

Palladium Nanoparticles on Silica Nanospheres for Switchable Reductive Coupling of Nitroarenes

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Abstract

In this study, we synthesized a robust and sustainable Pd/SiO_2 nanospheres catalyst. Further, its catalytic activity was demonstrated for the direct reductive coupling of nitroarenes under mild conditions. While the reaction with Pd nanoparticles on other supporting materials such as modified carbon materials and TiO₂, under similar conditions, resulted formation of amines exclusively. Therefore, it was confirmed that the SiO₂ was found to be the best supporting material towards the selective reductive coupling of nitroarenes. Also, the catalyst could be recycled up to five cycles with a marginal loss of product yield (<2% yield).

Graphic Abstract



Keywords Heterogeneous catalysis · Hydrogenation of nitroarenes · Nanocatalysis

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1 Introduction

Aromatic azo and azoxy compounds are vital and valuable ingredients for the synthesis of organic dyes, pigments, food additives, indicators, optical storage media, therapeutic agents and other drug derivatives [1–3]. Direct reductive coupling of nitroarenes is a challenging task to produce azo and azoxy aromatic compounds with controlled selectivity (without forming amines) at ambient temperature [3]. In general, industrially the azo and azoxy compounds are synthesized by diazotization (i.e. the coupling of diazonium

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salts with electron-rich aromatic compounds) [2]. This process is tedious and unfriendly with the environment, due to the formation of unstable diazo compounds as waste and harsh process condition is used in this conversion [2, 4]. In a green approach, azo compounds can be acquired via aerobic oxidation of amines by heterogeneous catalysis, however, this process requires a high amount of supported noble metal catalysts or expensive oxidants, which constrains broadscale applications [5, 6].

Heterogeneous catalysis demonstrates incredible potential in driving essential organic reactions (i.e. C-C couplings, reduction and oxidation reactions, etc.) and the innovation has along these lines pulled in significant consideration in the most recent decades [7-14]. The recent development of silica-supported metal nanoparticles has further boosted the fundamental research and industrial potential of heterogeneous catalysis, as these inexpensive and eco-friendly materials show the reasonable catalytic performance and stability, under mild conditions [15, 16]. Silica has a wide range surface area with broad applications in every field especially in catalysis. Also, silica-supported heterogeneous catalysts are more beneficial over traditional homogenous catalysts as they limit the ecological impact of organic transformations to a great extent [17]. Silica supported metal nanoparticles has some additional advantages over other heterogeneous solid supports. Because, modification of silica surface with organic, inorganic moieties and metal nanoparticles is relatively easy due to the presence of surface silanol groups (polar functional moiety) [18]. Also, having a huge surface area, which provides a large number of active sites. In addition, silica has good physicochemical properties and is inert under the reaction progression. Moreover, silica has tunable pore structures [19]. Therefore, based on the above reasons, silica is considered as the best solid support for the organic transformations.

Recently, a number of studies have been reported for the formation of aniline, azoxy and azo compounds via heterogeneous catalysis using supported metal nanoparticles shown in Table 1 [20–32]. The heterogeneous catalysts, such as, Pd [20, 23], Pd–Pt [21], and Rh [22] nanoparticles on various supporters such as PVP–iron powder, g-C₃N₄, Fe₃O₄ and SiO₂ coated Fe₃O₄, proved to be effective in producing quantitative yields of anilines and without the formation of self-coupled products [20–23]. Whereas, Au, Pt and Co nanoparticles supported by CeO₂, TiO₂, ZrO₂ and Mg–A1 hydrotalcite nano-structures, generated, exclusively the reductive self-coupled product instead of aniline [24–32]. In this study, for the first time, we describe Pd nanoparticles supported SiO₂ for direct reductive self-coupling of nitroarenes.

 Table 1
 Literature for nitroarenes reduction using supported metal nanoparticles



S. nos	Catalyst (loading mol%)	Conditions	% of Yield			References	
			2	3	4		
1	Pd/PVP-iron powder (1 mol%)	NaBH ₄ , H ₂ O, rt, 45 min	99	_	_	[20]	
2	$Pd-Pt/Fe_3O_4$ (1 mol%)	NH ₃ BH ₃ , MeOH, rt, 5 min	96	-	_	[21]	
3	Fe ₃ O ₄ @SiO ₂ -NH ₂ -Rh@mSiO ₂	N ₂ H ₄ ·H ₂ O, H ₂ O, 100 °C	99	-	-	[22]	
4	$Pd/g-C_3N_4$	НСООН, H ₂ O, 298 К	99	-	_	[23]	
5	Au/Mg–Al hydrotalcite	2 MPa H ₂ , toluene, 50 °C	1	1	98	[24]	
6	Au/meso-CeO ₂ (0.5 mol%)	5 atm CO, 150 °C, toluene, 5 h	1	-	99	[25]	
7	Au/CeO ₂ yolk shell nanostructure	KOH, IPA, 50 °C, under Ar atmosphere	7	2	91	[26]	
8	Au/meso CeO ₂	KOH, IPA:H ₂ O (5:1), 1 atm N ₂ , 30 °C, 5 h	_	94	1	[27]	
9	Au/TiO ₂ (1 mol%)	5 bar O ₂ , toluene, 100 °C, 22 h	_	99	_	[28]	
10	Au/ZrO ₂	KOH, IPA, 40 °C, under Ar atmosphere, 5 h	-	99	_	[29]	
11	Au/CeO ₂	4 bar H ₂ , 120 °C	_	-	98	[30]	
12	Co–N–C	3 MPa H ₂ , NaOH, <i>t</i> -BuOH, 80 °C, 1.5 h	_	-	97	[31]	
13	Pt nanowires	1 bar H ₂ , KOH, <i>p</i> -xylene, 80 °C	-	-	89	[32]	
14	Au/organic cage (OC_1^R)	hv, NaOH, 2-propanol, 30 °C	_	-	90	[33]	
15	NMC–Fe	N_2H_4 · H_2O , KOH, toluene, 100 °C	5	Trace	94	[34]	
16	Pd/SiO ₂ nano-spheres	NaBH ₄ , EtOH, rt, 1 h	5	92	-	Present work	





Fig. 2 PXRD pattern of Pd/SiO₂ nanospheres

2 Results and Discussion

2.1 Synthesis of SiO₂ Nanospheres

In a typical synthesis of SiO_2 nanospheres, initially, 200 mL of EtOH and 50 mL of water (4:1) were taken in a 500 mL round bottom flask on a magnetic stirrer. In addition, 4.5 mL of NH₄OH was added dropwise and immediately 12.9 mL of tetraethyl*orthosilicate* (TEOS) was added and stirred for 4 h at room temperature. Finally, the SiO₂ nanospheres were collected by centrifugation and washed with ethanol and water. The formed wet material was dried under a hot air oven at 60 °C.

2.2 Synthesis of Pd/SiO₂ Nanospheres

Initially, 84 mg of PdCl₂ was dispersed in 20 mL of EtOH in a separate vessel and stirred for 30 min. In another vessel, 500 mg of SiO₂ nanospheres were dispersed in 30 mL of EtOH and added PdCl₂ solution dropwise at room temperature and stirred on the magnetic stirrer. After 1 h, 0.5 mL of N₂H₄·H₂O was added to the stirred solution and then after 15 min the temperature increased from room temperature to 70 °C and stirred 12 h. Finally, the formed material was collected by filtration washing with ethanol and water. The resultant Pd/SiO₂ nanospheres were dried under vacuum oven for overnight. Figure 1 represents the diagrammatic representation of Pd/SiO₂ nanospheres synthesis.

2.3 Characterization of the Catalyst

2.3.1 XRD Analysis

The phase, crystalline nature and structural confirmation of as-prepared Pd/SiO₂ nanospheres were attained by powder X-ray diffraction (PXRD) studies. The PXRD pattern of Pd/SiO₂ shown in Fig. 2. The Pd nanoparticles showed the corresponding d-spacing values are 2.244 Å, 1.943 Å, 1.374 Å, 1.173 Å and 1.121 Å. These d-spacing values can be attributed to (111), (200), (220), (311) and (222) lattice planes of Pd (JCPDS No. 46-1043). The broad amorphous peak at 10° -35° indicates the presence of SiO₂ [35]. From the XRD data analysis, it was found that the Pd nanoparticles were dispersed/impregnated on the surface of the SiO₂.



Fig. 3 IR spectrum analysis of Pd/SiO₂ nanospheres

2.3.2 FTIR Spectrum Analysis

The FTIR spectra of SiO₂ nanospheres and Pd on SiO₂ nanospheres were scheduled in the range of 660–4000 cm⁻¹ and the spectral data shown in Fig. 3. In SiO₂ nanospheres, the observable peaks were attributed at 3704.8 cm^{-1} , 1514.0 cm^{-1} , 1059.3 cm^{-1} , 940.3 cm^{-1} and 787.4 cm^{-1} . The band due to adsorbed water shows an asymmetric broadband range from 3540 to 3660 cm^{-1} . This band attribute with the moisture water which exists everywhere around us [36]. Moisture on SiO₂ nanospheres is mainly trapped as Si-OH by breaking the bonds in the network of SiO₂ nanospheres [37, 38]. Therefore, the resultant stretching frequency of -OH band in Si-OH observed a sharp peak at 3704.8 cm⁻¹ and the bending mode of -OH band in Si-OH could be seen at around 1630 cm⁻¹ but which was hindered by many stretching peaks of Si-O [38]. The broad peaks can be seen between the ranges of 1400 and 1800 cm⁻¹ which indicates the stretching bands of Si-O [38]. The main and highest intense band SiO₂ nanospheres assigned at 1059.3 cm⁻¹, which indicates the antisymmetric stretching frequency of Si–O–Si bond [39–41]. Whereas, symmetric stretching frequency of Si–O–Si bond observed at 787.4 cm⁻¹ [40]. A weakly bonded silanols (Si–OH) on the SiO₂ nanospheres surface observed the vibrational band at 940.3 cm⁻¹ [39]. When Pd nanoparticles were dispersed on the surface of SiO₂ nanospheres, the highest intense Si–O–Si and Si–OH peaks shifted to lower frequency side i.e., 1050.8 cm⁻¹ and 936.5 cm⁻¹ respectively [39]. The shifting of Si–O–Si and Si–OH bands indicates that Pd nanoparticles were strongly adsorbed on the surface of the SiO₂ nanospheres [39].

2.3.3 XPS Analysis

To further analyze the oxidation state and bonding between the atoms and quantifications of the elements in the catalyst were characterized by X-ray photoelectron spectroscopy (XPS). The wide scan XPS spectra of Pd/SiO₂ and the



Fig. 4 XPS pattern of Pd/SiO₂ nanospheres

elements Pd 3d, Si 2p, O 1s core-level spectra's are shown in Fig. 4. In Fig. 4, the characteristic peaks $3d_{3/2}$ and $3d_{5/2}$ were showed at 335.4 eV and 342.4 eV and these peaks assigned to Pd (0) and the new peak at 347.9 eV is a plasmon loss associated with the peak 335.4 eV [42, 43]. Moreover, the core level spectra of Si 2p showed the binding energies at 107.6 eV, 109.0 eV and 110.2 eV respectively. These peaks accounted for the unique chemical state of Si atom (Si⁴⁺ from SiO₂) [44]. The oxygen atoms surrounded by the Si

atom in SiO₂ nanospheres which supplies a certain density to the Si atom. Therefore, the local position of the Si 2p shifted to higher binding energy side [44–46]. At the same time, Si 2s core-level spectra also shifted to higher binding energy side i.e., 158.8 eV and 160.3 eV. The O 1s core-level spectrum showed the three components of binding energy at 538.9 eV, 539.7 eV and 540.4 eV which indicates the oxygen atoms surrounded by the Si atom [44]. Also, C 1s



Fig. 5 SEM images of Pd/SiO₂ nanospheres

peak attributed at 289.3 eV and 291.6 eV which indicates the carbon atom surrounded by oxygen atoms [44].

2.3.4 SEM Analysis

The FE-SEM images of Pd/SiO_2 nanospheres were shown in Fig. 5. From Pd/SiO_2 nanospheres SEM images, we demonstrate that the morphology of SiO_2 is a smooth spherical in shape. Moreover, Fig. 5 reveals that the Pd nanoparticles are distributed on the surface of SiO_2 nanospheres. Also, some of the Pd nanoparticles are agglomerated. From SEM images of Pd/SiO_2 nanospheres, the average of spherical size in SiO_2 is 410.5 nm. Whereas, the Pd nanoparticles average particles is approximately 8.3 nm.

2.3.5 TEM Analysis

To further confirmation of morphology and particle size of SiO_2 and palladium, we investigated with transmission electron microscopy (TEM) shown in Fig. 6. In this TEM analysis, we observed the morphology of SiO_2 is a soft spherical in shape and the average particle size of each spherical is 410 nm. Whereas, the Pd nanoparticles size is 7.5 nm. These TEM results support with the SEM results.

2.4 Catalytic Performance

To find out the optimal reaction conditions, the reactions were screened for the direct reductive self-coupling of nitroarenes 1a (1 mmol) in the presence of various catalysts. The results are summarized in Table 2. Thus, initially, the reaction of nitrobenzene 1a was performed with hydrazine monohydrate as a reductant in the presence of catalyst Pd/ GO and ethanol as solvent at room temperature for 12 h. However, aniline was formed as the product, in 72% yield instead of reductive coupled product 3/4 (Table 2, entry 1). Similar results were noted with Pd-Au/TiO₂ catalyst (Table 2, entry 2). Also, the reaction under neat reaction conditions with hydrazine monohydrate and with various catalysts (Pd/GO, Pd-Au/TiO₂, Pd/TiO₂, Au/TiO₂, Pd/activated charcoal and Pd/SiO₂ nanospheres), furnished the aniline 2a (Table 2, entries 3 to 8). Even when water was used as the solvent, gave aniline 2a, as an exclusive product in the presence of Pd-Au/TiO₂ (Table 2, entry 9). The same results were observed by using NaBH₄ as the reducing agent and water as a solvent for 12 h (Table 2, entry 10). Notably, with the Pd/SiO₂ nanospheres catalyst, NaBH₄ as a reductant and in water, direct reductive self-coupling of nitrobenzene to the azoxybenzene 3a (84%) was noticed along with the formation of aniline 2a as a minor product (Table 2, entry 11). While the reaction in water and ethanol (1:1) mixture, with the same catalyst and reductant, gave 78% yield of azoxybenzene **3a** (Table 2, entry 12). Interestingly, when ethanol was used as the sole solvent, isolated **3a** in 92% (Table 2, entry 13). On the other hand, at 80 °C, the yield of 3a was decreased to 75% and without appreciable formation of aniline 2a (Table 2, entry 14). No progress was noted in the





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 Microscope Accelerating Voltage Magnification Camera Length
 Microscope Accelerating Voltage Magnification Camera Length

 JEM-2100
 200 kV
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 200 kV
 25000 x
 -200 nm



Fig. 6 TEM images and particle size distribution of Pd/SiO₂ nanospheres

absence of palladium catalyst and with SiO_2 nanospheres, even for prolonged reaction time (Table 2, entry 15).

2.5 Effect of NaBH₄ Concentration

In addition, we optimization study was screened with regards to the equivalents of NaBH₄. From Fig. 7, when increasing

the number of equivalents of NaBH₄ (1 to 5 equiv), the formation of by-product aniline **2a** was decreased and the yield of azoxybenzene **3a** was increased. When 1, 2, 3.5 and 5 equivalent of NaBH₄ was employed along with Pd/SiO₂ nanospheres and ethanol, the % of yields ratio of aniline **2a** and azoxybenzene **3a** are 33:35, 25:48, 20:56 and 5:92, respectively. From these results, it was concluded that

 Table 2
 Optimization for the switchable hydrogenative coupling of nitrobenzene



Entry	Catalyst	Reductant	Solvent	Yield (%)		
				2a	3a	4a
1	PdO/GO	$N_2H_4 \cdot H_2O(0.5 \text{ mL})$	EtOH	72	_	_
2	Pd–Au/TiO ₂	N_2H_4 · H_2O (0.5 mL)	EtOH	85	-	_
3	PdO/GO	N_2H_4 · H_2O (0.5 mL)	Neat	75	-	-
4	Pd–Au/TiO ₂	N_2H_4 · H_2O (0.5 mL)	Neat	96	-	-
5	Pd/TiO ₂	N_2H_4 · H_2O (0.5 mL)	Neat	82	-	_
6	Au/TiO ₂	$N_2H_4 \cdot H_2O(0.5 \text{ mL})$	Neat	80	-	_
7	Pd/activated charcoal	N_2H_4 · H_2O (0.5 mL)	Neat	46	-	_
8	Pd/SiO ₂ nanospheres	N_2H_4 · H_2O (0.5 mL)	Neat	35	-	_
9	Pd–Au/TiO ₂	N_2H_4 · H_2O (0.5 mL)	Water	84	-	_
10	Pd–Au/TiO ₂	NaBH4 (5 equiv)	Water	76	-	_
11	Pd/SiO ₂ nanospheres	NaBH ₄ (5 equiv)	Water	15	84	-
12	Pd/SiO ₂ nanospheres	NaBH ₄ (5 equiv)	Water:EtOH (1:1)	10	78	_
13	Pd/SiO ₂ nanospheres	NaBH ₄ (5 equiv)	EtOH	5	92	_
14 ^a	Pd/SiO ₂ nanospheres	NaBH ₄ (5 equiv)	EtOH	Trace	75	_
15 ^b	SiO ₂ nanospheres	NaBH ₄ (5 equiv)	EtOH	-	_	-

Bold highlighted in entry 13 indicates the highly active reaction condition (standard reaction condition)

Reaction conditions: nitrobenzene 1a (1 mmol), reductant (5 mmol), catalyst (1 mol%), solvent (1 mL) at rt. Isolated yields of products 2a and 3a

^aReaction conducted at 80 °C

^bThe reaction carried out up to 24 h



Fig. 7 Number of equivalents of NaBH₄ vs the % of products 2a and 3a yields. Reaction conditions: nitrobenzene 1a (1 mmol), NaBH₄, Pd/SiO₂ nanosphere (1 mol%), EtOH (1 mL) at rt. Isolated yields of products 2a and 3a

5 equiv of $NaBH_4$ is the optimized amount for the direct hydrogenative coupling of nitroarenes to form azoxybenzene **3a**.

With these optimized conditions in hand (Table 2, entry 13), we amplified the scope of the reaction and explored with various substituted nitroarenes **1a-q**, for the formation of hydrogenative coupled azoxybenzene products. The reaction was quite smooth and furnished the azoxybenzenes 3. The process showed broad functional group tolerance, for example, the reaction was amenable to nitrobenzenes having functional groups (H, Me, Br, Cl, F, NH₂, CH₂OH) and afforded the corresponding azoxybenzenes [3a (92%), 3b (73%), **3c** (94%), **3j** (20%) and **3m** (83%)] (Table 3). Particularly, the reaction was found to show excellent selectivity and tolerance with Br, Cl and F functionalities present the benzene ring of 1 [3d (65%), 3e (86%), 3f (88%), 3g (92%), **3h** (48%) and **3i** (52%)] (Table 3). The low yield in case of 3j may be attributed to slow reaction rate due to the presence of a strong electron-donating amino group of 1m. While nitrobenzaldehydes 1k-m, furnished azoxybenzenes/

Table 3Pd/SiO2 nanospherescatalyzed direct reductivecoupling of nitroarenes



azobenzenes and with relatively higher reaction rates. In addition, the aldehyde group also was reduced, which is usual in the presence of NaBH₄. This may be due to the

electron-withdrawing ability of aldehyde moiety. The protocol was also successful with 4-acylnitrobenzene **10**, exclusively afford secondary alcohol azobenzene **30**, in 90% yield.





Reaction conditions: nitroarenes 1a-q (1 mmol), NaBH₄, Pd/SiO₂ nanospheres (1 mol%), EtOH (1 mL) at rt. Isolated yields of products 3a-q/4q

On similar grounds, *para*-nitrobenzoyl chloride **1p** generated exclusively **4m**. The substrate nitrocinnamic acid ester **1q** was also found amenable and furnished a mixture of azoxy-/ azo-cinnamic acid esters **3q/4q**.

2.6 Recyclability Test

To check the sustainability of catalyst retains its activity, recyclability was also tested. Catalyst recovered by using centrifugation, ethanol washing, treatment with water and acetone and drying (vacuum oven at 60C for overnight) steps. Thus, the recovered Pd/SiO₂ nanospheres catalyst was then subjected to the next catalytic cycles. The recovered catalyst was found to be active without an appreciable reduction in the product **3f** yield, under the established conditions. Thus, based on the above results it was confirmed that the Pd/SiO₂ nanospheres catalyst is having enough stability and can be reused (Fig. 8).

2.7 Mechanism

The plausible reaction pathway for the conversion of nitrobenzene **1a** into azoxybenzene **3a** and azobenzene **4a** is shown in Fig. 9. Initially, the adsorbed nitrobenzene **1a** on the metal surface would undergo partial reduction



Fig. 8 Recyclability test of the catalyst Pd/SiO_2 nanospheres. Reaction conditions: 3-bromo nitrobenzene 1f (1 mmol), $NaBH_4$, Pd/SiO_2 nanospheres (1 mol%), EtOH (1 mL) at rt. Isolated yields of products 3f



Fig. 9 The reaction pathway for the reductive coupling of nitrobenzene

via a two-hydride ion transfer and furnish nitrosobenzene **A** and *N*-phenyl hydroxylamine **B**. The nitrosobenzene **A** and *N*-phenyl hydroxylamine **B** would combine and afford azoxybenzene **3a** (step I, Fig. 9). Reduction of azoxybenzene **3a** gives azobenzene **4a** (step II, Fig. 9). Further, azobenzene **4a** would reduce to produce aniline **2a** (step III, Fig. 9).

3 Conclusion

We have developed highly efficient and sustainable heterogeneous Pd/SiO_2 nanospheres for the direct hydrogenative coupling of nitroarenes environmentally benign conditions. The reaction proceeded at mild conditions and showed broad functional group tolerance. The catalyst was robust and recyclable.

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