

# Palladium Nanocatalysts Encapsulated on Porous Silica @ Magnetic Carbon-Coated Cobalt Nanoparticles for Sustainable Hydrogenation of Nitroarenes, Alkenes and Alkynes.

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Palladium nanoparticles were impregnated on porous silica shell carbon-coated cobalt nanoparticles, resulting in a magnetically retrievable material that was evaluated in the catalytic hydrogenation of nitroarenes, alkenes and alkynes. The prepared material was characterized by HR-XRD, HR-TEM, elemental mapping EDX, ICP-OES and XPS analyses, revealing highly dispersed palladium nanoparticles within the porous platform

that could account for the high activity observed. Mild reaction conditions, easy retrievability of the catalyst with the aid of an external magnet, recycling in four runs with a total leaching of 19 ppm (1.2% of the initially employed Pd amount), and high stability makes this material attractive for sustainable and environmentally benign applications.

## Introduction

Conventional metal catalysis can be broadly divided into two categories i.e. homogenous and heterogeneous catalysis. In homogenous catalysis, the catalyst and the reactants are in the same phase wherein all the catalytic sites are accessible providing high activity and selectivity through appropriate tuning of the metal center by ligands. However, the recovery of such catalysts is generally difficult, and moreover, contamination of the product by residual metal is hard to avoid, being especially problematic for the synthesis of pharmaceuticals. Nanoparticle (NP) based heterogeneous catalysis<sup>[1]</sup> offers supported metal as active sites which can be easily retrieved from the reaction mixture by filtration, thus improving on the above stated limitations. They are attractive for catalysis because of their large surface area-to-volume ratio and the possibility to modulate their size and hence, the catalytic potential of such materials can be tuned.<sup>[2]</sup> However, the high surface energy of NPs usually causes extensive aggregation,<sup>[3]</sup> which often prohibits a tailoring of the particle size. To overcome this problem stabilizers like ligand caps ranging from small to large organic

molecules are used, which however, might have an adverse effect for the catalytic activity.<sup>[4]</sup> Hence so forth, high surface area materials (e.g., carbon,<sup>[5]</sup> silica,<sup>[6]</sup> zeolites,<sup>[7]</sup> metal oxides<sup>[8]</sup> etc.) were suggested to obtain ultrafine and homogeneously distributed well-defined noble-metal NPs that not only function as barriers to prevent encapsulated NPs from coalescing but also improve the catalytic activity of such functionalized materials. Recently, novel systems such as dendrimers,<sup>[9]</sup> block copolymer nanospheres<sup>[10]</sup> and crosslinked lyotropic liquid crystals,<sup>[11]</sup> were employed to encapsulate metal nanoparticles.

Nano crystallization of heterogeneous catalysts has been hailed as a bridge between heterogeneous and homogeneous catalysis, but the recovery of such nanocatalysts is troublesome because of their small particle size, also augmenting their leaching of active component into the product. To resolve this problem nanoparticles supported on a magnetic core have emerged with the promise of facile recovery with the aid of an external magnet.<sup>[12]</sup>

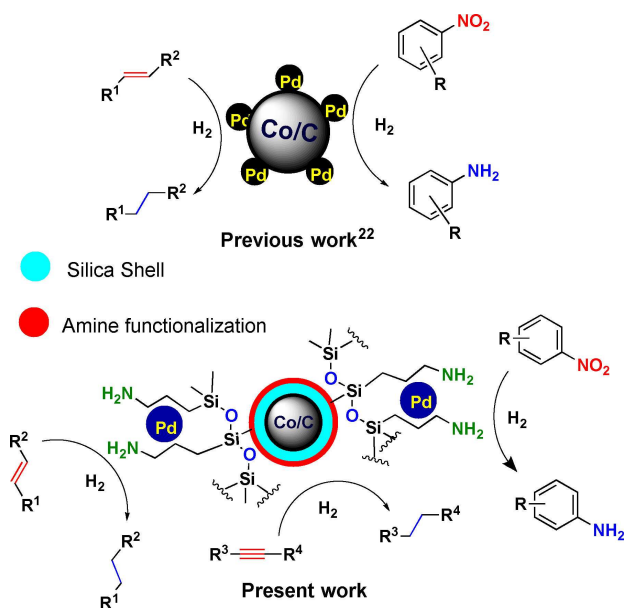
Catalytic hydrogenation of alkenes, alkynes and nitroarenes is an atom economic process being widely utilized in academia and industry. As a result, a great number of palladium nanocatalysts supported on silica,<sup>[13]</sup> alumina,<sup>[14]</sup> SWNT,<sup>[15]</sup> polymer,<sup>[16]</sup> boron nitrides,<sup>[17]</sup> phosphine functionalized supports,<sup>[18]</sup> carbon<sup>[19]</sup> including carbon coated Fe–Ni cores and other magnetic and non-magnetic materials<sup>[12,20]</sup> have been developed (for a representative overview see the Supporting information (SI); table S1). Recently, carbon coated cobalt Co/C nanoparticles emerged as an advantageous and versatile platform for magnetically supported catalysts and reagents.<sup>[21]</sup> Especially, the deposition of palladium nanoparticles on the surface of Co/C nanoparticles led to highly active and magnetically retrievable catalysts for the hydrogenation of alkenes in organic solvents (Figure 1a).<sup>[22]</sup> Although high turnover frequencies were achieved with this catalytic system (up to 4000 cycles/h at room temp. and ambient pressure for the hydrogenation of stilbene), the palladium nanoparticles aggregated on the

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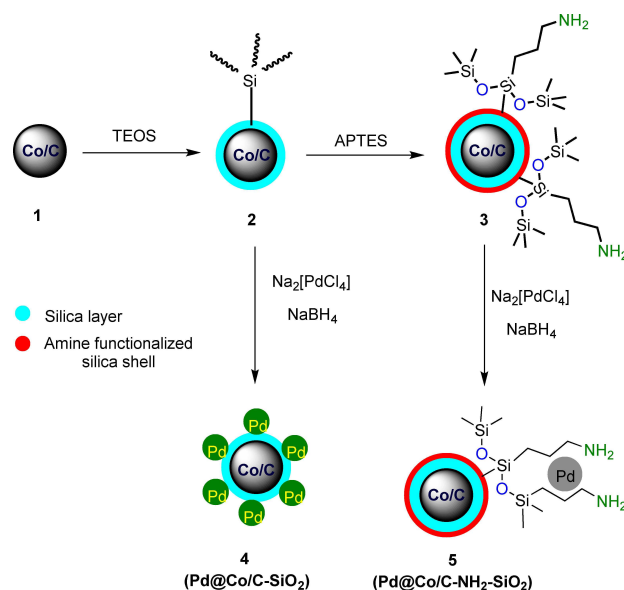
**Figure 1.** Hydrogenation reactions using (a) Pd@Co/C; (b) Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub>.

surface of the Co/C platform over time, thus reducing its activity. As a part of our ongoing effort to develop nanocatalysts for green and sustainable chemistry,<sup>[22,23]</sup> we herein report a nanoparticle hybrid system, which uses porous silica coated amine functionalized Co/C nanoparticles for the encapsulation of palladium nanoparticles (Figure 1b). Due to the amine groups this catalyst shows high stability in polar solvents including water as well as a high affinity for palladium. The fabricated Pd NPs display especially good catalytic efficiency for the reduction of the nitroarenes, and in particular of the anthropogenic pollutant 4-nitrophenol.

## Results and Discussion

Silica and carbon coated cobalt nanoparticles with amine functionalization in their outer shell (Co/C-SiO<sub>2</sub>-NH<sub>2</sub>) **3** were prepared from unfunctionalized Co/C nanobeads<sup>[24]</sup> **1**: Briefly, silica coating with tetraethyl orthosilicate (TEOS)<sup>[25]</sup> led to **2**, followed by amine functionalization using 3-aminopropyltriethoxysilane (APTES) yielding **3** with a high amine loading of 8.5 mmol/g nanomaterial (Scheme 1, characterization Figure S1–S5).

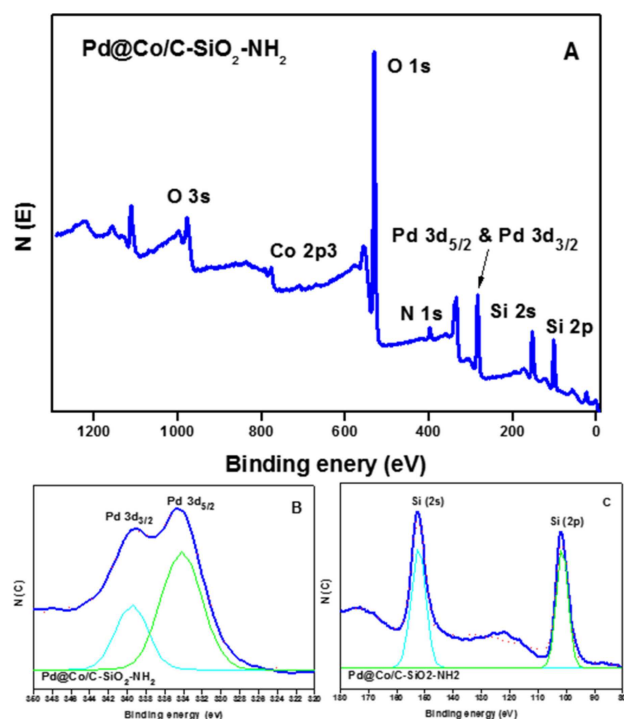
Reduction of Na<sub>2</sub>PdCl<sub>4</sub> with NaBH<sub>4</sub> in the presence of either **2** or **3** resulted in the encapsulation of palladium nanoparticles. Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> **5** (Scheme 1) was obtained with a palladium loading of 0.42 mmol/g (4.5 wt%), corresponding to 68% incorporation of the palladium amount originally employed. For comparison, Pd@Co/C-SiO<sub>2</sub> NPs **4** were synthesized analogously by encapsulating Pd NPs into **2**, resulting only in a negligible palladium loading of 1.22 × 10<sup>-4</sup> mmol/g (1.30 × 10<sup>-3</sup> wt%, < 2% Pd incorporation), demonstrating the benefit of the amine surface modification of the support. Due to the low incorpo-



**Scheme 1.** Preparation of Pd@Co/C-SiO<sub>2</sub> **4** and Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> **5**.

ration of palladium, **4** was not further evaluated. The oxidation state of palladium in Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> **5** was determined to be zero from the Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> binding energies in the X-ray photoelectron spectra (XPS, Figure 2).

Likewise, the presence of silica is confirmed from the binding energies corresponding to Si (2s) and Si (2p) (Figure 2(c)).



**Figure 2.** (a) XPS survey spectra of Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> (**5**). (b) Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> (c) Si(2s) and Si(2p) peaks.

The signal at 402 eV corresponds to nitrogen 1s in agreement with the amino functionalization of the silica coated Co/C. The XPS spectrum also showed an intense peak for oxygen 1s at 531.5 eV owing to the high abundance of oxygen present in the silica coated Co/C support. Additionally, X-ray powder diffraction (Figure 3) was performed: With Pd loadings of 0.421 mmol/g (4.5 wt% of Pd) only the characteristic lines at 2 theta values of 44.2°, 51.5° and 75.8° corresponding to the diffraction of (111), (200), and (220) of the cobalt core were observed together with one broad reflection at 2 theta of 39.9°, which is attributed as the diffraction (111) of crystalline Pd(0). The X-ray powder pattern confirms precipitated SiO<sub>2</sub> with a characteristic broad amorphous peak. Furthermore, the crystallite size of Pd NPs was found to be 4.17 nm as estimated using the Scherrer equation.

HR-TEM analysis (Figure 4) and particle size distribution maps of catalyst 5 (Figure 7a) further support the formation of small, well dispersed palladium nanoparticles (3–5 nm) around the amine functionalized silica coated Co/C nanobeads (Figure 4e). The interplanar spacings for the lattice fringes of Pd were 0.302 nm and 0.292 nm, which correspond to the (111) and (200) lattice planes of the face-centred cubic (fcc) Pd structure (Figure 4c). The selected-area electron diffraction (SAED) pattern corresponds to the (111), (200) and (220), of the expected fcc Pd (Figure 4d).

Elemental mapping of 5 showed a homogeneous distribution of carbon (from graphene), cobalt, silica, oxygen, nitrogen and palladium on the catalysts (Figure 5 A–H). The energy dispersive X-ray spectrometry (EDX) of the sample confirmed the presence of the same elements (Figure 6).

Thus, the prepared Pd@Co/C–SiO<sub>2</sub>–NH<sub>2</sub> material 5 has well-dispersed Pd(0) nanoparticles embedded in a highly porous amine functionalized silica shell support, and the data are in good agreement with previously reported nanocatalysts immobilized on the magnetic Co/C platform.<sup>[22,23]</sup> Next, we evaluated its catalytic activity initially for the reduction of nitrobenzene at room temperature and 1 atm hydrogen pressure (Table 1).

In the presence of non-polar solvents, i.e. toluene, no hydrogenated product was observed (Table 1, entry 3), while polar protic solvents such as EtOH, MeOH, gave rise to aniline, albeit in low yields (Table 1, entries 1,2). *i*-PrOH proved to be an excellent medium for catalyst 5, allowing the generation of aniline in quantitative yield within 2.5 h (Table 1, entry 5). Remarkably, catalyst 5 also performed well in water (Table 1, entry 4).

No conversion was observed in the absence of a catalyst 5 or by just using 2, excluding any significant catalytic activity by the support itself (entries 6,7, Table 1). In the absence of molecular hydrogen no conversion was observed indicating that 2-propanol is not taking part as a hydrogen donor for catalyst 5 (entry 8, Table 1). 5 compares well with literature reports wherein modified Pd/C (with Fe–Ni magnetic core),<sup>[19]</sup> Pd/C<sup>[26]</sup> or Pd/MgF<sub>2-x</sub><sup>[27]</sup> is used for the title reaction (see SI for details).

Next, we investigated the scope for catalyst 5 by applying it for the hydrogenation of various alkenes, alkynes, and nitroarenes (Table 2). Given that toluidines have wide applications in

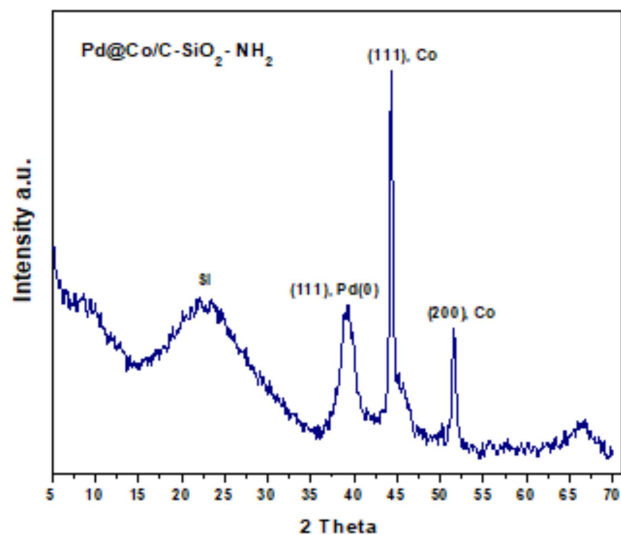


Figure 3. HR-XRD of Pd@Co/C–SiO<sub>2</sub>–NH<sub>2</sub> 5.

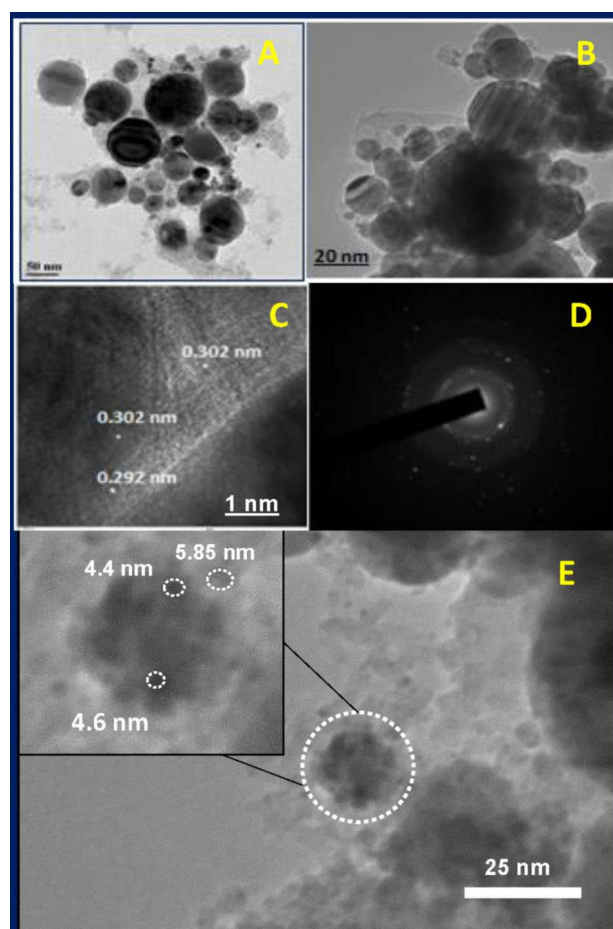


Figure 4. HRTEM images of Pd@Co/C–SiO<sub>2</sub>–NH<sub>2</sub> 5 (A–C); (D) The selected-area electron diffraction (SAED) pattern; (E) Impregnated Pd NPs on Co/C–NH<sub>2</sub>–SiO<sub>2</sub> support (see inset).

pesticides (*o*-toluidine) and in the dye industry (*p*-toluidine), nitrotoluenes (*o*-, *m*- and *p*-) we were pleased to find that the

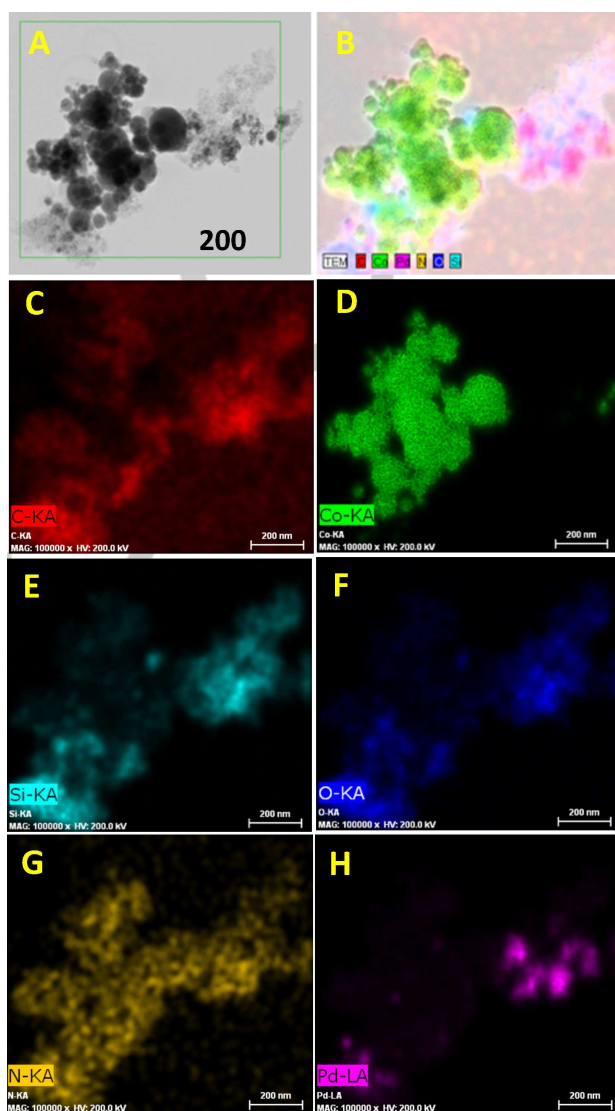


Figure 5. Elemental mapping (A–H) of Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> 5.

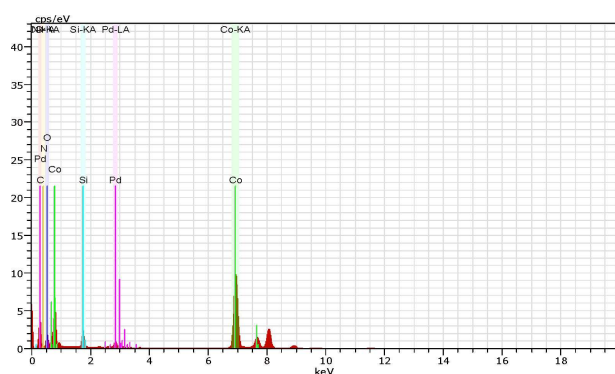


Figure 6. Energy dispersive X-ray spectrometry (EDX) analysis of Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> 5.

corresponding nitroarenes were successfully reduced to the corresponding anilines. Both electron donating (OH, OMe, Me)

Table 1. Optimization study for hydrogenation of nitrobenzene to aniline<sup>[a]</sup>

Entry	Catalyst	Solvent	t [min]	Pd [mol %]	Yield [%] <sup>[b]</sup>
1	5	EtOH	150	0.16	12.3
2	5	MeOH	150	0.16	39.5
3	5	Toluene	150	0.16	0
4	5	Water	150	0.16	94
5	5	<i>i</i> PrOH	150	0.16	100
6	2	<i>i</i> PrOH	1440	–	0
7	–	<i>i</i> PrOH	1440	–	0
8 <sup>[c]</sup>	5	<i>i</i> PrOH	1440	0.16	0

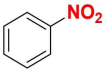
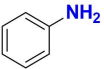
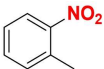
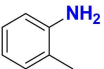
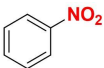
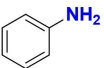
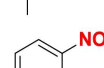
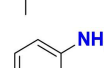
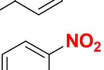
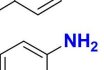
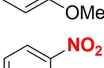
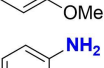
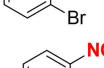
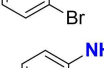
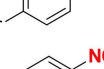
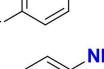
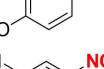
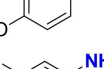
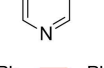
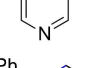
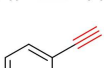
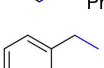
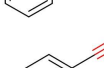
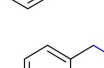
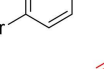
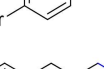
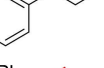
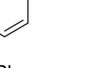
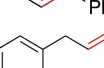
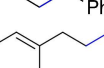
Reaction conditions: [a] Nitrobenzene (0.81 mmol), dodecane (0.89 mmol, internal standard), solvent (5 ml), and catalyst were stirred for the indicated time at an ambient atmosphere of molecular hydrogen and room temp, [b] Yield was determined by GC using dodecane as internal solvent, [c] In absence of molecular H<sub>2</sub>.

as well as electron withdrawing substituents (Br, Cl) or exchanging phenyl for pyridyl were tolerated well and especially showed no cross reactivity to undergo competitive reduction, contrasting other Pd based nanocatalysts that have been reported to effect hydrodehalogenation of bromo- and chloroarenes.<sup>[28]</sup> Particularly gratifying, the hydrogenation of 4-nitrophenol, being important for environmental reasons as well as for the synthesis of scaffolds relevant in medicinal chemistry proceeded with a TOF of 417 h<sup>-1</sup>, comparing well to reports in the literature.<sup>[29]</sup>

To ascertain the heterogeneity nature of the Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> catalyst, a filtration test was performed wherein hydrogenation reaction of nitrobenzene was stopped midway (75 min), and the catalyst was removed by the aid of an external magnet. The reaction was continued for 24 h: no additional formation of aniline was observed indicating that no active catalyst species leached in the reaction mixture (see SI).

Recyclability of the catalyst 5 was also studied (Table 3): The reduction of nitrobenzene was carried out on an 8.0 mmol scale again using with 0.16 mol% of catalyst 5. After completion of the reaction, the catalyst was separated from the reaction-mixture by the aid of an external magnet within seconds, washed with 2-propanol (2×5 mL) and acetone (2×5 mL), dried under vacuum and subjected to subsequent runs (total of four runs). Overall, good activity (> 139 TOF (h<sup>-1</sup>)) and low palladium leaching (3–8 ppm per cycle) was observed, nevertheless, some loss of activity was observed in subsequent cycles (Table 3, entry 1–4), reflected by an increase of reaction time to reach full conversion. Given the low palladium leaching and by and large unchanged particle sizes (Figure 7b, Figure S6), loss of palladium or agglomeration appear not to be a major factor for this observation. Since catalyst isolation and recycling was handled open to air, passivation of the surface by oxidation, which required a longer induction over time in the hydrogenation, seemed to be the most relevant factor for the prolonged reaction times. This is corroborated by XRD studies of recycled

**Table 2.** Substrate scope using Pd@Co/C–SiO<sub>2</sub>–NH<sub>2</sub> catalyst 5<sup>[a]</sup>.

Entry	Substrate	Product	t [min] <sup>[b]</sup>	TOF [h <sup>-1</sup> ] <sup>[c]</sup>	Isolated yield[%] <sup>[d]</sup>
1			150	250	96
2			120	312	94
3			120	312	N.D.
4			120	312	94
5			110	341	92
6			100	375	92
7			100	375	N.D.
8			90	417	N.D.
9			180	208	N.D.
10			30	1250	N.D.
11			40	937	N.D.
12			40	937	N.D.
13			30	1250	N.D.
14			25	1500	N.D.
15			25	1500	N.D.

Reaction Conditions: [a] Substrate (0.81 mmol), dodecane (0.89 mmol), 2-propanol (5 mL), catalyst 5 (3 mg, 0.0013 mmol, 0.16 mol%) were stirred at RT, [b] Time required for full conversion was determined by GC analysis (product selectivity 100%) using dodecane as an internal standard, [c] TOF values are calculated as mmol substrate per mmol palladium per time, [d] As in [a] without internal standard.

catalyst 5 (SI, Figure S7), showing that oxidation to Pd(II) has occurred.

## Conclusions

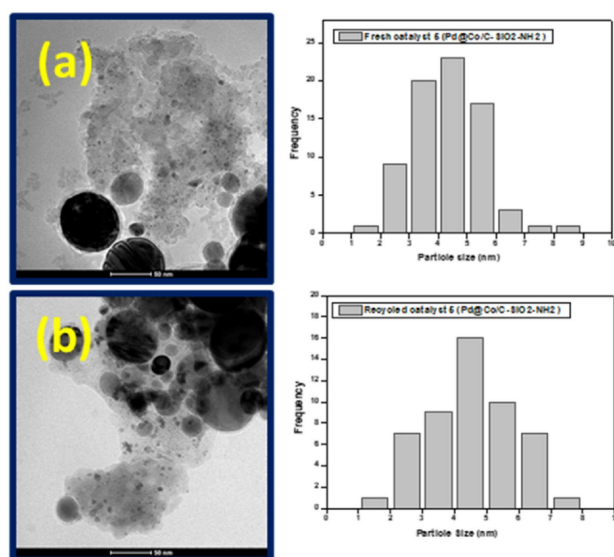
We have developed an amine functionalized-silica shell coated Pd nanomaterial i.e. Pd@Co/C–SiO<sub>2</sub>–NH<sub>2</sub> 5, being efficient in the hydrogenation of nitroarenes, alkenes and alkynes under ambient hydrogen pressure and room temperature. The

catalysts could be recycled at least four times, reaching a total turnover number of  $\geq 2500$ . The palladium nanoparticles are firmly embedded in the Co/C magnetic nanoparticles coated with an amine functionalized silica surface, resulting in a stable, magnetically retrievable nanocatalyst with a leaching of Pd below 8 ppm/cycle. Further investigations on the feasibility and pertinability of this catalyst for related organic transformations are currently underway.

**Table 3.** Recyclability and determination of the leaching in the hydrogenation of nitrobenzene.<sup>[a]</sup>

run	Full conversion time [min] <sup>[b]</sup>	TOF [h <sup>-1</sup> ] <sup>[c]</sup>	Leaching Pd [ppm]
1	150	250	5
2	165	227	3
3	180	208	8
4	270	139	3

Reaction conditions: [a] Nitrobenzene 1 (8.1 mmol), dodecane (8.9 mmol), Isopropanol (20 mL), catalyst 5 (30 mg, 0.013 mmol, 0.16 mol%) were stirred at RT, [b] Time required for full conversion was determined by GC analysis (product selectivity 100%) using dodecane as an internal standard, [c] TOF values are calculated as mmol substrate per mmol palladium per time.

**Figure 7.** Particle size distribution maps for (a) Pd@Co/C-SiO<sub>2</sub>-NH<sub>2</sub> 5 and (b) recycled catalyst 5 (after 4<sup>th</sup> run).

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Pd nanoparticles · Nitrobenzene · heterogeneous catalysis · Hydrogenation · immobilization

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