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## Selective hydrogenation of functionalized nitroarenes under mild conditions

Valerica Pandarus,<sup>a</sup> Rosaria Ciriminna,<sup>b</sup> François Béland<sup>\*a</sup> and Mario Pagliaro<sup>\*b</sup>

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Functionalized anilines are selectively synthesized from the corresponding nitroarenes by simple heterogeneous catalytic hydrogenation carried out under mild conditions over a very low amount (0.5 mol%) of a new sol–gel entrapped Pd(0) catalyst. Only halo-nitroarenes could not be selectively converted. The catalyst is leach-proof and can be reused in many consecutive reaction cycles.

### Introduction

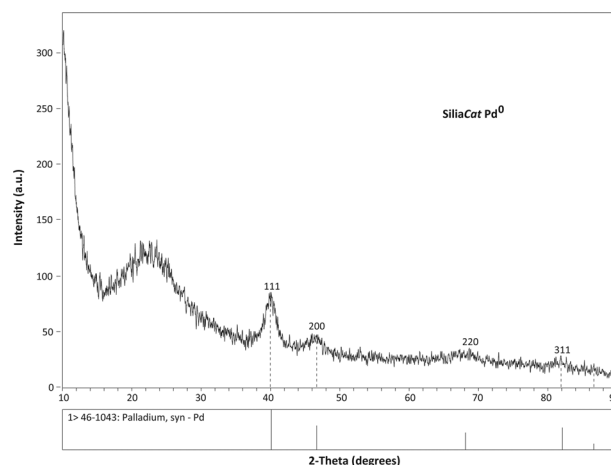
Functionalized anilines are important intermediates for pharmaceuticals, polymers, dyes, urethanes and other industrially important chemical products.<sup>1</sup> These aromatic amines are generally obtained by catalytic hydrogenation of nitroarenes with various heterogeneous metal catalysts (supported nickel, copper, cobalt) including Pd/C.<sup>2</sup> Yet, the selective reduction of a nitro group with H<sub>2</sub> when other reducible groups are present in the same molecule is generally not feasible with the above-mentioned catalysts, and requires either homogeneous catalysis,<sup>3</sup> or delicate strategies involving multi-component catalytic materials.<sup>4</sup>

The use of supported Pd(0) nanoparticles for the hydrogenation of nitro groups in the presence of “moderately” reducible functional groups under mild reaction conditions has been demonstrated, for example using Pd nanoparticles supported over carbon nanofibers,<sup>5</sup> in aluminium oxy-hydroxide,<sup>6</sup> and over magnesium oxide.<sup>7</sup> However, when more challenging substrates containing sensitive functionalities (such as double, and triple bonds, carbonyls, *etc.*) are involved, different strategies need to be undertaken to transform non-selective supported Pd or Pt catalysts into more selective species.<sup>8</sup> Yet, most of these strategies require the employment of relatively harsh conditions and typically require high amount of solid catalyst (for example 0.1 g catalyst for 0.5 g substrate at 70–140 °C under 10–40 bar H<sub>2</sub>).<sup>4</sup> It is thus of relevant interest the discovery reported herein of the chemoselective catalytic activity of new Pd(0) heterogeneous catalysts for the hydrogenation of a wide series of functionalized nitroarenes dissolved in methanol in a simple hydrogen balloon under remarkable mild conditions of room temperature and 1 bar H<sub>2</sub>.

### Results and discussion

#### Experimental section

Trademarked SiliaCat Pd<sup>0</sup>: this new series of patent-protected<sup>9</sup> sol–gel entrapped Pd nanocatalysts is made of highly dispersed Pd nanoparticles (uniformly in the range 4.0–6.0 nm) encapsulated within an organosilica matrix *via* an alcohol-free sol–gel process typical of enzyme sol–gel encapsulation.<sup>10</sup> Specifically



**Fig. 1** The crystalline nature of the active Pd(0) nano-phase in a SiliaCat Pd(0) catalysts is evident from the succession of X-ray diffraction peaks.

**Table 1** X-Ray Powder Diffraction (XRD) of SiliaCat Pd<sup>0</sup>–4

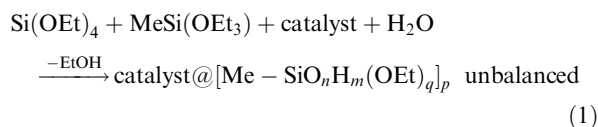
Catalyst	Diffraction angle 2θ				Mean crystallite size/nm
	111	200	220	311	
Pd(0) <sup>a</sup>	40.12	46.66	68.12	82.10	N.A.
SiliaCat Pd <sup>0</sup> –4	39.96	46.66	68.11	81.90	5.7

<sup>a</sup> The Powder Diffraction File of The International Centre for Diffraction Data is used to identify the diffraction peaks characteristic of crystalline Pd(0) with a face centered cubic (fcc) lattice identified Pd(0).

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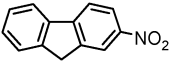
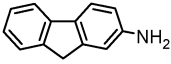
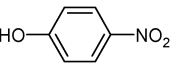
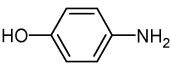
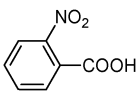
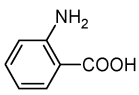
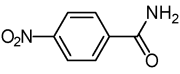
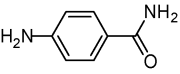
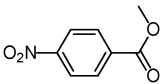
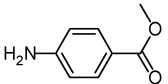
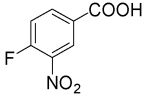
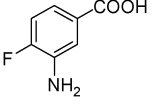
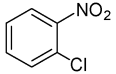
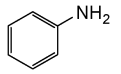
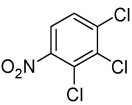
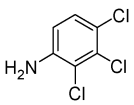
the entrapment process starts with controlled distillation in a rotovapor of the ethanol (a reductant) released with ongoing hydrolysis and condensation of the  $\text{MeSi}(\text{OEt})_3$  and  $\text{Si}(\text{OEt})_4$  precursors (eqn (1)):



The resulting alcohol-free sol is doped with a  $\text{Pd}(\text{II})$  salt and undergoes further basic or acid catalyzed polycondensation to yield a microporous hydrogel that is dried under mild conditions to afford a xerogel doped with  $\text{Pd}^{2+}$ . The latter material is eventually treated with a mild reductant such as  $\text{Na}(\text{AcO})_3\text{BH}$  to yield a *SiliaCat*  $\text{Pd}^0$  nanostructured encapsulated catalyst. In a typical preparation, a mixture of

methyltriethoxysilane (27 g, 30 mL, 151.4 mmol) and 10 mL of 0.042 M  $\text{HCl}$  was stirred for 15 minutes. The resulting solution was concentrated with a rotavapor under reduced pressure at 30 °C until complete ethanol removal (about 15 min). The alcohol-free sol thereby obtained was added with  $\text{K}_2\text{PdCl}_4$  (from 0.004 to 0.02 equiv.) dissolved in  $\text{H}_2\text{O}$  (from 5 to 10 mL) and 60 mL acetonitrile. This mixture was added with 1 M  $\text{NaOH}$  (from 0.023 to 0.053 equiv.) to favour gelation that indeed rapidly occurred. The resulting transparent gel was left to dry in air for 4 days after which the xerogel was reduced at room temperature under inert conditions with a solution of sodium triacetoxyborohydride ( $\text{Pd}:\text{Na}(\text{AcO})_3\text{BH} = 1:6$  molar ratio) in 80 mL THF, washed with THF and  $\text{H}_2\text{O}$  and dried in air to afford the *SiliaCat*  $\text{Pd}^0$ -4 catalyst used in the catalytic experiments described below.

**Table 2** Catalytic hydrogenation of different nitro compounds containing different functionalities with *SiliaCat*  $\text{Pd}^0$  hydrogel catalyst<sup>a</sup>

Entry	Substrate	Time/h	Product	Conv. (%) <sup>c</sup>	Selectivity (%)
1		1		100 <sup>b</sup>	100
2		1 2		80 100	100
3		1		100	98
4		1		100 <sup>b</sup>	100
5		0.5		100	99
6		1		100	100
7		1		100	100 <sup>d</sup>
8		1		100	97

<sup>a</sup> Reaction conditions: 0.5 mol% *SiliaCat*  $\text{Pd}^0$ ; MeOH solvent HPLC grade 0.1 M, molar concentration with respect to the substrate; room temperature under 1 bar  $\text{H}_2$ . <sup>b</sup> 1 mol% *SiliaCat*  $\text{Pd}^0$ ; MeOH solvent HPLC grade 0.05 M, molar concentration with respect to the substrate. <sup>c</sup> The conversion with respect to the hydrogenated product was evaluated by GC/MS analysis. <sup>d</sup> The hydrogenolysis of one chlorine is observed.

**Table 3** Catalytic hydrogenation of different nitroarenes with SiliaCat Pd<sup>0</sup> hydrogel catalyst<sup>a</sup>

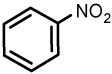
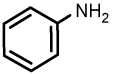
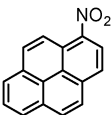
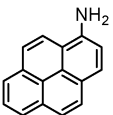
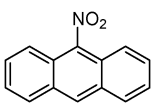
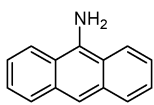
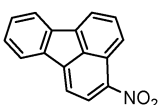
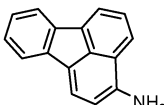
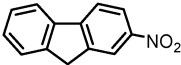
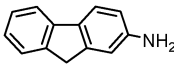
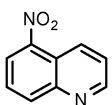
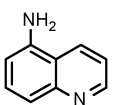
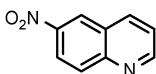
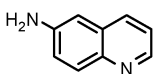
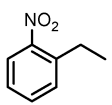
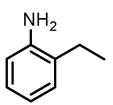
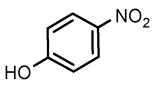
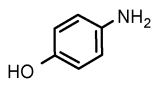
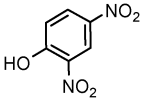
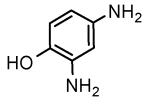
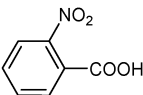
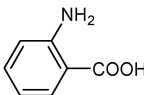
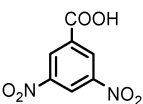
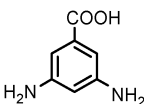
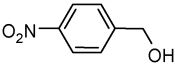
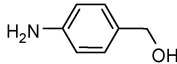
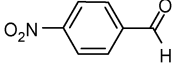
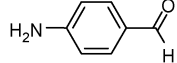
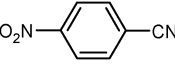
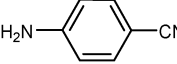
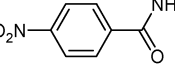
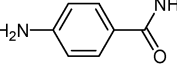
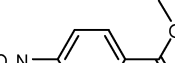
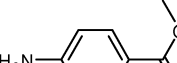


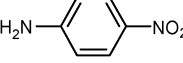
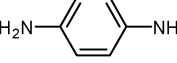
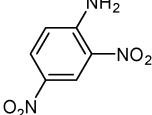
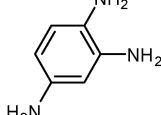
Entry	Substrate	Catalyst amount/mol%	Solvent <sup>b</sup> /M	Time/h	Product	Conv. <sup>a</sup> (%)	Selectivity (%)
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2		SiliaCat Pd <sup>0</sup> 1	MeOH (0.05 M)	1		100	100
3		SiliaCat Pd <sup>0</sup> 1	MeOH (0.05 M)	4		100	80 <sup>c</sup>
4		SiliaCat Pd <sup>0</sup> 1	MeOH (0.05 M)	1		100	95 <sup>d</sup>
5		SiliaCat Pd <sup>0</sup> 1	MeOH (0.05 M)	1		100	100
6		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
7		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.07 M)	1 2		80 100	100
8		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
9		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1 2		80 100	100
10		SiliaCat Pd <sup>0</sup> 1	MeOH (0.1 M)	1		100%	100
11		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	98
12		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100

Table 3 (continued)

Entry	Substrate	Catalyst amount/mol%	Solvent <sup>b</sup> /M	Time/h	Product	Conv. <sup>a</sup> (%)	Selectivity (%)
13		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	92 <sup>e</sup>
14		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	0 <sup>f</sup>
15		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	0.5		90	10
16		SiliaCat Pd <sup>0</sup> 1	MeOH (0.07 M)	1		100	100
17		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
18		SiliaCat Pd <sup>0</sup> 1	MeOH (0.1 M)	1		100	100
19		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	99
20		SiliaCat Pd <sup>0</sup> 1	MeOH (0.07 M)	1		100	100

<sup>a</sup> Reaction at room temperature under 1 bar H<sub>2</sub>. Conversion with respect to the desired product was evaluated by GC/MS analysis. <sup>b</sup> Molar concentration of MeOH with respect to the substrate. <sup>c</sup> 20% anthracene. <sup>d</sup> 5% fluorentene. <sup>e</sup> 8% aminotoluene. <sup>f</sup> 4-Nitrobenzaldehyde is reduced to 4-aminobenzyl alcohol.

The dopant metallite particles are made of nanostructured crystalline palladium(0) as clearly shown by the XRD pattern of the powder catalyst in which the diffraction peaks of a face centered cubic structure of metallic Pd are evident (Fig. 1), and for which a typical 5.7 nm metallite particle size was calculated using the Scherrer formula from the line broadening of (111) reflection (Table 1).

For each hydrogenation experiment, the substrate (2 mmol, 1 equiv.) and the catalyst SiliaCat Pd<sup>0</sup> (0.5 mol%; catalyst load = 0.063 mmol g<sup>-1</sup> measured using the CAMECA SX100 instrument equipped with an EPMA analyzer) were combined in MeOH (HPLC grade) and stirred in a hydrogen balloon at room temperature. Methanol was found to be the optimal reaction solvent after a screening that included other solvents (tetrahydrofuran, toluene and acetonitrile). Increasing the

loading of the catalyst in reactions performed under same conditions did not afford significant benefits in terms of reaction rate whereas decreasing its content below 0.5 mol% resulted in drastic reduction of the reaction rate. The conversion with respect to the final product was determined by GC/MS analysis. The preliminary test with substrates displayed in Table 2 shows that by using 0.5–1 mol% of catalyst, reaction proceeds at completion with a minimum 97% selectivity, and most often with complete selectivity.

Based on these promising results a wide variety of nitroarenes bearing different functionalities were tested in the catalytic hydrogenation in methanol over 0.5–1 mol% SiliaCat Pd<sup>0</sup> under the same mild conditions mentioned above. Table 2 shows that complete conversion was obtained typically after 1 hour, with very fast conversion (0.5 h) in the case of the

**Table 4** Hydrogenation of nitro-functionalized aryl halides in the presence of different halogen functionalities using SiliaCat Pd<sup>0</sup> catalyst

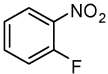
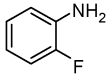
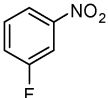
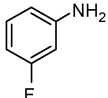
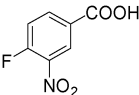
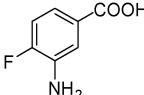
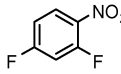
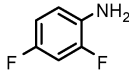
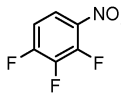

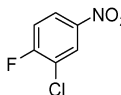
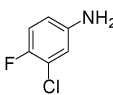
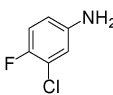
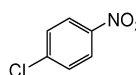
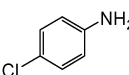
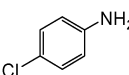
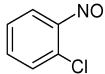
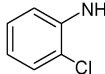
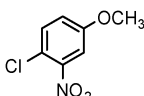
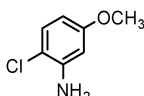
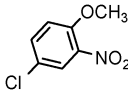
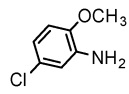
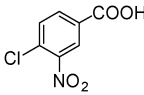
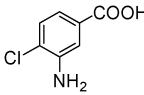


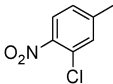
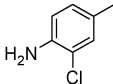
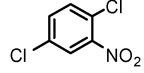
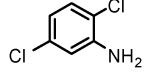
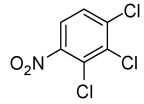
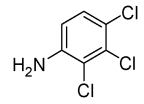
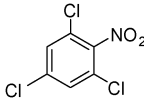
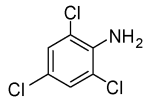
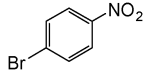
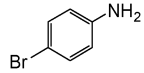
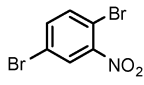
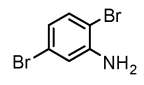
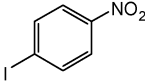
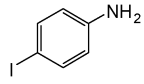
Entry	Substrates	Catalyst/mol%	Solvent <sup>b</sup> /M	Time/h	Product	Conv. <sup>a</sup> (%)	Selectivity (%)
1		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
2		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
3		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
4		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	100
5		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	99
6		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	2		90	30 <sup>c</sup>
				4		100	0
7		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	20
				2		100	0
8		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	0
9		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	2		100	65 <sup>c</sup>
10		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	4		99	14 <sup>c</sup>
11		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	2		99	5 <sup>c</sup>
12		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	2		99	28 <sup>c</sup>

Table 4 (continued)

Entry	Substrates	Catalyst/mol%	Solvent <sup>b</sup> /M	Time/h	Product	Conv. <sup>a</sup> (%)	Selectivity (%)
13		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	2		99	67 <sup>c</sup>
14		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		93	66 <sup>d</sup>
15		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	97 <sup>e</sup>
16		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1		100	90 <sup>e</sup>
17		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.07 M)	1		100	10 <sup>e</sup>
18		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.1 M)	1 4		54 100	0 0 <sup>f</sup>
19		SiliaCat Pd <sup>0</sup> 0.5	MeOH (0.05 M)	4		40	40

<sup>a</sup> Reaction conditions: room temperature under 1 bar H<sub>2</sub>. The conversion with respect to the desired product was evaluated by GC/MS analysis.

<sup>b</sup> Mc, molar concentration of the solvent with respect to the substrate. <sup>c</sup> Hydrogenolysis of halide is favored. <sup>d</sup> Hydrogenolysis of chloride is observed. <sup>e</sup> Hydrogenolysis of one chloride group is observed. <sup>f</sup> Hydrogenolysis of both Br residues is favored.

important pharmaceutical intermediate 4-nitrobenzonitrile; and requiring 4 h only in the case of 9-nitroanthracene, a nitro-polycyclic aromatic hydrocarbon also employed as intermediate in organic synthesis.

In detail, results in Table 3 show that the hydrogenation proceeds either at completion or with minimum 80% chemoselectivity independently of the substrate's molecular size (entries 1–5). Most importantly, the nitro groups can be reduced selectively with SiliaCat Pd<sup>0</sup> under mild conditions when other different functionalities are present in the same molecule, including easily reducible groups such as amide, nitrile, carboxylic acid and ester residues (entries 6–20). Only when such functionalities are carbonyl or nitrile groups, the nitro groups are not reduced selectively. For example, 4-nitrobenzaldehyde (entry 14 in Table 3) is reduced quantitatively to 4-aminobenzyl alcohol.

Finally, the SiliaCat Pd<sup>0</sup> catalyst was tested in the selective catalytic hydrogenation of different halo-nitroarenes. Again, rapid (0.5–2 h) and complete substrate conversion was observed for each molecule tested (Table 4). Now, however, dehalogenation generally takes place concomitant to reduction

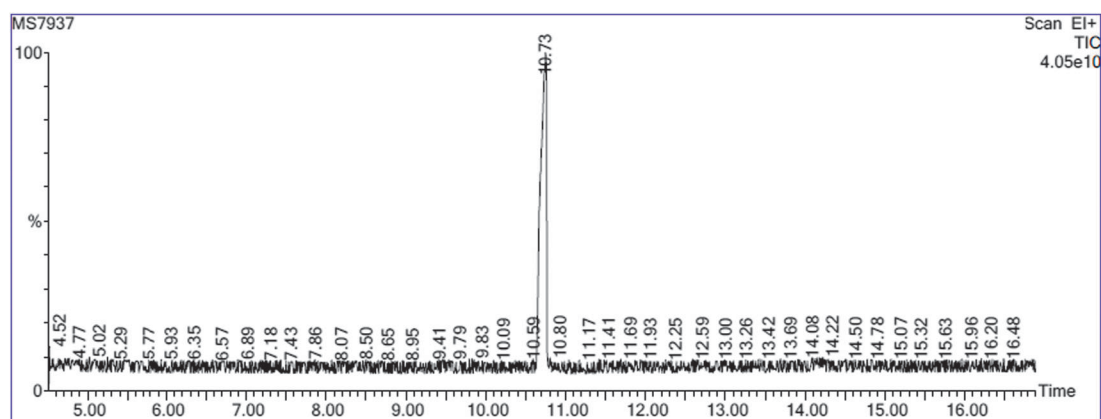
of the nitro group. Selective reduction of the –NO<sub>2</sub> functionality is observed only when strongly deactivating fluoride is bound to the aryl ring (entries 1–5 in Table 4).

When one chloride is present in the substrate molecule (entries 6–13 in Table 4) fast dechlorination generally takes place along with hydrogenation of the nitro residues; and only in the presence of three chlorine atoms de-halogenation is prevented and selectivity in the nitro group reduction was again >90% (entries 15 and 16). Finally, with bromide (entries 17 and 18) and iodide (entry 19) halo-nitroarenes, selectivity was also poor and now also conversion was not complete pointing to likely catalyst deactivation effect due to iodine and bromine atoms bound to the benzene ring.

#### Catalyst recycle

The reusability of the catalyst was studied using methyl-4-nitrobenzoate as substrate of choice. The substrate was dissolved in MeOH (HPLC grade, 0.1 M with respect to the substrate) and the hydrogenation was carried out in the presence of 0.5 mol% of the SiliaCat Pd<sup>0</sup> under the same conditions





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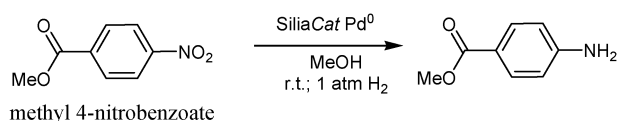
**Fig. 2** Profile of the GC/MS chromatogram after the 8th run in the hydrogenation of methyl-4-nitrobenzoate over 0.5 mol% SiliaCat Pd<sup>0</sup>.

**Table 5** Reusability of the SiliaCat Pd<sup>0</sup> heterogeneous catalyst in the hydrogenation of methyl-4-nitrobenzoate

Run	Catalyst/mol%	Solvent/cm	Time/h	Conversion <sup>a</sup> (%)	Yield <sup>b</sup> (%)	Leaching <sup>c</sup> /ppm	
						Pd	Si
1	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.7	1.6 (16)	1.3 (12.5)
2	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.6	0.2 (2.4)	0.8 (8.2)
3	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.6	0.14 (1.4)	0.9 (8.9)
4	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.2	0.2 (2)	0.5 (5)
5	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.7	0.1 (1.2)	0.6 (6)
6	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.6	0.3 (3.4)	1.1 (11)
7	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	99.3	0.2 (2.6)	1.1 (12)
8	SiliaCat Pd <sup>0</sup> 0.5	MeOH 0.1 M	1/2	100	98.9	0.25 (2.9)	1 (11)

<sup>a</sup> Reaction conditions: room temperature under 1 bar H<sub>2</sub>. Conversion in the final product determined by GS/MS analysis. <sup>b</sup> Isolated yield of the crude product. <sup>c</sup> Leaching determined by ICP analysis in solution (DMF solvent, 0.7 M) and in the solid crude product.

reported above (eqn (2)). The resulting mixture was degassed twice replacing each time the vacuum with H<sub>2</sub>. The reaction mixture, connected to a balloon of hydrogen, was stirred at room temperature for 30 minutes after which the catalyst was recovered by filtration, rinsed with MeOH and dried under vacuum. The conversion was assessed by GC/MS analysis and the filtrate was concentrated to give a crude product.



(2)

Fig. 2 and Table 5 show that total conversion of the substrate with 100% selectivity was obtained even after the 8th cycle.

From an applicative viewpoint, it is of crucial importance the fact that reused in 8 consecutive cycles (Table 5) the SiliaCat Pd<sup>0</sup> catalyst did not show any loss in catalytic activity

with minimal (1–2 ppm) leaching in solution of both Pd and Si (assessed by ICP-MS).

Finally, all nitroarenes hydrogenation reactions were monitored by TLC. In most cases the reactions were very clean, namely showing one product only (single spot on plate) during the reaction and at the end of the conversion. According to the findings in Table 4, however, this was not the case for halide functionalized nitroarenes when the presence of the azoxy compounds was detected both by TLC and in GC/MS analysis.

## Conclusions

In brief, we have developed a new catalyst made of an amorphous organosilica matrix entrapping active Pd nanoparticles suitable for the chemoselective hydrogenation of a wide variety of functionalized nitroarenes to the corresponding anilines under remarkably mild conditions (at room temperature and under 1 bar H<sub>2</sub>) using very low catalyst amount (0.5 mol%) due

to fast kinetics and high TON. Trademarked SiliaCat Pd<sup>0</sup>, the catalyst is highly stable and can be reused several times without loss in activity.

The catalyst, furthermore, offers a number of additional advantages over traditional Pd/C catalysts, including lot-to-lot reproducibility due to intrinsically accurate molecular sol-gel loading;<sup>11</sup> ease and safe handling (Pd/C is pyrophoric); high density (suitable for small volume work); leach-proof nature (ultra low metal contamination of product); and fast, simple recovery of catalyst (the catalyst does not stick to glassware; is mechanically and thermally stable, and solvent independent as organosilica neither shrinks nor swells in any solvent). Given all these features this new catalytic material is amenable to automation in solid phase syntheses, nowadays a well established technology providing with increased productivity in both R&D and manufacturing in the pharmaceutical and fine chemicals industries.<sup>12</sup>

## Acknowledgements

This article is dedicated to Professor John Seddon (Vanguard Consulting, UK) for all he has done for quality in the workplace in all these years.

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