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Polymethylhydrosiloxane derived palladium nanoparticles for chemo- and regioselective hydrogenation of aliphatic and aromatic nitro compounds in water†

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Chemo- and regioselective hydrogenation of a wide range of aliphatic, unsaturated, aromatic and heteroaromatic nitro compounds into their corresponding amines has been achieved with highly efficient polysiloxane-stabilised "Pd" nanoparticles on NAP-magnesium oxide supports using an environmentally friendly hydrogenating agent, polymethylhydrosiloxane [PMHS] in water. Highly stable and active Pd nanoparticles were prepared by the reduction of NAP-Mg-$PdCl_4$ with PMHS, which serves as a reducing agent as well as a capping agent. The well-dispersed palladium nanoparticles on NAP-MgO catalysts also exhibit excellent regioselectivity in the hydrogenation of dinitrobenzenes to the corresponding nitroanilines. The catalyst has high durability against sintering during the hydrogenation reaction and can be reused with no loss in its activity.

Introduction

The selective hydrogenation of functionalized nitro compounds to their corresponding amines is of paramount importance in organic synthesis since functionalized amines are vital intermediates and key precursors in the synthesis of dyes, pigments, agrochemicals, polymers, herbicides, and pharmaceuticals.[1–3] The use of several reducing agents[4] with transition metal-based catalysts[5] is limited by the expense of these reducing agents when used in stoichiometric amounts and is restricted based on safety and handling considerations because of their hazardous nature.[6–11] In this respect, catalytic hydrogenation[12] has garnered much attention as it is an effective and economical method, particularly in large-scale reactions. However, the selective hydrogenation of a functionalized nitro compound to the desired corresponding amine continues to remain in serious need of improvement. RANEY®nickel, palladium or platinum modified by special additives are the most commonly available catalysts used to carry out the selective hydrogenation of substituted nitroarenes.[13–16] Despite the efficiency of these catalysts, there are several reported disadvantages with one or the other of these catalysts, mainly moisture sensitivity, pyrophoric nature, lack of selectivity for the desired product, the requirement for a special reactor because of the high temperature and high pressure of the reaction, expense and long reaction time. In addition to the above drawbacks, in the case of Pd- and Pt-based catalysts the presence of trace impurities that deactivate the active catalyst and leaching of metals are added disadvantages. More recently, Corma *et al.* and Xia-Bing Lou *et al.*, have independently demonstrated and disclosed a heterogeneous gold-based catalyst that can hydrogenate nitro compounds selectively in the presence of a variety of functional groups.[17,18] In addition to the previously mentioned noble catalysts, heterogenized cobalt oxide catalyst, active copper nanoparticles prepared *in situ*, recyclable copper(II) as well as cobalt(II) phthalocyanines have been reported for the chemo- and regioselective reduction of aromatic nitro compounds.[19]

Nevertheless, so far there exist only a limited number of successful heterogeneous catalyst systems that allow a selective hydrogenation of all kinds of nitro compounds. In view of these impediments in selectivity and scale-up methods, there is enormous interest in developing an efficient, active and environmentally sustainable catalytic system that would perform the selective hydrogenation of nitro compounds in the presence of other reducible functional groups, such as ketones, aldehydes, alkenes or alkynes.[20–25] Such a catalytic system with high functional-group tolerance might also obviate the need for protecting groups and streamline more complex syntheses.

The development of new green methodologies has been a part of our research program. In a continuation of our earlier

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† Electronic supplementary information (ESI) available: General remarks, preparation of catalysts, SEM-EDX, TEM images, XRD and XPS of NAP-Mg-Pd(0) PS, spectroscopic characterizations (^{1}H NMR and ^{13}C NMR) of the products. See DOI: 10.1039/c4ra01333f

work,[26] we report here the preparation of highly efficient polysiloxane-stabilised "Pd" nanoparticles supported on nanocrystalline magnesium oxide [NAP-Mg-Pd(0)PS] by reducing NAP-Mg-$PdCl_4$ with polymethylhydrosiloxane [PMHS]. The basic NAP-MgO possesses inherently a high concentration of surface ions in its well-defined three-dimensional structure that leads to high surface reactivity. With these properties NAP-MgO acts as the finest support for good dispersion of Pd(0) nanoparticles and enhances the catalytic activity of the metal nanoparticles as well. The role of PMHS is to reduce the metal ion as well as to act as a capping agent to enhance the stability and durability of highly active nano Pd(0). The [NAP-Mg-Pd(0)PS] prepared was then used in chemo- and regio-selective hydrogenation of a wide range of aliphatic, unsaturated, aromatic and heteroaromatic nitro compounds into their corresponding amines using PMHS as a hydrogenating agent and water as a solvent. PMHS acts as a hydrogen source for economically favourable hydrogenating processes, being a non-toxic, biodegradable and inexpensive reducing agent.[27] Moreover, PMHS is more air and moisture stable than other silanes and can be stored for longer periods of time without loss of activity. To our knowledge, only a limited number of reports about the hydrogenation of nitro compounds using silanes/siloxanes have been published to date.[28–30]

Experimental procedure

Preparation of the catalyst

NAP-Mg-$PdCl_4$. The brown-colored NAP-Mg-$PdCl_4$ (ref. 31) was obtained by treating NAP-MgO (BET surface area of 600 m^2 g^{-1}, 1 g) with Na_2PdCl_4 (294 mg, 1 mmol) and dissolved in 100 mL decarbonated water with stirring for 12 h, maintained in a nitrogen atmosphere. The catalyst obtained was filtered, washed with deionized water, acetone and dried at 65 °C in an oven.

NAP-Mg-Pd(0)PS. NAP-Mg-$PdCl_4$ catalyst (1 g) was reduced with PMHS (Av. MW 2000, 33–35 Si–H units, 0.75 mL, 12 mmol) in 30 mL ethylene glycol (EG) for 2 h in a round-bottom flask under a nitrogen atmosphere (Fig. 1). Finally, black-colored, air-stable NAP-Mg-Pd(0)PS was obtained as crystalline material (Pd: 0.99 mmol g^{-1}). The other catalysts were synthesized based on methods found in the literature.[32]

General procedure for the hydrogenation of nitroarenes to amines

A 50 mL round-bottom flask was charged with nitroarene (1 mmol), triethylamine (0.75 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), and 3 mL water under stirring at room temperature. PMHS (4 mmol) was slowly added (dropwise), under a nitrogen atmosphere, to avoid violent evolution of gas. The reaction mixture was then stirred at 80 °C in a pre-heated oil bath until completion of the reaction as confirmed by TLC. The reaction flask was then opened to the atmosphere, cooled to room temperature and diluted with 5–10 mL of diethyl ether. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum. The resulting products were purified by flash column chromatography and the amines were characterized by ^1H NMR and ^{13}C NMR spectroscopic methods (see ESI†).

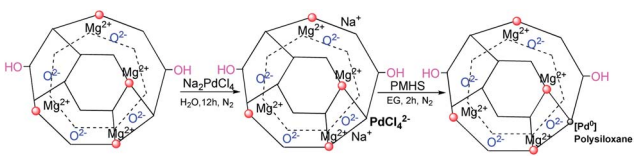

Fig. 1 Preparation of NAP-Mg-Pd(0)PS catalyst from NAP-Mg-$PdCl_4$ and PMHS.

Results and discussion

The stable NAP-Mg-Pd(0)PS catalyst was prepared and well characterized by XRD, XPS, SEM-EDX, and TEM methods. XRD and XPS determinations were compared with previous reports[33] (see ESI†). Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) of NAP-Mg-Pd(0)PS showed the presence of palladium (12.78%) in the sample, and TEM results showed quite well the dispersion of 6–7 nm sized Pd(0) nanoparticles on NAP-MgO. The complete reduction of the palladium ion was further confirmed by X-ray photoelectron spectroscopy (XPS) spectra, in which the 3d level of Pd shows a $3d_{5/2}$ line at 335.02 eV. The main objectives for the development of the NAP-Mg-Pd(0)PS catalyst from PMHS are that it is easy to handle and acts as an environmentally friendly reducing agent (for the reduction of Pd(II) to Pd(0)) as well as a hydrogenating agent (for nitro to aniline). Secondarily, in the reduction of Pd(II) to Pd(0), PMHS acts as a capping agent and thereby enhances the stability and efficiency of the catalyst.

Screening of catalysts

Initially, the catalytic hydrogenation was examined using 4-nitropyridine as a model substrate with various hydrogen sources in combination with different bases and polar solvents. It was observed that the reaction was highly effective in polar solvents, such as CH_3OH, THF, DMF and water, whereas a very low yield of the desired product was observed with the non-polar solvent, toluene. The highest yields of 4-aminopyridine were obtained in water (92%) and a mixture of THF + water solvents (93%). These yields are nearly identical to one another, so water was used as the preferred reaction medium in the subsequent hydrogenation of various nitro compounds (Table 1).

To confirm the high catalytic activity of NAP-Mg-Pd(0)PS over Pd(0) on other supports, we prepared Pd(0) reduced by PMHS on various supports and screened for hydrogenation of 4-nitropyridine in water (Fig. 2). While screening the various catalysts, we found that the hydrogenation reaction can also be catalysed by Pd(0) supported on HAP, FAP, TiO_2, Al_2O_3, MgO and SiO_2. The purpose of selecting different supports was to investigate the effect of supports and dispersion and the stability of the Pd(0) nanoparticles with suitable supports. Pd(0) supported on SiO_2 and commercial MgO display higher catalytic

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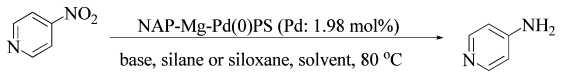
Table 1 Screening of base, solvent, and silane/siloxanes for the hydrogenation of 4-nitropyridine[a]



Entry	Si–H species	Solvent	Base	Isolated yield[b] (%)
1	PMHS	DMF	TEA	63
2	PMHS	Toluene	TEA	Trace
3	PMHS	THF	TEA	65
4	PMHS	MeOH	TEA	68
5	PMHS	H_2O	TEA	92
6	PMHS	THF : H_2O (50 : 50)	TEA	93
7	Et_3SiH	H_2O	TEA	61
8	$EtO(Me)_2SiH$	H_2O	TEA	67
9	$Et(Me)_2SiH$	H_2O	TEA	62
10	PMHS	H_2O	—	77
11	PMHS	H_2O	K_3PO_4	74
12	PMHS	H_2O	KOH	72
13	—	H_2O	TEA	n.r.
14	PMHS	H_2O	K_2CO_3	61
15	PMHS	H_2O	CS_2CO_3	64

[a] Reaction conditions: 4-nitropyridine (1.0 mmol), catalyst (0.020 g, Pd: 1.98 mol%), base (0.75 mmol), silane (hydrogen source) (4 mmol), solvent (3 mL), 80 °C, 6 h. [b] Isolated yield of product. n.r. = no reaction.

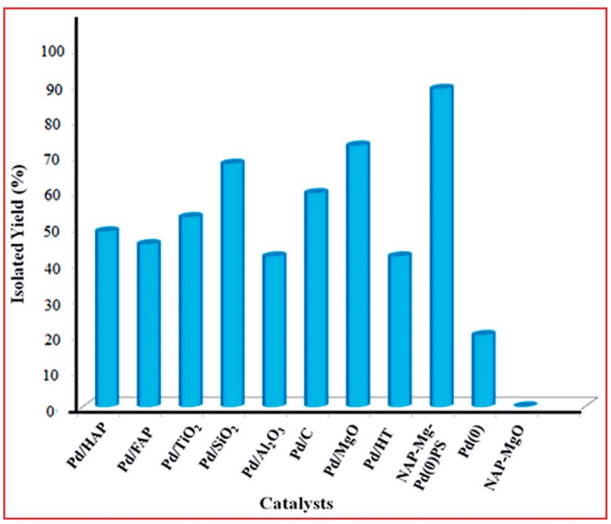


Fig. 2 Hydrogenation of 4-nitropyridine using various Pd catalysts. [a]Reaction conditions: 4-nitropyridine (1.0 mmol), catalyst (0.020 g, Pd: 1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL), 80 °C, 6 h.

activity (72% and 76%, respectively) than Pd(0) supported on HAP, FAP, Al_2O_3 and HT (45–50%). Pd(0) supported on NAP-MgO (NAP-Mg-Pd(0)PS) catalyst efficiently catalyzes the hydrogenation of 4-nitropyridine and afforded excellent yield of product (92%) due to the high surface area and high basicity of the NAP-MgO support.

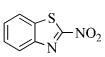
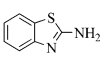
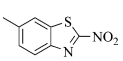
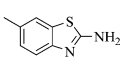
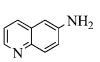
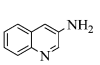
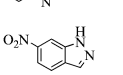
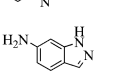
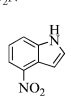
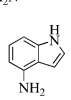
Eventually, the system consisting of polysiloxane-stabilised Pd(0) nanoparticles on NAP-magnesium oxide support, NAP-Mg-Pd(0)PS with triethylamine and water solvent was the catalytic system chosen for the hydrogenation of various functionalized nitro compounds.

Hydrogenation of heteroaromatic nitro compounds

After the success in hydrogenation of 4-nitropyridine with an optimized set of reaction conditions, we investigated the scope of selective hydrogenation of a variety of heteroaromatic nitro compounds (Table 2, entries 2–16).

There are several advantages to using of water as a solvent. It is environmentally safe, readily and abundantly available, and inexpensive. Moreover, the use of water rather than organic solvents is an important theme of current research, and hydrogen has good solubility in water.[34] Nevertheless, the development of eco-friendly efficient processes using metal

Table 2 Hydrogenation of various heterocyclic nitro compounds[a]

Entry	Substrate	Product	Time (h)	Conv./selectivity (%)	Yield[b] (%)
1			6	99/99	92, 90[c]
2			4	98/99	92
3			8	93/99	90
4			6	99/99	91
5			4	97/99	90
6			4	97/99	91
7			8	96/99	90
8			6	96/99	92
9			4	97/99	91
10			6	95/99	89
11			4	98/100	91
12			4	99/100	92
13			4	98/99	93
14			6	97/99	90
15			6	94/99	90
16			4	98/99	91

[a] Reaction conditions: nitro compound (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL), 80 °C. [b] Isolated yield of product. [c] Yield after 5th reuse.

nanoparticles that are stable in the aqueous phase remains a challenge.[35]

The results in Table 2 show that a wide variety of heteroaromatic nitro compounds were hydrogenated in water to their corresponding amines in almost quantitative yields. Essentially, the fused heterocyclic rings such as 2-aminobenzothiazole, 6-aminoindazole, 5-aminobezoxazole and amino group-containing quinolines and indoles (Table 2, entries 8–16) were obtained in excellent yields and the ring systems remained intact under reaction conditions. In the cases of 2-nitropyrimidine and 2-nitrothiazole, the entire nitro group was hydrogenated within 8 h.

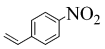
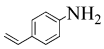
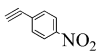
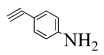
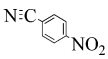
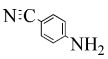
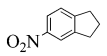
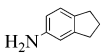
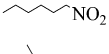
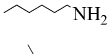
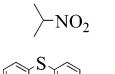
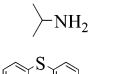
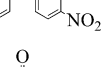
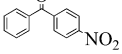
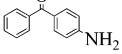
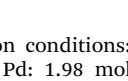
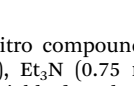
Hydrogenation of functionalized and saturated nitro compounds

Recently, Corma and Serna have achieved good chemoselectivity, in the presence of unsaturated bonds using a supported gold catalyst.[17] However, no examples were reported of gold-catalysed hydrogenation of nitro compounds containing other reducible substituents such as alkynes, iodides or heteroarenes.

We examined the catalytic activity of NAP-Mg-Pd(0)PS in the hydrogenation of the most challenging substrates that bear other easily reducible functional groups such as cyano and C–C double and triple bonds, and found that the chemoselective hydrogenation of the nitro group even in the presence of alkenes, alkynes, and cyano functional groups could proceed with high conversion and with no contemporaneous hydrogenation of the unsaturated unit (Table 3, entries 1–3).

We were delighted to observe the hydrogenation of a wide variety of alicyclic and linear aliphatic nitro compounds. In the hydrogenation of nitrocyclohexane, cyclohexylamine was obtained as the corresponding hydrogenated product with a 92% yield within 2 h (Table 3, entry 8). In addition to hydrogenation of fused aromatic-ring compounds (Table 3, entries 5 and 6), (4-nitrophenyl)(phenyl)methanone and (4-nitrophenyl)(phenyl) sulfane were also selectively hydrogenated smoothly with good yields (Table 3, entries 14 and 15).

Table 3 Hydrogenation of functionalized, alicyclic and linear alkyl nitro compounds[a]

Entry	Substrate	Product	Time (h)	Conv./sel. (%)	Yield[b] (%)
1			6	98/99	92
2			4	99/99	93
3			8	99/98	92
4			4	98/99	91
5			5	97/100	91
6			4	98/99	92
7			2	96/99	91
8			2	99/100	92, 90[c]
9			4	98/100	91
10			2	99/100	93
11			2	98/100	91
12			2	99/100	92
13			1.5	98/100	91
14			6	97/99	92
15			6	97/99	91

[a] Reaction conditions: nitro compound (1.0 mmol), NAP-Mg-Pd(0)PS (0.20 g, Pd: 1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL), 80 °C. [b] Isolated yield of product. [c] Yield after 5th reuse.

Hydrogenation of various aromatic nitro compounds

Finally, various nitro aromatics with different halides (Cl, Br, I and F) were studied for the selective hydrogenation in the presence of a NAP-Mg-Pd(0)PS catalyst and PMHS. The corresponding anilines were obtained with excellent yield, and no dehalogenated anilines were observed as by-products (Table 4, entries 2 and 3). The selective hydrogenation of chloro-substituted nitrobenzene without dechlorination is an important industrial reaction and the NAP-Mg-Pd(0)PS catalyst with PMHS afforded excellent selectivity for, and yield of, the desired corresponding anilines.

To examine the stability and efficiency of the catalyst in a large-scale reaction, we performed the selective hydrogenation of 2-chloronitrobenzene (10 mmol) (Table 4, entry 13), and obtained an excellent yield of the desired hydrogenated 2-chloroaniline with 97% selectivity which signifies that the present catalytic system can be applied for the selective hydrogenation of 2-chloronitrobenzene at the industrial scale. Interestingly, in the case of hydrogenation of 1,4-dinitrobenzene, we found that NAP-Mg-Pd(0)PS and PMHS could selectively hydrogenate one nitro group to 4-nitroaniline with an excellent yield (97%). It has been observed that many conventional hydrogenation procedures involving hydride reducing agents fail to give high regioselectivity.[4b,33a] The regioselective hydrogenation of one nitro group in dinitrobenzene is one of the most exciting results of our present study. The regioselective hydrogenation of *o*-, *m*-, and *p*-dinitrobenzene with NAP-Mg-Pd(0)PS and PMHS also afforded corresponding nitroanilines in excellent yields under our reaction conditions (Table 4, entries 5–7) and no phenylenediamine was detected. These results indicate a high regioselectivity in hydrogenation of dinitro compounds under set optimized reaction conditions with NAP-Mg-Pd(0)PS catalyst and PMHS.

The selectivity, which is highly desirable in the chemical industry, simplifies the product separation and avoids

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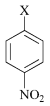
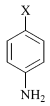
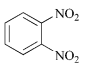
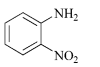
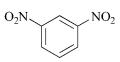
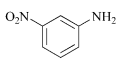
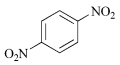
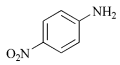
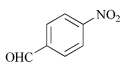
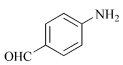
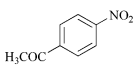
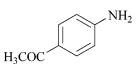
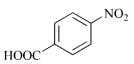
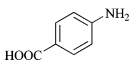
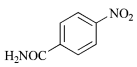
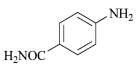
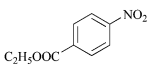
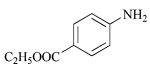
Table 4 Hydrogenation of various aromatic nitro compounds[a]

Entry	Substrate	Product	Time (h)	Conv./selectivity (%)		Yield[b] (%)
1			2	98/99		96
2			2	99/99	X = CH_3	98
			2	100/100	X = $CH(CH_3)_2$	99
			2	99/99	X = $C(CH_3)_3$	98
			2	100/100	X = OCH_3	99
			3	95/100	X = F	94
			3	97/100	X = Cl	95
			3	97/100	X = Br	94
			2	100/100	X = OH	97
			3	98/100	X = NH_2	96
3			2	98/100	Y = CH_3	95
			2	95/100	Y = F	93
			2	97/100	Y = Cl	93
			2	98/99	Y = Br	94
			2	99/99	Y = I	96
4			2	99/100		97
5			2	97/99		95
6			2	96/99		94
7			2	97/99		95
8			2	96/99		91
9			2	96/99		92
10			2	98/100		93
11			2	95/100		90
12			2	96/100		91
13[c]			2	97/100		91

[a] Reaction conditions: nitro compound (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL), 80 °C. [b] Isolated yield of product. [c] Reaction conditions: 2-chloro nitrobenzene (10 mmol), NAP-Mg-Pd(0)PS (0.20 g, Pd: 1.98 mol%), Et_3N (7.5 mmol), PMHS (40 mmol), H_2O (30 mL), 80 °C for 2 h.

unwanted disposal, which makes the processes environmentally friendly. The substrates containing sensitive functional groups such as aldehydes or ketones were investigated for the hydrogenation reaction, and we found that the selected nitro group was converted into the corresponding aniline without altering sensitive functional groups (entries 8 and 9). Furthermore, carboxylic acid derivatives, such as esters and amides, were also tolerated well by hydrogenation under set optimized reaction conditions and yielded selective corresponding anilines in good to excellent yields (Table 4, entries 10–12).

Kinetic study of hydrogenation of 4-nitropyridine

To understand the hydrogenation process we performed a kinetic study. The hydrogenation of 4-nitropyridine using NAP-Mg-Pd(0)PS (Pd: 1.98 mol%) was investigated at different intervals of time as shown in Fig. 3. The reaction time (h) *versus* concentration or selectivity is plotted in the graph to study the effect of increase in time on conversion and selectivity of the product in the hydrogenation reaction. It was observed that the yield of 4-aminopyridine increased with time and the concentration of 4-nitropyridine gradually decreased to zero mmol

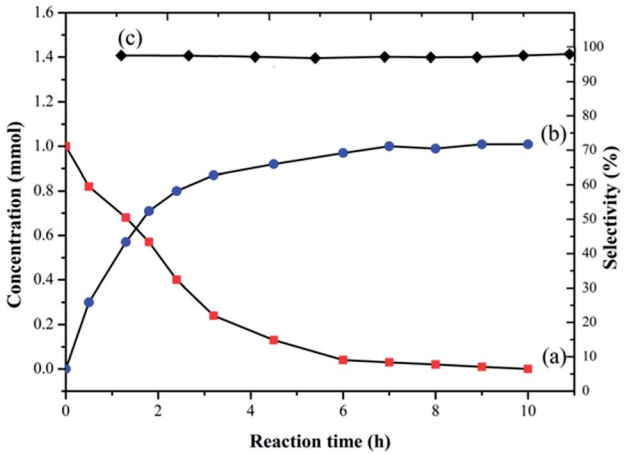


Fig. 3 Hydrogenation of 4-nitropyridine: (a) concentration of 4-nitropyridine; (b) concentration of 4-aminopyridine; (c) selectivity of 4-aminopyridine at different reaction times.

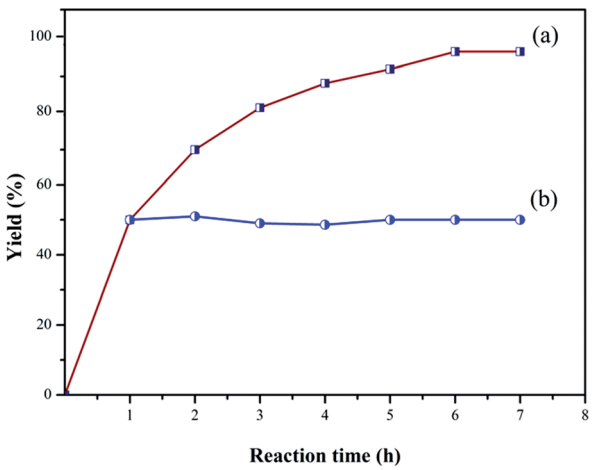


Fig. 4 (a) The kinetic plot of hydrogenation of 4-nitropyridine; and (b) the reaction kinetics when the catalyst NAP-Mg-Pd(0)PS was removed from the reaction mixture after 1 h.

Table 5 The reusability of the NAP-Mg-Pd(0)PS for the hydrogenation of nitrocyclohexane[a]

	Yields of isolated products[b] (%)				
Substrate	Run 1	Run 2	Run 3	Run 4	Run 5
Nitrocyclohexane	92	92	91	90	90
4-Nitrobenzaldehyde	91	90	90	89	89

[a] Reaction conditions: nitrocompound (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL). [b] Isolated yield of product.

after 10 h. There is no change observed in selectivity with increase in time.

To examine the true heterogeneity of NAP-Mg-Pd(0)PS in the hydrogenation of 4-nitropyridine, the reaction was terminated after 60 min (50% conversion) and the catalyst was filtered under hot conditions (Fig. 4(b)). The reaction mixture (filtrate) was continued for more than 7 h. During this time period, the progress of the reaction was monitored by GC every hour. The results illustrated in the graph (yield (%) *vs.* reaction time) suggest that there is no product formation after removal of the catalyst from the reaction mixture and that hydrogenation of the nitro compounds is carried out solely by NAP-Mg-Pd(0)PS catalyst and not by the leached palladium.

Reusability study of catalyst

The synthesized catalyst was reused five times without significant loss of catalytic activity. The SEM and TEM analyses showed that the particle size and morphology of NAP-Mg-Pd(0)PS is identical before and after the reaction (see ESI†) (Table 5).

Conclusion

We have developed an efficient and eco-friendly protocol using NAP-Mg-Pd(0)PS as the catalyst and PMHS as the hydrogenating source with high chemo- and regio-selectivity in hydrogenation of a wide range of heteroaromatic, functionalized aromatic, alicyclic, and linear aliphatic nitro compounds in an aqueous medium under mild reaction conditions. The simple operation, easy recovery, reusable catalytic systems and short reaction times are the main advantages of this system, and this work contributes to the development of environmentally safe chemical processes.

The advantages of the present report are highlighted by two main features that are also among the 12 principles of green chemistry.[36] One is energy efficiency, as the reaction is carried out with the hydrogen source PMHS, which is a by-product of the silicon industry and which is also used for the reduction of palladium(II). The role of PMHS is not only to reduce the palladium but also to act as a capping agent for the long-term stable activity of the catalyst. The second feature is atom economy in achieving a very high selectivity for the desired products.

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