Synthesis, characterization, and application of easily accessible resin-encapsulated nickel nanocatalyst for efficient reduction of functionalized nitroarenes under mild conditions

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Abstract. A novel resin-encapsulated nickel nanocatalyst has been synthesized by a modified impregnation method using nickel acetate tetrahydrate in presence of sodium borohydride as a mild reducing agent. The synthesized nanocatalyst was characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The concentration of nickel nanoparticles encapsulated on resin was determined by inductively coupled plasma-mass spectroscopy (ICP-MS). Further, synthesized resin-encapsulated nickel nanocatalyst was found to be stable and efficient in micromolar concentrations, for the selective reduction of functionalized nitroarenes to corresponding amines in good to high yield, under mild reaction conditions. The nanocatalyst shows excellent reusability.

Keywords. Resin-encapsulated nickel nanocatalyst; impregnation; stability; recyclability; reduction; nitroarenes; aromatic amines.

1. Introduction

Nitroarenes are generally employed in a wide range of industries for the synthesis of many valuable materials such as dyes, pesticides, explosives, polymers, pharmaceuticals, *etc.* Excessive discharge of these nitro compounds from industries into the wastewater has led to environmental pollution.¹ Their mutagenic and carcinogenic nature affect extensively the entire range of living organisms including humans as they are heavily dependent on water and aquatic products in everyday life. Moreover, these nitro compounds have been declared as the second largest group of organic environmental pollutants.² Therefore, it is necessary to eliminate these nitro compounds from the waste water and land. Principles of green chemistry endorse the replacement of hazardous chemicals by using environment-friendly alternatives. Among the various reported methods,^{3–6} the transformation of nitroarenes to their corresponding amines is the most significant and sustaining strategy that contributes to the environmental fate of nitroarenes. The aromatic

amines so obtained are generally employed as the important building blocks in the synthesis of drugs, biologically active compounds, dyes, agrochemicals, pharmaceuticals, polymers, corrosion inhibitors, surfactant, herbicides, *etc.*^{7–9} Conventional methods for the reduction of nitroarenes include certain drawbacks such as long reaction time, use of toxic and carcinogenic solvents, expensive noble metal complexes, generation of a large amount of waste and non-reusability of the catalysts, *etc.*^{10–12}

The importance of amines in the above-mentioned industries and efforts in surface science have led to the discovery of new heterogeneous catalysts either by impregnation of unsupported metal nanoparticles or highly dispersed metal precursors to different supports for the reduction of nitroarenes using various reducing agents such as H₂, NaBH₄, N₂H₄·H₂O and so on.^{13–15} Many support materials such as polymers, dendrimers, carbonaceous porous materials, metal oxide, *etc.*, are in trend to arrest the agglomeration and the high surface energy of metal nanoparticles.^{16–20}

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Usually, heterogeneous catalysts including noble metals (palladium, platinum, gold, and silver) are the most widely sourced supported catalysts for the reduction of nitroarenes.^{21–25} The high price of these precious noble metals limit their large-scale applications. Current research activities in this area are mainly focused on the development of the heterogeneous catalysts based on base-metals (nickel, iron, copper, and cobalt) for efficient and cost-effective catalytic selective reduction of nitroarenes.^{26–29}

Many supported nickel nanocatalysts and their versatile applications in the field of medical diagnosis,³⁰ supercapacitors,³¹ and catalysis^{32–35} especially for the reduction of nitroarenes are reported in the literature. Kalbasi and co-workers developed nickel nanoparticles@polyvinylamine/SBA-15 composite (PVAm/SBA-15), to be used in most of the solvents as an efficient heterogeneous catalyst for hydrogenation of aromatic nitro compounds to corresponding aromatic amino compounds in good yields by employing sodium borohydride as a reducing agent.³⁶ Figueiredo *et al.* generated nickel nanoparticles by metal disintegration. These were stabilized on the top of the filamentous carbon. This nanocomposite was tested as a catalyst for the reduction of nitrobenzene under 1.5 MPa hydrogen pressure at 120 °C with excellent performance producing clean aniline (approx. 99% yield).³⁷ Ranu and co-workers reported the excellent use of Fe(0) nanoparticles stabilized by citric acid, for reduction of nitroarenes. The reaction was done using 3 equiv. nanoparticles per 1 equiv. of substrate in water for 3–4 h to obtain desired products in good yield.³⁸ The commercially available amberlite XAD-4 resin used as a solid support for nanoparticles has advantages like easy to handle, non-reactive, easily available, porous nature, thermal and chemical stability.³⁹ This has not been so far explored for the synthesis of nickel nanoparticles.

We have synthesized the amberlite XAD-4 resin-encapsulated nickel nanocatalyst by the chemical reduction of nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) in ethanol. Further, we have investigated the reduction of functionalized nitroarenes by the resin-encapsulated nickel nanocatalyst as a heterogeneous catalyst, using sodium borohydride as a reducing agent under mild reaction conditions. Thus, catalytic reduction of nitroarenes by resin-encapsulated nickel nanocatalyst may be of direct use in the treatment of waters contaminated with nitroarenes if the resulting amines can be removed by subsequent treatment. The resin-encapsulated nickel nanocatalyst was recycled five times without any significant loss of its catalytic activity.

2. Experimental

2.1 Materials and methods

Unless otherwise stated, all reactions were carried out without taking precautions to exclude air and moisture. Nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 98%) was procured from Qualikems, India, sodium borohydride (NaBH_4 , >96%) from Spectrochem, India, absolute ethanol (99.9%) from Changshu chemicals, China, and amberlite XAD-4 resin (of high purity) from Sigma-Aldrich, Germany, and used as received. Hydrochloric acid (37%) and other solvents were of analytical grade and supplied by qualigens chemicals, India and were used after purification by standard procedures. All reaction temperatures refer to oil bath temperatures. Silica gel (230–400 mesh) (of high purity grade) for column chromatography, was purchased from Fisher Scientific Ltd, India. ^1H NMR and ^{13}C NMR spectra were recorded on model Avance-II (Bruker) 400 spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C). FESEM images were recorded using HITACHI SU8010 field emission scanning electron microscope. HR-TEM images and TEM-EDS analysis were obtained using a TecnaiTM G2 20, 120kV transmission electron microscope with embedded CCD Camera. ICP-MS study was done on Agilent's 7700x, ICP-MS system. UV-Vis study for reduction of functionalized nitroarenes was carried out using UV-Visible spectrophotometer JASCO model V-530 using a 1 cm path length quartz cell.

2.2 Synthesis of resin-encapsulated nickel nanocatalyst

In a typical synthetic protocol, 5 g of resin beads were added to 25 mL of 5.0 mmol nickel acetate tetrahydrate solution prepared in ethanol and stirred at room temperature for 3–4 h followed by dropwise addition of 0.1 M aq. NaBH_4 solution (10 mL). The addition of NaBH_4 solution turns resin beads black, indicating the formation of nickel nanoparticles. The synthesized nanoparticles were first washed with distilled water followed by ethanol to control surface oxidation. This synthesized resin-encapsulated nickel nanocatalyst was then stored in absolute ethanol and is referred to as resin stabilized nickel nanocatalyst ($\text{Ni}@XAD-4$ nanocatalyst).

2.3 General procedure for catalytic reduction

To an oven dried 50 mL round bottom flask, charged with nitroarene (1.5 mmol) and 10 mL of methanol: water (3:7) was added resin-encapsulated nickel nanocatalyst (300 mg of resin) (0.161 mg of $\text{Ni} \approx 0.00275$ mmol of Ni). The solution was stirred at room temperature for 5–10 min. To this solution, solid sodium borohydride (0.567 g, 10 equiv. 15 mmol) was added in small instalments and the reaction mixture was heated at 50 °C for the required time (almost 30 min) to complete the reaction as monitored by using TLC. It was cooled to room temperature and then filtered. The filtrate was extracted with ethyl acetate (3×10 mL). The

combined organic extract was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude material so obtained was purified by column chromatography.

3. Results and Discussion

3.1 Characterization of resin-encapsulated nickel nanocatalyst

3.1.1 Field emission Scanning Electron Microscopy (FESEM) and High-Resolution Transmission Electron Microscopy (HR-TEM): FESEM was carried out to study topography and elemental information of the surface of resin beads encapsulated with nickel nanoparticles. FESEM images depict the smooth dispersion of nickel nanoparticles into the matrix and on the surface of beads. FESEM images show no obvious contamination or agglomeration of metal nanoparticles on the surface of the resin beads (Figure 1).

The resin beads were immersed in ethanol that developed the nanopores in microporous resins. The nanopores of the microporous XAD-4 resin can control the growth of metal nanoparticles resulting in concise distribution in the size of nickel nanoparticles. Figure 2 depicts the HR-TEM images of synthesized nickel nanocatalyst. HR-TEM analysis was used to know the morphology and dimension of nickel nanoparticles embedded in the matrix of resin. Resin beads were dispersed in ethanol through sonication. The analysis was done by putting a drop of this dispersion on carbon-coated copper grids. The typical TEM images of freshly prepared nickel nanocatalyst show uniform and well-dispersed spherical nickel nanoparticles with a dimension between 5 and 8 nm (average size 6.7 ± 3.03 nm) as revealed through particle size distribution TEM-histogram (Figure 2c).

TEM-EDS analysis reveals the presence of only nickel metal and it is found to be 10.24 wt% in elemental composition. The inset TEM shows the SAED pattern of nickel nanocatalyst displayed with bright spots and good ring pattern that specifies the crystallinity of nickel nanoparticles.

3.1.2 Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS): The concentration of nickel nanoparticles deposited on resin could be figured out by ICP-MS. 500 mg of resin-encapsulated nanocatalyst was incinerated in a silica crucible for 4 h at 550 °C, and then the residue was dissolved in 1 mL of Aqua-regia and diluted up to 5 mL with distilled water. The average concentration of nickel metal deposited on resin was calculated as 0.00916 mmol/g or 0.538 mg/g of the resin in at least three trials.

3.2 Optimization of the reaction conditions for the reduction of nitroarenes

The catalytic performance of resin-encapsulated nickel nanocatalyst has been investigated in the reduction of nitroarenes. For the optimization of the reaction conditions, a series of experiments were carried out, involving the variation in reducing agent, amount of resin-encapsulated nickel nanocatalyst, temperature, and solvent combinations. The reduction of 4-nitrotoluene (0.205 g, 1.5 mmol) was chosen as the model reaction to give the 4-aminotoluene. Increasing the amount of sodium borohydride from 5 equivalents to 10 equivalents for 4-nitrotoluene, the yield of the desired product increased from 70 to 95% (Table 1, entries 2–4). Further increase in the amount of sodium borohydride did not result in any increase in the yield (Table 1, entry 12). Decreasing the amount of nickel nanocatalyst resulted in the decrease in the yield of the product. However,

Figure 1. FESEM images of resin bead with nickel nanoparticles (1–2).

Figure 2. HR-TEM images (a–b), particle size distribution histogram (c), SAED pattern (d) and TEM-EDS images (e) of freshly prepared resin-encapsulated nickel nanocatalyst.

the yield did not improve on increasing the amount of nickel nanocatalyst (from 300 to 350 mg) under similar conditions (Table 1, entries 5, 8–11).

The effect of solvent on the yield and time of the reaction was also examined. Water and methanol were more efficient compared to other solvents like ethanol, DCM and THF (Table 1, entries 5, 13, and 15–19). The best yield was obtained using a combination of methanol: water ($v/v = 3/7$) at 50 °C. Even when the reaction was carried out in water only, the desired product 4-aminotoluene (Table 1, entry 17) was obtained in good yield (68%). When the reduction was carried out at room temperature, the product was obtained in a lower yield (Table 1, entry 14). However, no reaction occurred in the absence of either catalyst or reducing agent (Table 1, entries 1, 20). The best results were obtained using 4-nitrotoluene (0.205 g, 1.5 mmol), 300 mg resin-encapsulated nickel nanocatalyst with sodium borohydride (0.567 g, 10 equiv. 15 mmol) in 10 mL of $\text{CH}_3\text{OH} : \text{H}_2\text{O}$ (3:7) at 50 °C (Table 1, entry 5).

3.3 General scope of the reaction

With the optimized reaction conditions in hand, resin-encapsulated nickel nanocatalyst was further evaluated for the reduction of different functionalized nitroarenes. The synthesized resin-encapsulated nickel nanocatalyst was found to be compatible with arenes having electron-donating as well as electron-withdrawing substituents at any position (Table 2). Amino, methoxy, and methyl substituted nitroarenes were reduced to corresponding amines in good yield.

It was found that both 4-chloro and 4-bromo substituted nitroarenes were reduced to their corresponding amines without any dehalogenation taking place (Table 2, entries 8, 9). The 4-chloroaniline so obtained is an important ingredient for the synthesis of antimalarial drug paludrine. The nitro group in the heterocyclic system was reduced to give the corresponding amine in good yield (Table 2, entries 11, 15). 8-Aminoquinoline (**2k**) is an important ingredient for the synthesis of antimalarial drugs primaquine and pamaquine.

Table 1. Optimization of reaction conditions for reduction of 4-nitrotoluene.

Entry	Substrate 1a (mmol)	NaBH ₄ (equiv.)	Amount of resin (mg)	Solvent	Temp. (°C)	Time (h)	Yield ^a (%)
1.	1.5	5	0	CH ₃ OH : H ₂ O (3:7)	50	1	0
2.	1.5	5	300	CH ₃ OH : H ₂ O (3:7)	50	2	70
3.	1.5	7	300	CH ₃ OH : H ₂ O (3:7)	50	2	85
4.	1.5	10	300	CH ₃ OH : H ₂ O (3:7)	50	1	95
5.	1.5	10	300	CH ₃ OH : H ₂ O (3 : 7)	50	0.5	95
6.	1.5	10	300	CH ₃ OH : H ₂ O (3:7)	50	0.35	90
7.	1.5	10	300	CH ₃ OH : H ₂ O (3:7)	50	1	95
8.	1.5	10	350	CH ₃ OH : H ₂ O (3:7)	50	1	95
9.	1.5	10	250	CH ₃ OH : H ₂ O (3:7)	50	1	80
10.	1.5	10	200	CH ₃ OH : H ₂ O (3:7)	50	1	70
11.	1.5	10	100	CH ₃ OH : H ₂ O (3:7)	50	1	50
12.	1.5	12	300	CH ₃ OH : H ₂ O (3:7)	50	0.5	95
13.	1.5	10	300	CH ₃ OH : H ₂ O (1:1)	50	1	85
14.	1.5	10	300	CH ₃ OH : H ₂ O (3:7)	25	2	60
15.	1.5	10	300	CH ₃ OH	50	1	65
16.	1.5	10	300	EtOH	50	1	50
17.	1.5	10	300	H ₂ O	50	1	68
18.	1.5	10	300	DCM	50	1	30
19.	1.5	10	300	THF	50	1	Trace
20.	1.5	-	300	CH ₃ OH : H ₂ O (3:7)	50	1	0

^aIsolated yield.**Table 2.** Reduction of nitroarenes using resin-encapsulated nickel nanocatalyst and NaBH₄ as mild reducing agent^a.

Entry no.	Reactant 1	Product 2	Time (h)	Yield ^b (%)
1.	4-Nitrotoluene (1a)	4-Aminotoluene (2a)	0.5	95
2.	3-Nitrotoluene (1b)	3-Aminotoluene (2b)	2	82
3.	Nitrobenzene (1c)	Aniline (2c)	1	90
4.	4-Nitrophenol (1d)	4-Aminophenol (2d)	0.5	80
5.	4-Methoxynitrobenzene (1e)	4-Methoxyaniline (2e)	1	90
6.	3-Methoxynitrobenzene (1f)	3-Methoxyaniline (2f)	2	86
7.	4-Nitrobenzaldehyde (1g)	4-Aminobenzylalcohol (2g)	2	82
8.	4-Chloronitrobenzene (1h)	4-Aminochlorobenzene (2h)	2	88
9.	4-Bromonitrobenzene (1i)	4-Aminobromobenzene (2i)	2	80
10.	1-Nitronaphthalene (1j)	1-Aminonaphthalene (2j)	2	90
11.	8-Nitroquinoline (1k)	8-Aminoquinoline (2k)	2	80
12.	4-Aminonitrobenzene (1l)	1,4-Diaminobenzene (2l)	1	93
13.	3-Aminonitrobenzene (1m)	1,3-Diaminobenzene (2m)	2	79
14.	2-Aminonitrobenzene (1n)	1,2-Diaminobenzene (2n)	2	92
15.	2-Nitropyridine (1o)	2-Aminopyridine (2o)	2	80

^aReaction conditions: **1a** (1.5 mmol), Resin-encapsulated nickel nanocatalyst (300 mg of resin $\approx$ 0.00275 mmol of Ni), NaBH₄ (0.567 g, 10 equiv., 15 mmol) at 0 °C, CH₃OH : H₂O (3:7), 50 °C. ^bisolated yield after column chromatography.

3.4 UV-Vis study of the reduction reaction

The reduction of nitroarenes can be effectively catalyzed by metal nanocatalyst only when the

potential of metal nanocatalyst is located in between the potential of BH₄⁻ and nitroarenes. Bordbar *et al.*,⁴⁰ have described the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using borohydride ion in the

presence of immobilized nickel nanoparticles on polymer/mesoporous composite. Also, Song and coworkers⁴¹ reported the catalytic activity of Ru nanoparticles as an efficient catalyst for the reduction of 4-nitrophenol to 4-aminophenol using NaBH_4 . We have also studied the catalytic activity of synthesized resin-encapsulated nickel nanocatalyst by the selective reduction of 4-nitrophenol to 4-aminophenol using NaBH_4 as a mild reducing agent. This reaction is easy to follow using UV-Visible spectroscopy.⁴² The reaction was started by dissolving 4-nitrophenol (0.208 g, 1.5 mmol) in 10 mL of $\text{CH}_3\text{OH} : \text{H}_2\text{O}$ (3:7), followed by addition of nickel nanocatalyst (300 mg) and NaBH_4 (0.567 g, 10 equiv. 15 mmol). The reaction mixture was heated to 50 °C and then subjected to UV-Visible study by taking 0.3 mL aliquot, from the reaction mixture at regular intervals and diluting it to 5 mL with 10% HCl. Dilute HCl was used to decompose the excess amount of NaBH_4 present in the sample aliquot. The UV-Visible absorption

spectrum of the aqueous solution of 4-nitrophenol and the resin-encapsulated nickel nanocatalyst showed an absorption peak at 317 nm. On the addition of NaBH_4 into the 4-nitrophenol solution, the absorption peak shifted to 400 nm, with a change in the color from original light yellow to intense yellow (Figure S4 (A–E), Supplementary Information). This is due to the transformation of 4-nitrophenol to the 4-nitrophenolate anion. The progress of the catalytic reduction of the 4-nitrophenol to 4-aminophenol was monitored by the change in the intensity of the absorbance peak at 317 nm in the UV-Visible spectrum. The time-dependent UV-Visible absorption spectra of 4-nitrophenol and NaBH_4 solution in the presence of as-prepared nickel nanocatalyst is shown in Figure S5, Supplementary Information. It has been observed that with the progress of the reaction, the intensity of the absorption peak of 4-nitrophenol at 317 nm decreased gradually and finally disappeared and a new peak at 295 nm appeared, signifying that 4-nitrophenol gradually converted to the

Figure 3. HR-TEM images, particle size distribution histogram, SAED pattern and TEM-EDS images (a–e) of resin-encapsulated nickel nanocatalyst after fifth cycle for reduction of 4-nitrotoluene.

Table 3. Comparison of catalytic activity of present nanocatalyst with the earlier reported results

Entry no.	Nanocatalyst	Time	Conditions	Reusability	Reference
1.	Ni@organic modifier	8 h	0.8 MPa pressure, 100 °C, anhydrous ethanol	Up to four cycles	43
2.	Ni@ <i>p</i> (4-VP) cryogels	60 min	Nitro compound (0.01 M), NaBH ₄ (0.4 M), 30 °C, 800 rpm	Up to four cycles	44
3.	Ni@ carbon filaments	12–24 h	1.5 MPa of H ₂ , 120 °C	Single time	45
4.	Nanosized Nickel decorated sisal fibers	10 min	Substrate (1.0 mmol), NaBH ₄ (100 mmol) catalyst (3.39%)	Up to seven cycles	45
5.	Ni/Carbide-Ni/carbon nanofibers nanocomposite	2.5 h	2.0 MPa of H ₂ , 140 °C	Up to five cycles	46
6.	Fe(0) nps	3–4 h	80–96%, Substrate (1.0 mmol), catalyst (3 equiv.)	Single time	38
7.	Ni@XAD-4 nanocatalyst	20–80 min	95–80%, 0.00275 mmol nanocatalyst for 1.5 mmol of substrate, NaBH ₄ (10 equiv.)	Up to five cycles	Present work

corresponding 4-aminophenol. This was accompanied by the change in color from yellow to colorless.

3.5 Recyclability of resin-encapsulated nickel nanocatalyst

The recyclability and reusability of resin-encapsulated nickel nanocatalyst was demonstrated in the reduction of 4-nitrotoluene. The reaction was carried out with 4-nitrotoluene (0.205 g, 1.5 mmol) and nickel-encapsulated nickel nanocatalyst (300 mg) in 10 mL of CH₃OH : H₂O (3:7) at 0 °C and followed by the addition of NaBH₄ (0.567 g, 10 equiv.) in small instalments. The reaction mixture was heated to 50 °C and stirred at the same temperature for 30 min. After completion of the reaction, as monitored by TLC nickel nanocatalyst was recovered by filtration, and washed with distilled water, followed by ethanol and reused as such in the next reaction. The nanocatalyst was successfully recycled and reused up to five cycles without a significant decrease in its catalytic efficiency (95%, 95%, 94%, 90% and 90%) as shown in Figure S6 (Supplementary Information). The characterization of used nickel nanocatalyst through HR-TEM analysis shows that the morphology and size of nickel nanocatalyst remains almost the same (spherical and average size 8.1 ± 2.55 nm) after use for the fifth cycle. Slight variation in the concentration of nickel impregnation is there as revealed by the HR-TEM images and TEM-EDS analysis (Figure 3).

3.6 Comparison of catalytic activity of present nanocatalyst with the earlier reported nickel and other nanocatalysts towards reduction of nitroarenes

This section features Table 3.

4. Conclusions

In conclusion, an inexpensive and recyclable resin-encapsulated nickel nanocatalyst has been synthesized using a modified impregnation method and characterized by using FESEM, HR-TEM, TEM-EDS, and ICP-MS techniques. This protocol offers advantages such as easy accessibility, easy product isolation, eco-friendly, and recyclability of the nanocatalyst for the reduction of nitroarenes.

Supplementary Information (SI)

The synthesized resin-encapsulated nickel nanocatalyst is characterized by FESEM, HR-TEM, TEM-EDS, and ICP-MS techniques. FESEM and HR-TEM, particle size distribution histogram, and TEM-EDS images of the synthesized resin-encapsulated nickel nanocatalyst are given in SI (Figures S1, S2 and S3). The ¹H NMR and ¹³C NMR spectral data and spectra of aromatic amines obtained on the reduction of nitroarenes with resin-encapsulated nickel nanocatalyst are given in Appendix A of Supplementary Information, available at www.ias.ac.in/chemsci.

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