32.0 (NCH₂CH₂CH₂CH₃), 49.7 (NCH₂CH₂CH₂CH₃), 50.6 (CH₃OSi), 52.0 (SiCH₂CH₂CH₂N), 115.5, 118.6, 121.7 (CF₃), 123.5 (NCH₂CH₂N), 124.8 (CF₃), and 138.0 (NCHN). Yield: 5.3 g; 95%.

3. Synthesis of the **sg0–sgB4** organosilica supports

As a general procedure, a mixture of IL (**B1–B4**), TEOS, and H₂O with a molar ratio of 0.05:1.0:10.5 was dissolved in acetone (0.35 × V_{TEOS}) and heated

at 60°C under vigorous stirring. After 10 min, aqueous HF (5.0 M, molar ratio of HF to TEOS of 1:100) was added to the solution. After 24 h, the resultant solid material was cooled to room temperature, washed with acetone and dried under reduced pressure at 60°C to remove the volatile components, thus providing the supports (**sgB1–sgB4**). The support **sg0** was synthesised in the absence of IL. The white powders were recovered and stored under inert atmosphere for their further characterisation and application.

4. Sputtering deposition of Pd-NPs onto organosilica supports

As a general procedure, each support (2.0 g of **sg0**, **sgB1**, **sgB2**, **sgB3** and **sgB4**) was placed into a conical aluminium flask and placed inside the vacuum chamber. Then, the chamber was closed and its pressure lowered to a base pressure of 4 µbar, with the supports being evacuated at this pressure for 4 h. Then, the vacuum chamber was placed under a sputtering working pressure of 4 mbar by adding Ar flow. The supports were continuously homogenised by revolving the aluminium flask at a vibration frequency of 24 Hz. The Pd was sputtered onto the revolving support at 35 mA of discharge current during 3.0 min to give the Pd/**sg0**–Pd/**sgB4** catalysts. After the deposition, the chamber was vented with N₂ and the grey powders were recovered and stored under an inert atmosphere for their further characterisation and application.

5. Hydrogenation of 1,3-dienes

As a general procedure, 10 mL of a solution of the corresponding 1,3-diene (diene/Pd = 5000) dissolved in CH₂Cl₂ was added to a Fischer-Porter reactor containing the appropriate amount of catalysts (0.1 µmol Pd). After that, the reactor was pressurised with 4 bar of H₂ at 40°C. Samples were taken from the reaction mixture every 5 min. After the desired reaction time, the reactor was cooled to room temperature and then depressurised. The conversion and selectivity was determined by GC-analysis of the reaction samples. The activity values were calculated from the slope of plots of time vs. TON at low substrate conversions: TOF = mol 1,3-diene converted/(mol Pd surface × time).

Table S1. ^{13}C CP-MAS NMR spectra of **sg0–sgB4** supports.

Support	Carbon/ ppm							
	(a), (j) ^[a]	(b)	(c)	(d), (h) ^[a]	(e)	(f), (g) ^[a]	(i)	MeOH
sg0	—	—	—	—	—	—	—	—
sgB1	11.3	19.4	32.0	50.4	135.9	123.3	23.5	—
sgB2	11.3	19.4	32.0	50.4	135.2	122.5	24.2	58.4
sgB3	12.8	19.4	31.5	50.2	135.0	122.3	23.9	58.5
sgB4	12.3	17.3	32.4	51.1	136.3	123.6	24.3	59.1

^[a] Overlapped signals.

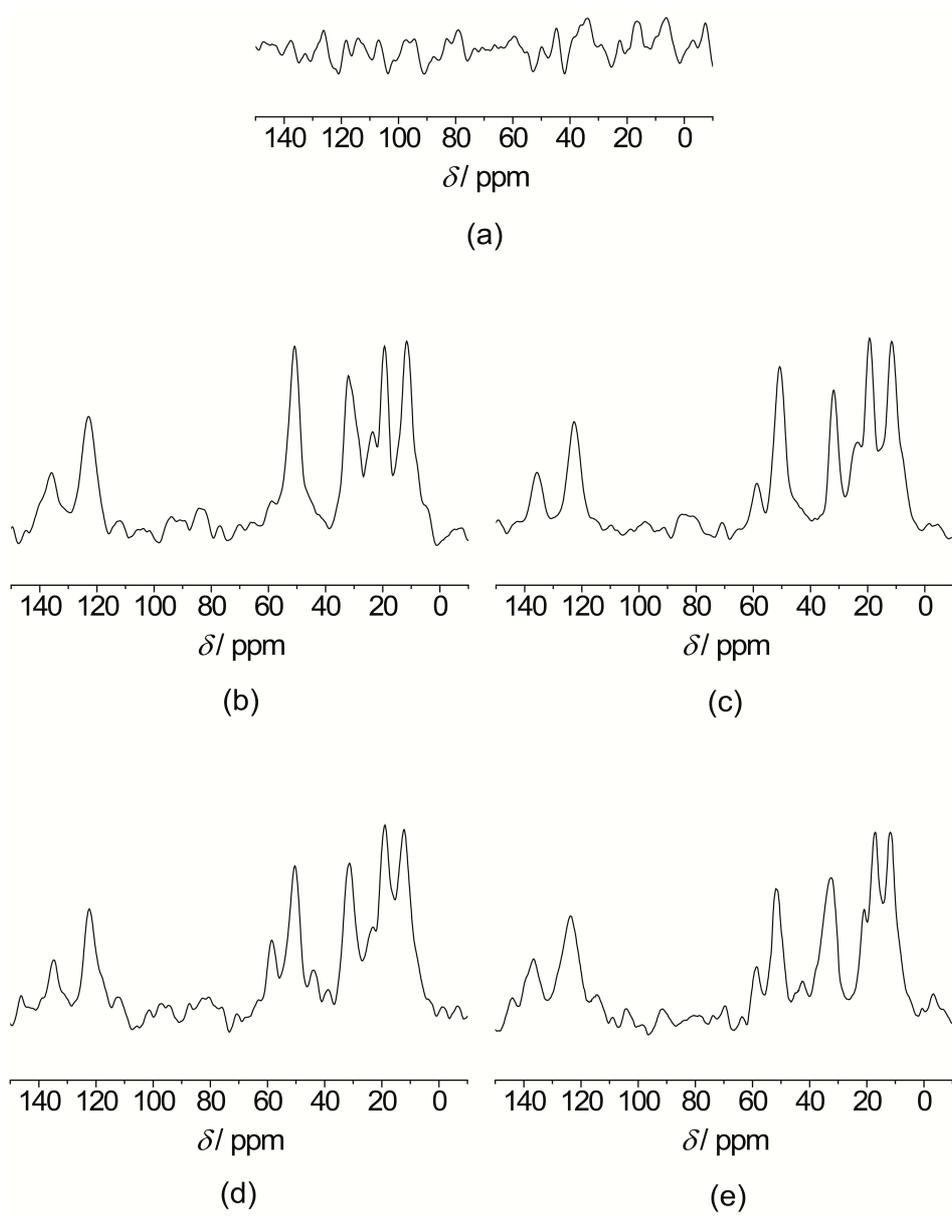
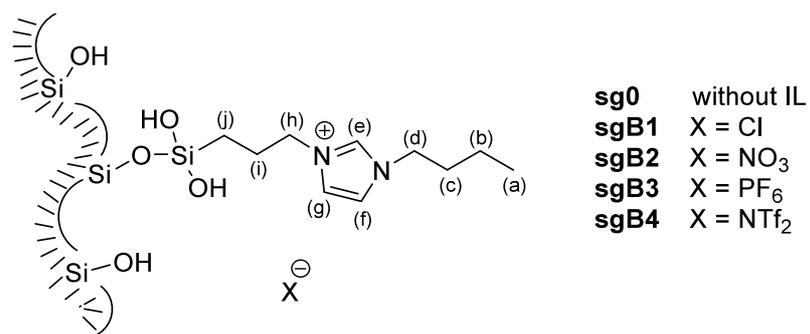
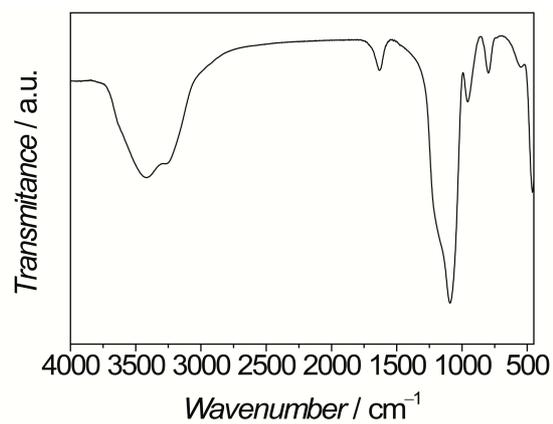


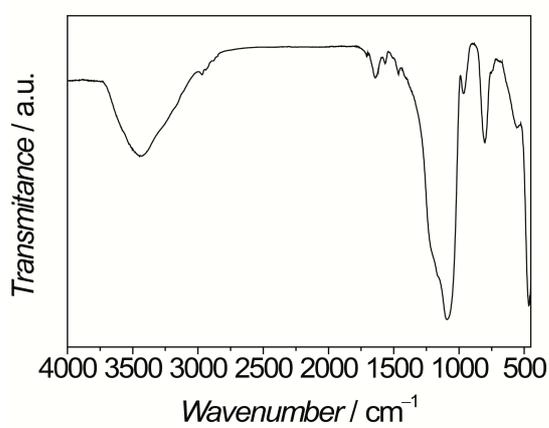
Figure S1. ¹³C CP-MAS NMR spectra of (a) **sg0**, (b) **sgB1**, (c) **sgB2**, (d) **sgB3** and (e) **sgB4** supports.

Table S2. FT-IR spectra of **sg0–sgB4** supports.

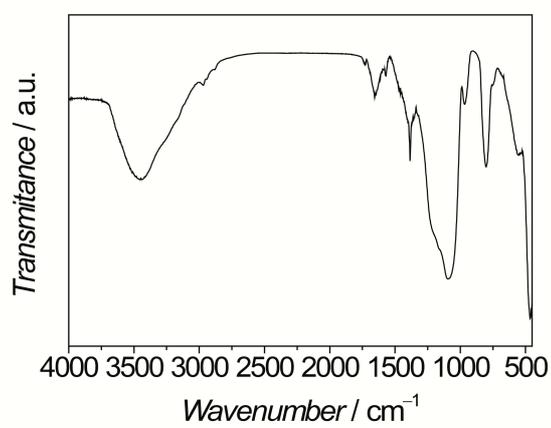
Attribution	Wavenumber/ cm^{-1}				
	sg0	sgB1	sgB2	sgB3	sgB4
ν (OH)	3420	3440	3450	3450	3446
ν (=C-H)	—	3149	3155	3157	3154
ν_{as} (C-H)	—	2968	2970	2970	2974
ν_{as} (C-H)	—	2941	2941	2941	2941
ν (C-H)	—	2881	2881	2879	2883
δ (H-O-H)	1631	1641	1654	1652	1641
ν (C=N)	—	1566	1571	1571	1570
ν (C=C)	—	1566	1571	1571	1570
δ (CH ₂)	—	1463	1467	1458	1465
ν (N-O)	—	—	1385	—	—
ν_{as} (SO ₂)	—	—	—	—	1352
ν_{as} (SO ₂)	—	—	—	—	1332
ν_{as} (CF ₃)	—	—	—	—	1207
ν_{as} (Si-O-Si) _L	1191	1190	1188	1189	1197
ν_{as} (Si-O-Si) _T	1091	1087	1093	1089	1095
ν (S-N-S)	—	—	—	—	1064
ν (Si-OH)	956	964	960	962	962
ν (P-F)	—	—	—	846	—
ν (Si-O-Si) _T	796	798	798	798	796
ν_{as} (P-F)	—	—	—	741	—



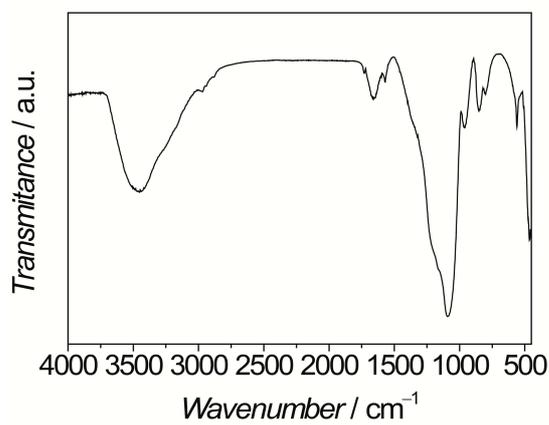
(a)



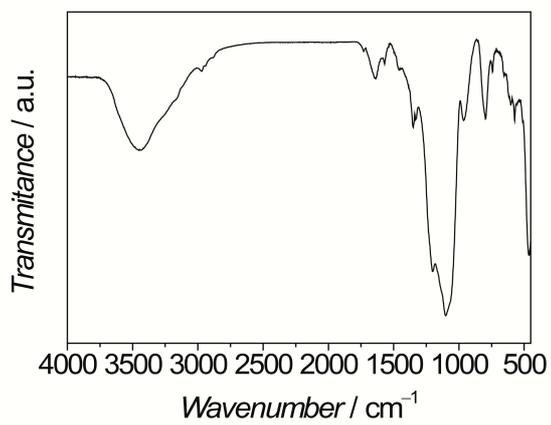
(b)



(c)

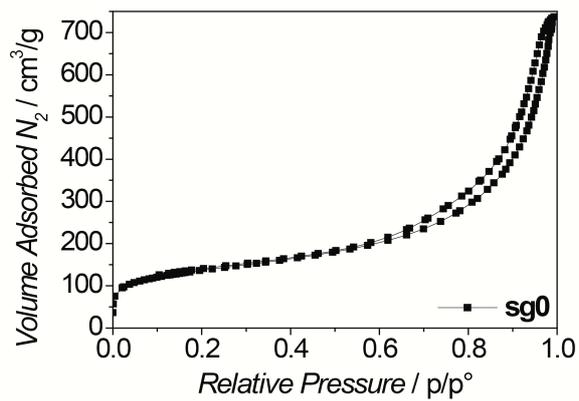


(d)

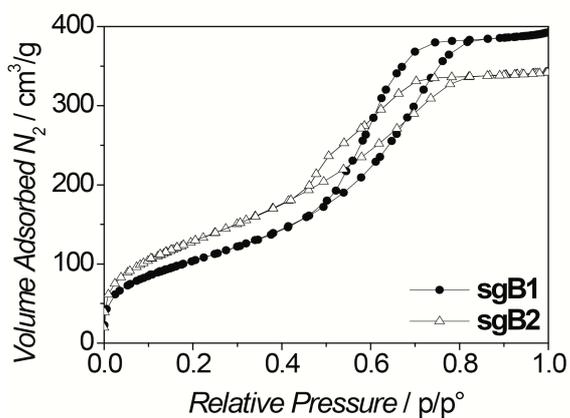


(e)

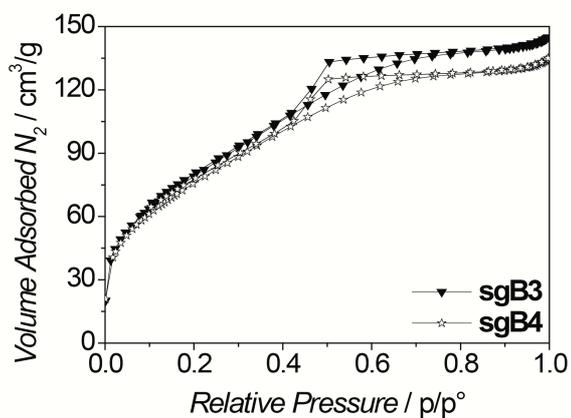
Figure S2. FT-IR spectra of (a) **sg0**, (b) **sgB1**, (c) **sgB2**, (d) **sgB3** and (e) **sgB4** supports.



(a)



(b)



(c)

Figure S3. Nitrogen adsorption/desorption isotherms of (a) **sg0**, (b) **sgB1** and **sgB2**, and (c) **sgB3** and **sgB4** supports.

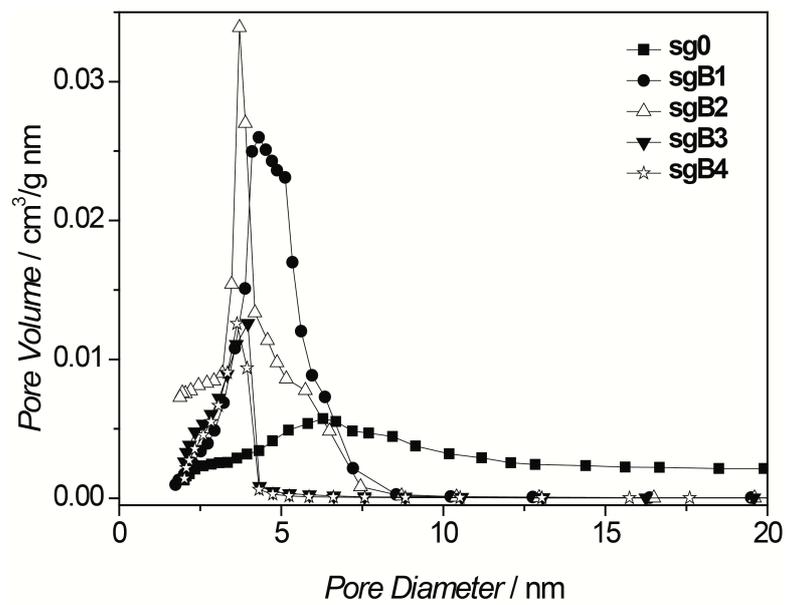
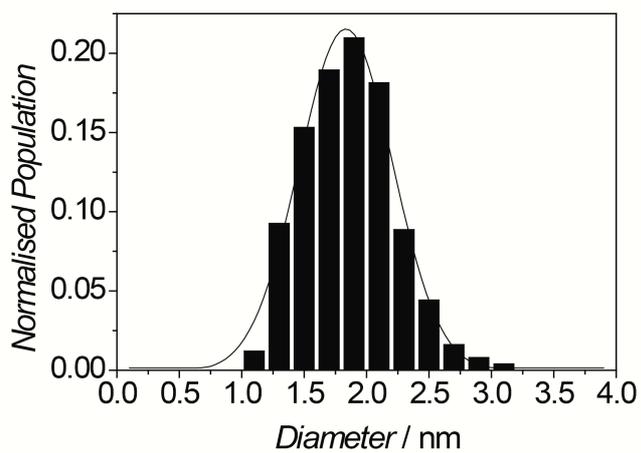
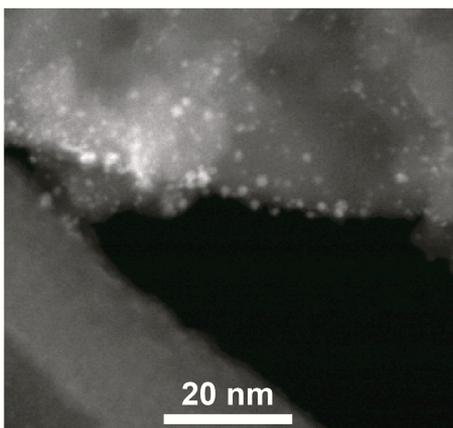
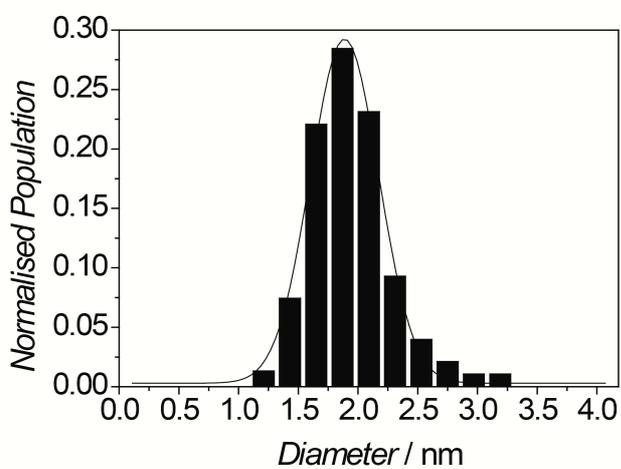
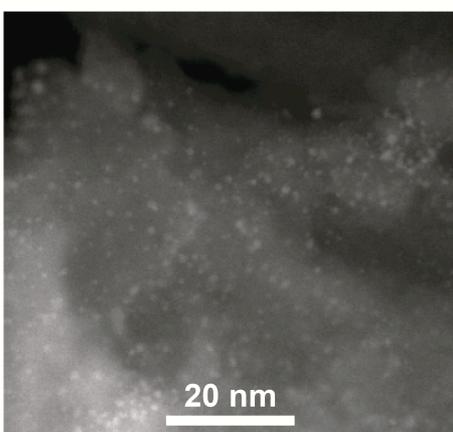


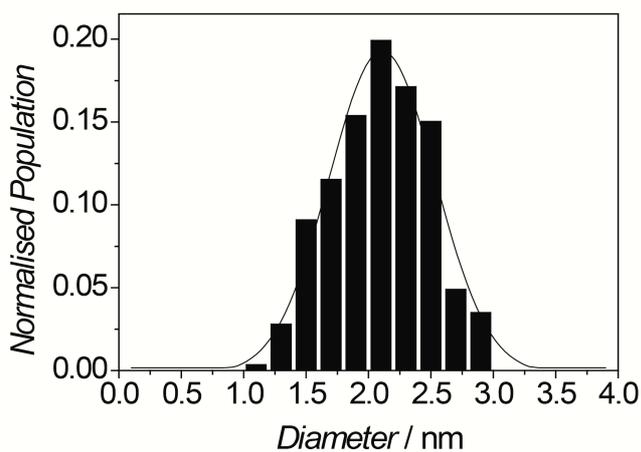
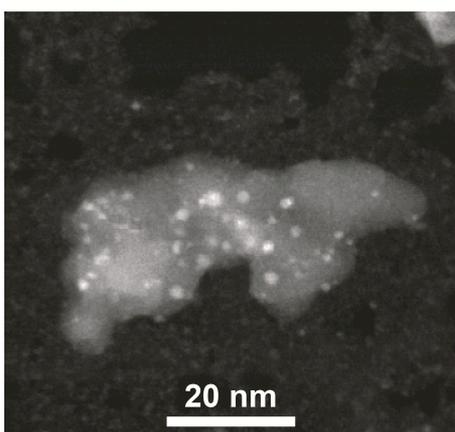
Figure S4. Pore diameter distribution of **sg0–sgB4** supports.



(a)



(b)



(c)

Figure S5. STEM images and histograms of the (a) Pd/sgB1, (b) Pd/sgB2 and (c) Pd/sgB3 catalysts.

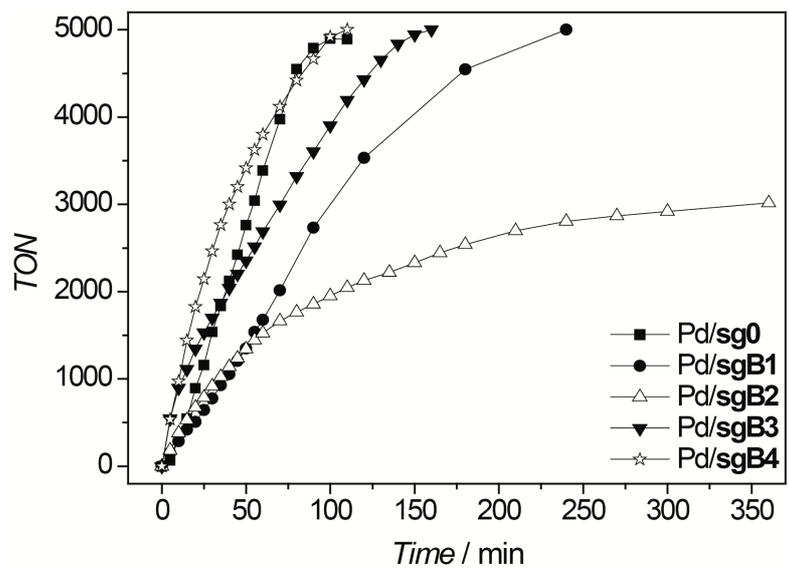
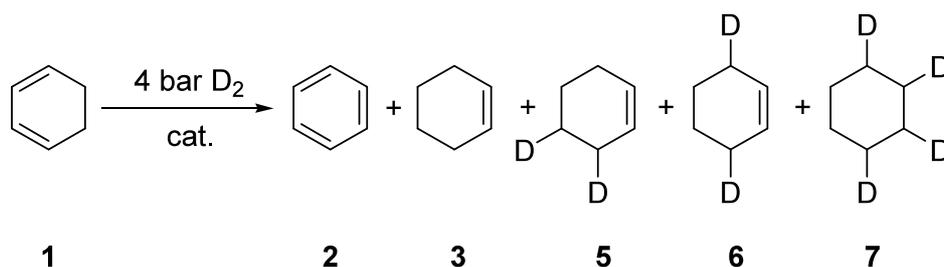


Figure S6. Hydrogenation of 1,3-cyclohexadiene: time [min] vs. TON with Pd/sg0–Pd/sgB4 catalysts.

Table S3. Deuteration of 1,3-cyclohexadiene by Pd/**sg0** and Pd/**sgB4** catalysts.



Entry [a,b]	Catalyst	Conv./ % [t/ h]	2/ %	3/ %	5/ %	6/ %	7/ %	TOF/ s ⁻¹ [c,d]
1	Pd/ sg0	100 [7.00]	3	3	58	34	2	1.37
2	Pd/ sgB4	100 [5.00]	2	2	58	34	4	1.44

[a] Reaction conditions: 0.1 μmol Pd, 1,3-cyclohexadiene/Pd = 5000, 10 mL of CH_2Cl_2 , 4 bar D_2 , 40°C; [b] Conversion and selectivity determined by GC and NMR- $^1\text{H}/^2\text{H}$ analysis; [c] TOF = mol 1,3-cyclohexadiene converted/(mol Pd surface \times time); [d] Calculated from the slope of plots of time vs. TON at low substrate conversions.