Polymethylhydrosiloxane Derived Palladium Nanoparticles for Chemo- and Regioselective Hydrogenation of Aliphatic and Aromatic Nitro Compounds in Water

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-02-2014-001333.R2
Article Type:	Paper
Date Submitted by the Author:	12-Apr-2014
Complete List of Authors:	LIKHAR, PRAVIN; Indian Institute of Chemical Technology, IandPC Dept Damodar, Dandu; CSIR-IICT, I&PC Division Arundhathi, Racha; CSIR-IICT, I&PC Division; Graduate School of Engineering Science, Osaka University, Thota, Ramesh; CSIR-IICT, I&PC Division Legan, Margaret; University of Wisconsin, Department of Chemistry Kumpaty, Hephzibah; University of Wisconsin- Whitewater, Chemistry

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Polymethylhydrosiloxane Derived Palladium Nanoparticles for Chemo- and Regioselective Hydrogenation of Aliphatic and Aromatic Nitro Compounds in Water

Dandu Damodara,[a] Racha Arundhathi,[a] T. Venkata Ramesh Babu,[a] Margaret K. Legan,[b] Hephzibah J. Kumpaty,[b] Pravin R Likhar[a]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 support using an environmentally-amiable 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 catalyst also exhibits 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 corresponding amines is of paramount importance in organic synthesis as functionalized amines are vital intermediates and key precursors in the synthesis of dyes, pigments, agrochemicals, polymers, herbicides, and pharmaceuticals.[1-3] Several reducing agents[4] with transition metal based catalysts[5] reported till date confine the use of expensive and hazardous stoichiometric reducing agents based on safety and handling considerations.[6-11] In this regard, catalytic hydrogenation[12] has gained much attention as it is an effective and economical method, particularly in large scale reactions. However, the selective hydrogenation of the functionalized nitro compounds to the desired corresponding amine continues to remain a serious concern for improvement. Raney–nickel, palladium or platinum modified by special additives are most commonly available catalysts to carry out the selective hydrogenation of substituted nitroarenes.[13-16] Despite the efficiency of these catalysts, there are some disadvantages reported with one or the other catalysts mainly moisture sensitive, pyrophoric nature, lack of selectivity to desired product, high temperature and high pressure hence requirement of special reactor, expensiveness and longer reaction time. In addition to above drawbacks in case of Pd- and Pt -based catalysts, the presence of trace impurities 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 afore mentioned noble catalysts, heterogenized cobalt oxide catalyst, in situ prepared active copper nanoparticles, recyclable copper(II) as well as cobalt(II) phthalocyanines are reported for chemo- and regioselective reduction of aromatic nitro compounds.[19] Nevertheless, so far there exist only a limited number of successful heterogeneous catalyst systems, which allows a selective hydrogenation of all kinds of nitrocompounds. In view of these impediments in selectivity and scale up methods, there is stupendous interest to develop 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 catalytic system with high functional-group tolerance might also omit the need of protecting groups and streamline more-complex syntheses.

The development of new green methodologies has been a part of our research program. In continuation of our earlier work,[26] we here-in report highly efficient polysiloxane-stabilised "Pd" nanoparticles supported on nanocrystalline magnesium oxide catalyst [NAP-Mg-Pd(0)PS] prepared by the reduction of 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 a finest support for well dispersion of Pd(0) nanoparticles and enhances the catalytic activity of metal nano particles as well. The role of PMHS is to reduce the metal ion as well as act as a capping agent to enhance the stability and durability of highly active nano Pd(0). The prepared [NAP-Mg-Pd(0)PS] was then used in chemo- and regioselective hydrogenation of 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 benign hydrogenating processes, being a non-toxic, bio-degradable and inexpensive reducing agent.[27] Moreover PMHS is 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 has been published till now for the hydrogenation of nitro compounds using silanes/siloxanes.[28-30]

Experimental procedure

Preparation of the Catalyst

NAP-Mg-PdCl$_4$: The brown colored NAP-Mg-PdCl$_4$[31] was obtained by treating NAP-MgO (BET 600 m^{2}g^{-1}, 1 g) with Na$_2$PdCl$_4$ (294 mg, 1 mmol) and dissolved in 100 mL decarbonated water with stirring for 12 h, maintaining a nitrogen atmosphere. The obtained catalyst was filtered, washed with deionized water, acetone and dried at 65 °C in oven.

NAP-Mg-Pd(0)PS: NAP-Mg-PdCl$_4$ (1 g) catalyst 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 nitrogen atmosphere (Fig.1). Finally, black-colored, air-stable NAP-Mg-Pd(0)PS was obtained as crystalline material (Pd: 0.99 mmolg^{-1}). The other catalysts were synthesized based on the literature reports.[32]

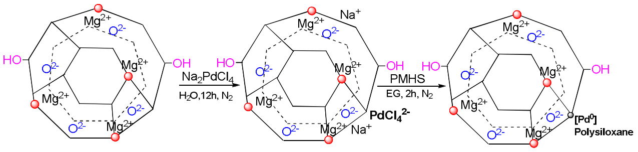


Fig. 1 Preparation of NAP-Mg-Pd(0)PS catalyst from NAP-Mg-PdCl$_4$ and PMHS.

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 condition at room temperature. PMHS (4 mmol) was slowly added (drop-wise) to avoid violent evolution of gas under nitrogen atmosphere. The reaction was then stirred for a required period of time at 80 °C in a pre-heated oil bath. After completion of the reaction as judged 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$_2$SO$_4$, filtered, and concentrated in vacuum. The resulting products were purified by flash column chromatography and amines were characterized by ^{1}H NMR and ^{13}C NMR (see the Supporting Information) spectroscopic methods.

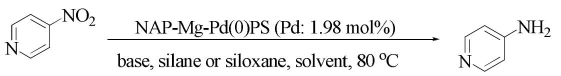
Results and Discussion

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

Screening of Catalysts

Initially, the catalytic hydrogenation was examined with 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$_3$OH, THF, DMF and water, whereas very low yield of the desired product was observed with non-polar solvent toluene. The highest and relatively similar yields of 4-aminopyridine were obtained in water (92%) and mixture of THF + water solvents (93%). Therefore water was used as a preferred reaction media in the subsequent hydrogenation of various nitro compounds (Table 1).

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



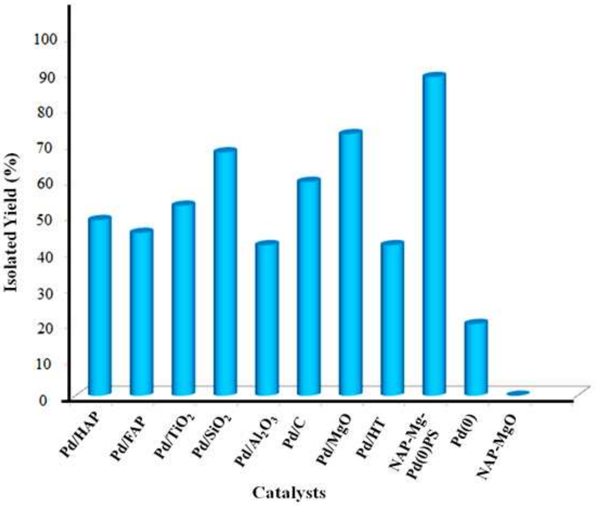
Entry	Si-H Species	Solvent	Base	Isolated yield[b] (%)
1	PMHS	DMF	TEA	63
2	PMHS	Toluene	TEA	trace
3	PMHS	THF	TEA	65
4	PMHS	MeOH	TEA	68
5	**PMHS**	**H_2O**	**TEA**	**92**
6	PMHS	THF:H_2O (50:50)	TEA	93
7	Et_3SiH	H_2O	TEA	61
8	$EtO(Me)_2SiH$	H_2O	TEA	67
9	$Et(Me)_2SiH$	H_2O	TEA	62
10	PMHS	H_2O	-	77
11	PMHS	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 NAP-Mg-Pd(0)PS (0.020 g, Pd:1.98 mol%), base (0.75 mmol), PMHS (4 mmol), solvent (3 mL), 80 ^{0}C, 6h. [b] Isolated yield of product. n. r. = no reaction.

To confirm the high catalytic activity of NAP-Mg-Pd(0)PS over the Pd(0) on other supports, we prepared Pd(0) reduced by PMHS on various support 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 is to investigate the effect of supports and dispersion and stability of the Pd(0) nanoparticles with suitable supports. Pd(0) supported on SiO_2 and commercial MgO display higher catalytic 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 high surface area and high basicity of NAP-MgO support.

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



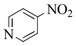
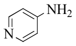
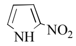
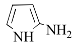
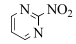
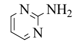
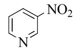
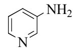
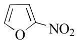
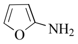
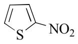
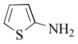
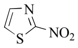
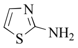
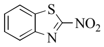
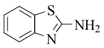
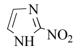
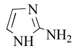
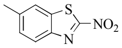
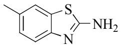
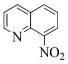
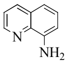
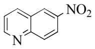
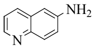
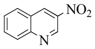
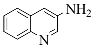
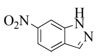
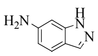
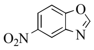
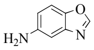
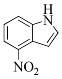
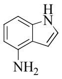
[a]Reaction conditions: 4-nitropyridine (1.0 mmol), catalyst (0.020 g, Pd:1.98 mol%), Et_3N (0.75 mmol), PMHS (4 mmol), H_2O (3 mL), 80 ^{0}C, 6h.

Fig. 2 Hydrogenation of 4-nitropyridine using various Pd catalysts[a]

Hydrogenation of heteroaromatic nitro compounds

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

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 ^{o}C. [b] Isolated yield of product. [c]Yield after 5th reuse.

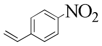
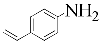
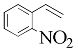
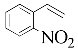
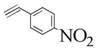
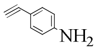
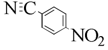
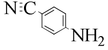
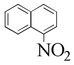
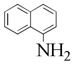
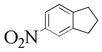
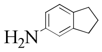
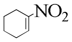
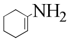
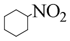
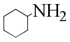
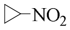
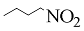
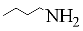
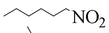
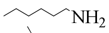
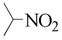
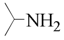
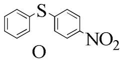
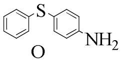
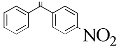
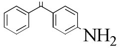
The advantages of using of water as solvent are: environmentally benign solvent, readily and abundantly available, inexpensive, the use of water rather than organic solvents is an important theme of current research, and moreover hydrogen has good solubility in water.[34] The development of eco-friendly process using metal nanoparticles that are highly efficient and stable in aqueous phase is still a challenge.[35]

The results in the Table 2 showed 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 quinoline, indole (Table 2, entries 8-16) were obtained in excellent yields and ring system remained intact under reaction conditions. In 2-nitropyrimidine and 2-nitrothiazole case, the entire nitro group was hydrogenated within 8h.

Hydrogenation of functionalized and saturated nitro compounds

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

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	98/100	92
13			1.5	99/100	91
14			6	97/99	92
15			6	97/99	91

[a] Reaction conditions: nitro compound (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 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.

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, C-C double and triple bonds, and found that the chemoselective hydrogenation of nitro group even in the presence of alkenes, alkynes, and cyano functional groups could be proceeded 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 hydrogenation of nitrocyclohexane, cyclohexylamine was obtained as corresponding hydrogenated product in 92% yield within 2h (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 in good yields (Table 3, entries 14 and 15).

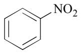
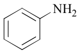
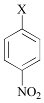
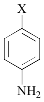
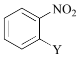
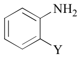
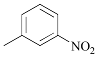
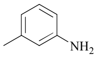
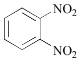
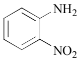
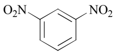
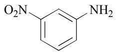
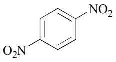
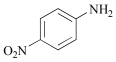
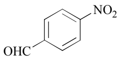
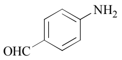
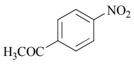
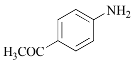
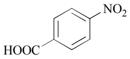
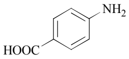
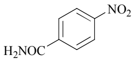
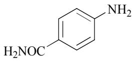
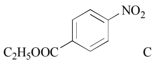
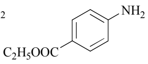
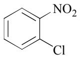
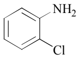
Hydrogenation of various aromatic nitro compounds

Finally, various nitro aromatics with different halides (Cl, Br, I and F) were studied for the selective hydrogenation in presence of NAP-Mg-Pd(0)PS catalyst and PMHS. The corresponding anilines were obtained in 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 NAP-Mg-Pd(0)PS catalyst with PMHS afforded excellent selectivity and yield of desired corresponding anilines.

To examine the stability and efficiency of the catalyst in a large scale reaction, we performed the selective hydrogenation of 2-chloro nitrobenzene (10 mmol), (Table 4, entry 13) and obtained excellent yield of desired hydrogenated 2-chloroaniline with 97% selectivity which signifies that the present catalytic system can be applied for the selective hydrogenation of 2-chloro nitrobenzene at industrial scale. Interestingly, in 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-nitro aniline with 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 in 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 condition (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 is highly desirable in chemical industry which simplifies the product separation, avoid unwanted disposal which makes the processes as greener. The substrates containing sensitive functional groups such as aldehyde or ketone were investigated for the hydrogenation reaction and found that selective nitro group was converted into the corresponding anilines without change in sensitive functional groups. (entries 8 and 9). Furthermore, carboxylic acid derivatives, such as ester and amide, were also tolerated well in hydrogenation under set optimized reaction conditions and yielded selective corresponding anilines in good to excellent yields.(Table 4, entries 10-12)

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 ºC. [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 ºC for 2h.

Kinetic study of hydrogenation of 4-nitropyridine

To understand the hydrogenation process we performed the 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 hydrogenation reaction. It was observed that the yield of 4-aminopyridine increased with time and the concentration of 4-nitropyridine gradually disappeared after 6h. There is no change observed in selectivity with increase in time.

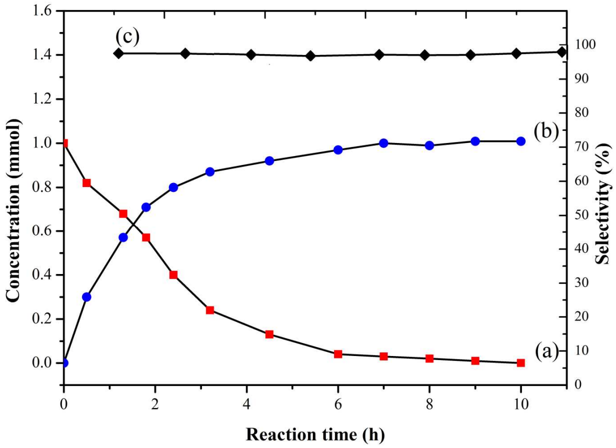


Fig. 3 Hydrogenation of 4-nitropyridine: (a) concentration of 4-nitropyridine; (b) concentration of 4-aminopyridine; (c) selectivity of 4-aminopyridine at different reaction times.

To examine the true heterogeneity of the NAP-Mg-Pd(0)PS in 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 7h. During this time the progress of reaction was monitored by GC after every 1h time. The results illustrated in the graph (Yield (%) vs Reaction time) suggest that there is no product formation after removal of catalyst from reaction mixture and hydrogenation of nitro compounds is purely carried by heterogeneous NAP-Mg-Pd(0)PS catalyst and not by leached catalyst.

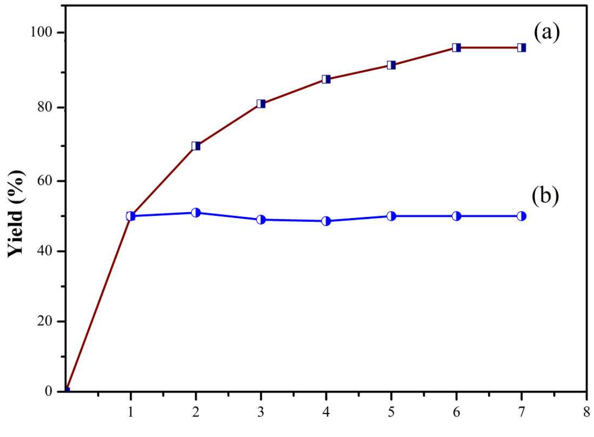


Fig. 4 (a) The kinetic plot of hydrogenation of 4-nitropyridine; (b) The reaction kinetics after the catalyst NAP-Mg-Pd(0)PS removed from the reaction mixture after 1h.

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 supporting information).

Table 6 The reusability of the NAP-Mg-Pd(0)PS for the hydrogenation of nitrocyclohexane[a]

Substrate	Yields of Isolated products[b] (%)				
	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.

Conclusion

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

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

Notes and references

[a]*Organometallic Gp., Inorganic and Physical Chemistry Division, Indian Institute of chemical Technology, Hyderabad-500607, India. Fax: +91-040-27160921; Tel: +91-040-27191667; E-mail: plikhar@iict.res.in*
[b]*Department of Chemistry, University of Wisconsin, Whitewater,WI-53190-1790 USA.*

† 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/b000000x/

1 N. Ono, *The Nitro Group in Organic Synthesis,* Wiley-VCH: New York, 2001.
2 (*a*) A. M. Tafesh and J. Weiguny, *Chem. Rev.,* 1996, **96**, 2035; (*b*) S. Chandrasekhar, S. J. Prakash and C. L. Rao, *J. Org. Chem.,* 2006, **71**, 2196; (*c*) Q. Shi, R. Lu, L. Lu, X. Fu and D. Zhao, *Adv. Synth. Catal.,* 2007, **349**, 1877; (*d*) P. K. Mandal and J. S. McMurray, *J. Org. Chem.,* 2007, **72**, 6599; (*e*) B. Chen, U. Dingerdissen, J. G. E. Krauter, H. G. J. L. Rotgerink, K. Mobus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke and H. Trauthwein, *Appl. Catal., A,* 2005, **280**, 17; (*f*) G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Klesczewski, D. Koch, R. Kumpf, H. Orzesek, H. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Appl. Catal., A,* 2001, **221**, 303.
3 (*a*) T. Joseph, K. Vijay Kumar, A. V. Ramaswamy and S. B. Halligudi, *Catal. Commun.,* 2007, **8**, 629; (*b*) M. Kumarraja and K. Pitchumani, *Appl. Catal., A: General,* 2004, **265**, 135; (*c*) D. J. Dale, P. J. Dunn, C. Golighty, M. L. Hughes, P. C. Levett, A. K. Pearce, P. M. Searle, G. Ward, and A. S. Wood, *Org. Process Res. DeV.,* 2000, **4**, 17.
4 (*a*) J. W. Bae, Y. J. Cho, S. H. Lee, C. O. M. Yoon and C. M. Yoon, *Chem. Commun.,* 2000, 1857; (*b*) R. J. Rahaim Jr and R. E. Maleczka Jr, *Org. Lett.,* 2005, **7**, 5087; (*c*) R. G. D. Noronha, C. C. Romao and A. C. Farnandes, *J. Org. Chem.,* 2009, **74**, 6960; (*d*) H. Imai, T. Nishiguchi and K. Fukuzumi, *Chem. Lett.,* 1976, 655; (*e*) H. Berthold, T. Schotten and H. Honig, *Synthesis*, 2002, 1607; (*f*) Y. Watanabe, T. Ohta, Y. Tsuji, T. Hiyoshi and Y. Tsuji, *Bull. Chem. Soc. Jpn.,* 1984, **57,** 2440; (*g*) A. B. Taleb and G. Jenner, *J. Mol. Catal.,* 1994, **91**, 149.
5 (*a*) D. C. Gowda and B. Mahesh, *Synth. Commun.,* 2000, **30**, 3639; (*b*) M. C. Kimber, A. C. Try, L. Painter, M. M. Harding and P. Turner, *J. Org. Chem.,* 2000, **65**, 3042; (*c*) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed.,* 2009, **48**, 9538; (*d*) Y. Motoyama, K. Kamo and H. Nagashima, *Org. Lett.,* 2009, **6**, 1345.
6 (*a*) P. Baumeister, H. U. Blaser and M. Studer, *Catal. Lett.,* 1997, **49**, 219; (*b*) H. U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner and M. Studer, *Adv. Synth. Catal.,* 2003, **345**, 103.
7 (*a*) B. K. Banik, C. Mukhopadhyay, M. S. Venkattman and F. F. Becker, *Tetrahedron Lett.,* 1998, **39**, 7243; (*b*) Y. S. Cho, B. K. Jun, S. Kim, J. H. Cha, A. N. Pae, H. Y. Koh, M. H. Chang and S. Y. Han, *Bull. Korean Chem. Soc.,* 2003, **24**, 653; (*c*) J. G. Lee, K. I. Choi, H. Y. Koh, Y. Kim, Y. Kang and Y. S. Cho, *Synthesis*, 2001, **1,** 81; (*d*) C. J. Moody and M. R. Pitts, *Synlett*, 1998, **9,** 1028; (*e*) D. Nagaraja and M. A. Pasha, *Tetrahedron Lett.,* 1999, **40**, 7855; (*f*) R. Shundberg and W. Pitts, *J. Org. Chem.,* 1991, **56**, 3048; (*g*) H. Y. Lee and M. An, *Bull. Korean Chem. Soc.,* 2004, **25**, 1717; (*h*) S. Iyer and G. M. Kulkarni, *Synth. Commun*., 2004, **34**, 721; (*i*) P. De, *Synlett.,* 2004, **10,** 1835.
8 (*a*) A. Vass, J. Dudar and R. S. Varma, *Tetrahedron Lett.,* 2001, **42**, 5347; (*b*) H. M. Meshram, Y. S. S. Ganesh, K. C. Sekhar and J. S. Yadav, *Synlett,* 2000, 993; (*c*) J. W. Bae, Y. J. Cho, S. H. Lee and C. M. Yoon, *Tetrahedron Lett.,* 2000, **41**, 175; (*d*) S. Gowda, B. K. K. Gowda and D. C. Gowda, *Synth. Commun.,* 2003, **33**, 281; (*e*) T. Hirao, J. Shiori and N. Okahata, *Bull. Chem. Soc. Jpn.,* 2004, **77**, 1763; (*f*) F. Yuste, M. Saldana and F. Walls, *Tetrahedron Lett.,* 1982, **23**, 147; (*g*) A. Yasuhara, A. Kasano and T. Sakamoto, *J. Org. Chem.,* 1999, **64**, 2301; (*h*) P. S. Kumbhar, J. S. Valente and F. Figueras, *Tetrahedron Lett.,* 1998, **39**, 2573; (*i*) C. Yu, B. Liu and L. Hu, *J. Org. Chem.,* 2001, **66**, 919.
9 (*a*) F. Ragaini and S. Cenini, *J. Mol. Catal. A,* 1996, **105**, 145; (*b*) K. Nomura, M. Ishino and M. Hazama, *Bull. Chem. Soc. Jpn.,* 1991, **64**, 2624; (*c*) A. J. Pardey, M. Fernandez, A. B. Rivas, M. C. Ortega, C. Urbina, D. Moronta, C. Longo, M. Mediavilla, P. J. Baricelli and S. A. Moya, *Inorg. Chim. Acta,* 2002, **329**, 22; (*d*) J. Y. Jiang, J. T. Mei, Y. H. Wang, F. Wen and Z. L. Jin, *Appl. Catal. A,* 2002, **224**, 21; (*e*) R. E. Harmon, S. K. Gupta and D. J. Brown, *Chem Rev.,* 1973, **73**, 21.
10 H.-U. Blaser, U. Siegrist and M. Studer, *In Fine Chemicals Through Heterogeneous Catalysis,* ed. R. A. Sheldon, H. van Bekkum, Wiley-VCH, Weinheim, 2001, p. 389.
11 (*a*) T. Mitsudome and K. Kaneda, *Green Chem.,* 2013, **15**, 2636; (*b*) Y. Liu, Y. Lu, M. Prashad, O. Repic and T. J. Blacklock, *Adv. Synth. Catal.,* 2005, **347**, 217; (*c*) V. Polshettiwar and R. S. Varma, *Green Chem.,* 2010, **12**, 743.
12 (*a*)Y. Chen, J. Qiu, X. Wang and J. Xiu, *J. Catal.,* 2006, **242**, 227; (*b*) H. Wua, L. Zhuo, Q. He, X. Liao and B. Shi, *Appl. Catal., A,* 2009, **366**, 44.
13 (a) U. Siegrist, P. Baumeister and H.-U. Blaser, H-U. In Catalysis of Organic Reactions, ed. F. Herkes, 207–219 (Chemical Industries Series 75, Marcel Dekker, 1998); (b) S. Xu, X. Xi, J. Shi, S. Cao, J. Mol. Catal. A: Chem., 2000, **160**, 287.
14 R. Raja, V. B. Golovko, J. M. Thomas, A. Berenguer-Murcia, W. Zhou, S. Xiee and B. F. G. Johnsona, *Chem. Commun.,* 2005, 2026.
15 A. Saha and B. C. Ranu, *J. Org. Chem.,* 2008, **73**, 6867.
16 H-U. Blaser, H. Steiner and M. Studer, *ChemCatChem*, 2009, **1**, 210.
17 A. Corma and P. Serna, *Science*, 2006, **313**, 332.
18 *(a)* A. Corma, C. Gonalez-Arellano, M. Iglesias and F. Sanchez, *Appl. Catal. A,* 2009, **356**, 99; *(b)* A. Corma, P. Serna, P. Concepcion

and J. Calvino, *J. Am. Chem. Soc.,* 2008, **30**, 8748; *(c)* X.-B. Lou, L. He, Y. Qian, Y.-M. Liu, Y. Cao and K.-N. Fan, *Adv. Synth. Catal.,* 2011, **353**, 281.

19 *(a)* F. A. Westerhaus, R. V. Jagadeesh, G. Wienhofer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M.Nielsen, A. Bruckner and M. Beller, *Nature Chemistry,* 2013*,* **5**, 537; *(b)* H. K. Kadama and S. G. Tilve, *RSC Adv.*, 2012,**2**, 6057; *(c)* U. Sharma, P. Kumar, N. Kumar, V. Kumar, and B. Singh, *Adv. Synth. Catal.,* 2010, **352**, 1834.

20 (*a*) P. M. Reis and B. Royo, *Tetrahedron Lett.,* 2009, **50**, 949; (*b*) L. Liu, B. Qiao, Z. Chen, J. Zhang and Y. Deng, *Chem. Commun.,* 2009, 653; (*c*) S. Cao, S. Xu and S. Xu, *Polym. Adv. Technol.,*1999, **10**, 43.

21 (*a*) C. Boix and M. Poliakoff, *J. Chem. Soc. Perkin Trans.,* 1999, **1**, 1487; (*b*) F. Cardenas-Lizana, S. Gomez-Quero, A. Hugon, L. Delannoy, C. Louis and M. A. Keane, *J. Catal.,* 2009, **262**, 235.

22 (*a*) F. Cardenas-Lizana, S. Gomez-Quero and M. A. Keane, *ChemSusChem,* 2008, **1**, 215; (*b*) S. Ichikawa, M. Tada, Y. Iwasawab and T. Ikariya, *Chem. Commun.,* 2005, 924.

23 (*a*) J. F. Knifton, *J. Org. Chem.,* 1976, **41**, 1200; (*b*) R. Joshi and U. Chudasama, *Ind. Eng. Chem. Res.,* 2010, **49**, 2543.

24 (*a*) A. A. Deshmukh, A. K. Prashar, A. K. Kinage, R. Kumar and R. Meijboom, *Ind. Eng. Chem. Res.,* 2010, **49**, 12180.

25 (*a*) A. M. Tafesh and M. Beller, *Tetrahedron Lett.,* 1995, **36**, 9305; (*b*) D. Savoia, C. Trombini, A. Umani-Ronchi and G. Verardo, *J. Chem. Soc. Chem. Comm.,* 1981, 540.

26 (*a*) R. Arundhathi, D. Damodara, P. R. Likhar, M. L. Kantam, P. Saravanan, T. Magdaleno and Sun Hee Kwon, *Adv. Synth. Catal.* 2011, **353**, 1591; (*b*) D. Damodara, R. Arundhathi and P. R. Likhar, *Catal. Sci. Technol.*, 2013, **3**, 797; (*c*) R. Arundhathi, D. Damodara, K. Veera Mohan, M. L.Kantam and P. R. Likhar, *Adv. Synth. Catal.* 2013, **355**, 751.

27 (*a*) R. J. Rahaim Jr. and R. E. Maleczka Jr., *Tetrahedron Lett.,* 2002, **43**, 8823; (*b*) B. P. S. Chauhan, J. S. Rathore, and T. Bandoo, *J. AM. CHEM. SOC.* 2004, **126**, 8493.

28 (*a*) H. Vorbruggen, *Silicon-mediated Transformations of Functional Groups*, Wiley-VCH: New York, 2004; (*b*) K. Junge, B. Wendt, N. Shaikh and M. Beller, *Chem. Commun.,* 2010, **46**, 1769.

29 (*a*) K. A. Andrianov, V. I. Sidorov and M. I. Filimonova, *Zh. Obshch. Khim.,* 1977, **47**, 485; (*b*) K. A. Andrianov, L. M. Tartakovskaya and B. I. Shapiro, *Zh. Obshch. Khim.,* 1972, **42**, 176; (*c*) K. A. Andrianov, V. I. Sidorov, L. M. Tartakovskaya, A. I. Anpilogova, V. V. Nepomnina and K. S. Pushchevaya, *Dokl. Akad. Nauk.* 1970, **195**, 352.

30 (*a*) J. Lipowitz and S. A. Bowman, *J. Org. Chem.,* 1973, **38**, 162; (*b*) B. P. S. Chauhan, J. S. Rathore, M. Chauhan and A. Krawicz, *J. Am. Chem. Soc.,* 2003,**125**, 2876.

31 M. L. Kantam, S. Roy, M. Roy, B. Sreedhar and B. M. Choudary, *Adv. Synth. Catal.,* 2005, **347**, 2002.

32 (*a*) A. Cwik, Z. Hell and F. Figueras, *Adv. Synth. Catal.,* 2006, **348**, 523; (*b*) J. M. D. Consul, C. A. Peralta, E. V. Benvenutti, J. A. C. Ruiz, H. O. Pastore and I. M. Baibich, *J. Mol. Catal. A: Chem.,* 2006, **246**, 33. (*c*) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K, Kaneda, *J. Am. Chem. Soc.*, 2002, **124**, 11572; (*d*) M. L. Kantam, K. B. S. Kumar, P. Srinivas, B. Sreedhar, *Adv. Synth. Catal.*, 2007, **349**, 1141.

33 (*a*) M. L. Kantam, R. Chakravarti, U. Pal, B. Sreedhar and S. Bhargava, *Adv. Synth. Catal.,* 2008, **350**, 822; (*b*) K. Layek, H. Maheswaran, R. Arundhathi, M. L. Kantam and S. K. Bhargava, *Adv. Synth. Catal.,* 2011, **353**, 606.

34 (*a*) M. O. Simon and C. J. Li, *Chem. Soc. Rev.,* 2012, **41**, 1415; (*b*) H. Syska, W. A. Herrmann and F. E. Kuehn, *J. Organomet. Chem.,* 2012, **703**, 56; (*c*) D. B. Bagal, Z. S. Qureshi, K. P. Dhake, S. R. Khan and B. M. Bhanage, *Green Chem.,* 2011, **13**, 1490; (*d*) Y. Q. Sun, G. H. Liu, H. Y. Gu, T. Z. Huang, Y. L. Zhang and H. X. Li, *Chem. Commun.,* 2011, **47**, 2583; (*e*) I. Nieto, M. S. Livings, J. B. Sacci, L. E. Reuther, M. Zeller and E. T. Papish, *Organometallics,* 2011, **30**, 6339; (*f*) K. H. Shaughnessy, *Chem. Rev.,* 2009, **109**, 643; (i) R. A. Sheldon, *Green Chem.,* 2005, **7**, 267; (*g*) H. U. Blaser and M. Studer, *Green Chem.,* 2003, **5**, 112.

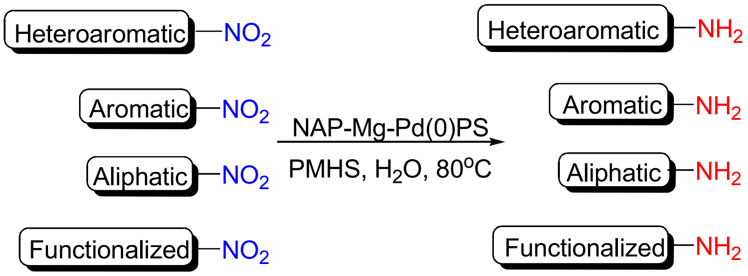
35 (*a*) Y. Piao, Y. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, *small* 2007, **3**, 255; (*b*) Y. Lee, J. Lee, C. J. Bae, J. G. Park, H. J. Noh, J. H. Park, T. Hyeon, *Adv. Funct. Mater.* 2005, **15**, 503.

Polymethylhydrosiloxane Derived Palladium Nanoparticles for Chemo- and Regioselective Hydrogenation of Aliphatic and Aromatic Nitro Compounds in Water

Dandu Damodara,[a] Racha Arundhathi,[a] T. Venkata Ramesh Babu,[a] Margaret K. Legan,[b] Hephzibah J. Kumpaty,[b] Pravin R Likhar[a]*

[a]*Organometallic Gp., Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500706 India.*

[b]*Department of Chemistry, University of Wisconsin, White water, WI-53190-1790 USA.*



chemo- and regioselective hydrogenation of nitro compounds

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-MgO support using an environmentally-amiable 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 catalyst also exhibits 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.