2.1 Synthesis and characterization of palladium(0) nanoparticles immobilized onto starch grafted amine functionalized magnetite nanoparticles

The preparation of nanopalladium immobilized onto starch grafted amine functionalized magnetite nanoparticles (Pd@Fe₃O₄-NH₂/Starch) was carried out in three steps (Scheme 1). Initially, amine functionalized magnetite nanoparticles were synthesized by solvo-thermal process. Stability of amine functionalized magnetite nanoparticles was enhanced by the incorporation of starch on Fe₃O₄-NH₂. Finally, Pd(0) nanoparticles were successfully immobilized onto the starch supported amine functionalized magnetite nanoparticles using Pd(OAc)₂, followed by reduction with aqueous NaBH₄.

Scheme 1. General scheme for the synthesis of Pd@Fe₃O₄-NH₂/Starch.
**General procedure for the preparation of Pd@Fe₃O₄-NH₂/Starch**

The preparation of Pd@Fe₃O₄-NH₂/Starch was carried out by the following three steps:

**Synthesis of amine-functionalized magnetic nanoparticles [Fe₃O₄-NH₂]**

Amine functionalized magnetic nanoparticles were prepared according to the procedure reported by Li *et. al.*¹ with slight modification. FeCl₃.6H₂O (1 g), 1,6-hexanediamine (6.5 g), anhyd. sodium acetate (2 g) and ethylene glycol (30 mL) were taken in a round bottom flask (100 mL), and the mixture was stirred at 60 °C till clear solution was obtained. After that, the reaction mixture was stirred at 200 °C for 6 h. The magnetic nanoparticles so obtained were washed successively with deionized water (2 × 15 mL) and ethanol (2 × 15 mL), and finally, dried under vacuum at 50 °C to obtain a black powder (1.26 g).

**Synthesis of starch supported amine functionalized magnetite nanoparticles [Fe₃O₄-NH₂/Starch]**

A mixture of amine functionalized magnetite nanoparticles (5 g), starch chloride² (2 g), triethyl amine (0.5 mL) and chloroform (30 mL) were taken in a round bottom flask (100 mL), and the reaction mixture was stirred at 70 °C for 12 h. Fe₃O₄-NH₂/Starch was filtered and washed with deionized water (2 × 15 mL) followed by chloroform (2 × 15 mL). The black powder so obtained was dried in the oven at 70 °C for 2 h to get Fe₃O₄-NH₂/Starch (5.98 g).

**Synthesis of palladium onto starch supported amine functionalized magnetite nanoparticles [Pd@Fe₃O₄-NH₂/Starch]**

To a mixture of Pd(OAc)₂ (0.18 g) and starch supported amine functionalized magnetite support (3 g) in a round bottom flask (100 mL), ethanol (25 mL) was added, and the reaction mixture was stirred at room temperature for 30 min, followed by the slow addition of aqueous solution of NaBH₄ (1.5 mmol, 4 mL) during 10 h with constant stirring. After the completion, the reaction mixture was filtered using vacuum pump and the residue was washed firstly with deionized water (2 × 30 mL), followed chloroform (2 × 30 mL). Finally it was dried under vacuum at 60 °C for 1 h to get final catalyst (2.93 g).
Characterization of Pd@Fe₃O₄-NH₂/Starch

Pd@Fe₃O₄-NH₂/Starch was characterized by different techniques such as FTIR, VSM, SEM, HR-TEM, EDX, XRD, CHN, ICP-AES and TGA.

Fourier Transform Infrared Spectroscopy (FT-IR)

The presence of various functional groups in Pd@Fe₃O₄-NH₂/Starch was investigated by FTIR spectroscopy. FTIR spectra of Fe₃O₄-NH₂, Fe₃O₄-NH₂/Starch and Pd@Fe₃O₄-NH₂/Starch are shown in Fig. 1a-c respectively. The bands at 3382, 2922, 1632, 1087, 878 and 634 cm⁻¹ (Fig. 1a) correspond to N-H stretching, CH₂ stretching, N-H bending, C-N stretching, CH₂ rocking and C-C bending of hexane diamine moiety respectively. Moreover, bands at 3327, 2358, 1641, 1408, 1151 and 1024 cm⁻¹ (Fig. 1b-c) were due to stretching vibrations of O-H, C-H, C-O-C, C-C and C-O moieties of starch respectively. These observations clearly suggests that naked magnetite nanoparticles were effectively functionalized with hexane-1,6-diamine and starch moiety.

![Fig. 1a FTIR of Fe₃O₄-NH₂.](image)
Fig. 1b FTIR of Fe₃O₄-NH₂/Starch.

Fig.1c FTIR spectra of Pd@Fe₃O₄-NH₂/Starch.
Vibrating Sample Magnetometer (VSM)

The magnetic properties of the synthesized materials were studied by vibrating sample magnetometry (VSM) at room temperature. VSM of Fe$_3$O$_4$-NH$_2$, Fe$_3$O$_4$-NH$_2$/Starch and Pd@Fe$_3$O$_4$-NH$_2$/Starch are shown in Fig. 2a-c respectively. The magnetic saturation values of Fe$_3$O$_4$-NH$_2$, Fe$_3$O$_4$-NH$_2$/Starch and Pd@Fe$_3$O$_4$-NH$_2$/Starch were observed at 39.3, 37.6 and 37.2 emu/g respectively. The small decrease in the magnetic saturation values as shown in Fig. 2b-c was due to the grafting of non-magnetic material on the surface of magnetic material. It was depicted that intrinsic magnetic behaviour of synthesized nanoparticles does not change with surface modification. This may occur due to the decrease in magnetization of Fe$_3$O$_4$-NH$_2$ with time as oxide layer is formed over

![Fig. 2 VSM of (a) Fe$_3$O$_4$-NH$_2$; (b) Fe$_3$O$_4$-NH$_2$/Starch; (c) Pd@Fe$_3$O$_4$-NH$_2$/Starch.](image-url)
the surface, leading to the shrinking of the magnetic core. Besides, the grafting of starch over Fe₃O₄-NH₂ relatively well protects them from oxidation and reinforces the magnetic stability. The reported catalyst was magnetic enough to be proficiently separated from the reaction mixture via external magnet.

**Scanning Electron Microscopy (SEM)**

The SEM images of Fe₃O₄-NH₂ and Pd@Fe₃O₄-NH₂/Starch Fig. 3a-d depicted the surface morphology of the synthesized catalyst. The SEM images of Fe₃O₄-NH₂ (3a,b) showed that hexyl-1,2-diamine moieties were uniformly spread over the surface of Fe₃O₄ nanoparticles and homogenous in nature. From the SEM images of Pd@Fe₃O₄-NH₂/Starch (3c,d), it was clearly revealed that the synthesized catalyst is homogenous powder, starch and palladium nanoparticles are homogeneously dispersed over the amine functionalized magnetite nanoparticles. Moreover, most nanoparticles of the synthesized
catalyst assumed spherical shape and aggregated in clusters, thus responsible for the increased surface area of the catalyst.

**High Resolution Transmission Electron Microscopy (HR-TEM)**

The HR-TEM images of the Pd@Fe$_3$O$_4$-NH$_2$/Starch (Fig. 4) revealed the information about the morphology and distribution of palladium nanoparticles onto the surface of Fe$_3$O$_4$-NH$_2$/Starch magnetic support. **Fig. 4a** clearly deciphered that spherical Pd nanoparticles of mean size 8.4 nm were uniformly dispersed on the magnetite support. Furthermore, HR-TEM image of Pd@Fe$_3$O$_4$-NH$_2$/Starch (**Fig. 4d**) showed the lattice

![HR-TEM images](image)

**Fig. 4** HR-TEM images of Pd@Fe$_3$O$_4$-NH$_2$/Starch.
fringe with an interplanar spacing of approximately 0.23 nm, corresponds to the [111]
lattice plane of fcc Pd nanoparticles. Besides palladium nanoparticles, nanoparticles of
mean size 24.81 nm (Fig. 4a) were also observed in the HR TEM image which
corresponded to magnetite support material.

Energy Dispersive X-ray (EDX)

The elemental composition of Pd@Fe₃O₄-NH₂/Starch was investigated by the energy
dispersive X-ray analysis (EDX). The EDX analysis (Fig. 5) showed that the developed
catalyst composed of C, O, Fe and Pd elements, which indicated that starch was
successfully incorporated over the amine functionalized magnetite nanoparticles.

![EDX spectrum of Pd@Fe₃O₄-NH₂/Starch.](image)

X-ray Powder Diffraction (XRD)

XRD pattern of Fe₃O₄-NH₂ (Fig. 6a) showed diffraction patterns at 2θ = 35.6, 43.5 and
62.8°, which corresponds to [220], [311] and [511] planes of cubic phase of Fe₃O₄ lattice.
Whereas, XRD pattern of Pd@Fe₃O₄-NH₂/Starch (Fig. 6b) showed two new
characteristics peaks at 2θ = 40.1 and 68.2° corresponding to the [111] and [220]
crystalline planes of face-centered cubic Pd(0) nanoparticles. The broad peaks observed
in Pd@Fe₃O₄-NH₂/Starch and Fe₃O₄-NH₂ may be due to the small crystallite size of the
nanoparticles\textsuperscript{5}. Thus, XRD spectra indicated that Pd nanoparticles have been successfully immobilized onto the starch stabilized amine functionalized magnetite nanoparticles.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{xrd_spectra.png}
\caption{XRD spectra of: (a) Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}; (b) Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch.}
\end{figure}

**Carbon Hydrogen Nitrogen (CHN) analysis**

The presence of amino group in the Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch was further established from the CHN analysis (Fig. 7). It was observed that carbon content of the catalyst was higher than that of nitrogen and hydrogen. This is owing to the presence of hexane-1,6-diamine and starch molecules in the Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{chn_analysis.png}
\caption{CHN analysis of Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch.}
\end{figure}
Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

In order to calculate the content of Pd supported on Fe₃O₄-NH₂/Starch, the synthesized catalyst was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results indicated that the content of Pd loaded onto 0.1 g of Fe₃O₄-NH₂/Starch was 2.52 wt%.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used to investigate the thermal stability of the Pd@Fe₃O₄-NH₂/Starch catalyst. The TGA was recorded by heating at the rate of 10 °C min⁻¹. TGA of Fe₃O₄-NH₂, Fe₃O₄-NH₂/Starch and Pd@Fe₃O₄-NH₂/Starch are shown in Fig. 8a-c respectively.

![Fig. 8a TGA of Fe₃O₄-NH₂.](image)

The thermal stability of the catalyst was increased with the grafting of starch onto the amine functionalized magnetite nanoparticles. Here, Pd@Fe₃O₄-NH₂/Starch showed highest thermal stability, wherein 5% weight loss occurs at 166.39 °C due to the loss of entrapped solvent and water molecules. Further, weight loss occurs beyond 328.51 °C may be owing to the thermal decomposition of starch and chemisorbed molecules of hexane diamine present in the Pd@Fe₃O₄-NH₂/Starch catalyst. Thus, from the TGA data,
we found that the synthesized catalyst showed highest thermal stability than its precursors, Fe$_3$O$_4$-NH$_2$ and Fe$_3$O$_4$-NH$_2$/Starch.

**Fig. 8b** TGA of Fe$_3$O$_4$-NH$_2$/Starch.

**Fig. 8c** TGA of Pd@Fe$_3$O$_4$-NH$_2$/Starch.
REFERENCES


2.2 Pd@Fe₃O₄-NH₂/Starch catalyzed selective oxidation of benzyl alcohols using H₂O₂ as an oxidant and EtOH:H₂O as solvent

Oxidation is an important methodology for the introduction and modification of functional groups in the synthetic organic chemistry.¹ Selective oxidation of benzyl alcohols into subsequent aldehydes becomes a fundamental research area in the synthetic organic chemistry owing to their broad range of applications from pharmaceuticals to material science²,³. Numerous homogeneous metal complexes have been developed for the oxidation of alcohols such as copper, gold and palladium⁴,⁵. Nowadays, heterogenization of such metal complexes on various supports and in particular, magnetic supports has recently gained research impetus⁶,⁷.

Earlier approaches for the selective oxidation of substituted benzyl alcohols

The selective oxidation of substituted benzyl alcohols to corresponding aldehydes is widely recognized as one of the most essential transformations in organic synthesis. Traditionally, oxidizing reagents such as peroxides, nitric acid, KMnO₄ and K₂Cr₂O₇ have been employed for the oxidation of benzyl alcohols. But these stoichiometric oxidants are expensive and/or toxic, non-selective and generates a large amount of heavy-metal wastes⁸,⁹. Although, hydrogen peroxide, molecular oxygen have appeared as ideal oxidants, yet they are not very reactive towards organic molecules. To make them more reactive, appropriate catalyst is required which will activate the oxidant molecule and mediates the oxidation potential to right oxidation reaction. In recent years, particular attention has been paved on the development of green methodology for the selective oxidation of benzyl alcohols, and in this perspective, transition metal nanoparticles immobilized onto heterogeneous support have been shown to be effective for catalyzing oxidation of benzyl alcohols.

Aktas et al. have reported the synthesis of peripherally tetra-substituted Co(II) and Fe(II) phthalocyanine complexes bearing (2-{2-[2,3,5,6- tetrafluorophenoxy]ethoxy}ethoxy) groups (Scheme 1). Fe(II) and Co(II) phthalocyanines so synthesized showed good catalytic activity for the oxidation of benzyl alcohols with different oxygen sources. It was reported that out of two synthesized complexes, Co(II) phthalocyanine showed
somewhat better catalytic performance on benzyl alcohol oxidation with high yield and selectivity.\textsuperscript{10}

**Scheme 1**

\[
\text{Benzyl alcohol} \xrightarrow{\text{oxidant, 90 °C}} \text{Benzaldehyde} + \text{Benzoquinone} + \text{Benzoic acid} + \text{Benzyl benzoate}
\]

Wang et al.\textsuperscript{11} have reported a new and simple PdCl\textsubscript{2}/DMA catalytic system for the alcohol oxidation using molecular oxygen as the sole oxidant under milder conditions (\textbf{Scheme 2}). It has been shown that a wide range of active and non-active alcohols were oxidized to their corresponding carbonyl compounds in good to excellent yields. Moreover, the catalytic system could be reused up to three runs without significant loss of catalytic activity. Gas-uptake kinetics for the reported catalytic system was also investigated, which suggested the \textit{insitu} formation of H\textsubscript{2}O\textsubscript{2}.

**Scheme 2**

\[
\text{Benzyl alcohol} \xrightarrow{\text{PdCl}_2 (0.1 \text{ mmol}), \text{DMA (4 mL)}, \text{NaOAc (0.2 mmol), 60 °C}} \text{Benzylic aldehyde}
\]

Literature studies revealed that transition metals have played important role in catalyzing oxidation of array of substituted benzyl alcohols. But, owing to their homogeneous nature, they undergo agglomeration, as a result, their efficiency decreases. Further, due to
the difficulty in their separation from reaction mixture, these processes become highly expensive. In this perspective, active metal species immobilized onto different heterogeneous supports have appeared as cost-effective alternative to homogeneous transition metals for the selective oxidation of benzyl alcohols.

Feng et al. have reported the facile synthesis of copper nanoparticles immobilized on reduced graphene oxide (Cu@rGO) by one-pot reduction of graphene oxide and copper ions. The Cu@rGO nanocomposite has appeared as an efficient, easily retrieved and recycled catalyst for the selective oxidation of benzyl alcohols to aldehydes in water with 97% conversion and 98% selectivity\textsuperscript{12} (Scheme 3).

**Scheme 3**

\[
\text{RCH(OH)R} \xrightarrow{\text{Cat, 80 °C}} \text{RCHO}
\]

Kimi et al.\textsuperscript{13} have reported the synthesis of bimetallic copper-nickel nanoparticles supported on activated carbon (AC) via deposition-precipitation method. CuNi/AC has showed the best catalytic activity for the oxidation of benzyl alcohols to the corresponding aldehyde within a short reaction period at 80 °C. It has been shown that the catalytic performance has significantly enhanced by the addition of equal amount of Ni as compared to the other monometallic counterparts.

Assal et al.\textsuperscript{14} have reported the synthesis of an efficient ZrO\textsubscript{x} doped MnCO\textsubscript{3} on highly reduced graphene oxide (HRG) catalyst for the selective oxidation of substituted benzyl alcohols to corresponding aldehydes using molecular O\textsubscript{2} as an environmentally friendly
oxidizing agent. Broad range of substituted benzyl alcohols have been successfully converted to their corresponding aldehydes in short reaction time.

Ouyang et al. have reported TiO$_2$ nanoparticles immobilized onto wheat bran (a residue from the agricultural industry), a novel and effective catalytic system for the selective conversion of benzyl alcohol to benzoaldehyde$^{15}$. It has been observed that 10% Ti-Bran showed better selectivity for the oxidation of benzyl alcohols as compared to commercial pure TiO$_2$. The higher selectivity of Ti-Bran nanocomposites towards benzoaldehyde was due to the incorporation of carbon atoms on the TiO$_2$ lattice.

Qi et al.$^{16}$ have reported the synthesis of Pd$^{2+}$ ions supported on [CTA$^+$]MCM-41 materials through adsorption method. The catalytic activity of Pd-M41-AE has been evaluated in the solvent-free conditions for the selective oxidation of benzyl alcohols using molecular oxygen under atmospheric pressure. It has showed excellent catalytic activity for the oxidation of benzyl alcohols, due to the adsorption of smaller Pd particles in Pd-M41-AE.

Dell’Anna et al.$^{17}$ have reported the synthesis of palladium nanoparticles immobilized onto polymer support (methacrylic material). The synthesized catalyst (Pd-Pol) has showed significant catalytic activity for the oxidation of primary and secondary aromatic alcohols to their corresponding carbonyl compounds in the presence of a low loading of palladium (0.5 mol%) in shorter time. Furthermore, the catalyst could be easily recovered and reused up to six cycles.

Recently, magnetite nanoparticles have emerged as a feasible alternative to conventional supports owing to their robust, high surface area, readily available, magnetic nature, etc. Besides, magnetite nanoparticles have offered additional advantage of being magnetically separable, thereby eliminating the tedious workup procedures.

Sun et al. have reported the synthesis of a novel iron-doped graphene supported Au-based catalyst by the deposition precipitation method (Scheme 4). The catalyst has showed the selective-switchable oxidation of benzylic alcohols to corresponding aldehydes or alkyl benzoates with dioxygen as an oxidant. The Au/Fe-Gr-K$_2$CO$_3$ catalyst has showed a very high catalytic performance for the selective oxidation of benzyl alcohol to methyl
benzoate, in which 96.2% conversion of \(1\) and 99.9% selectivity of \(3\) was obtained in methanol. Besides, the oxidation of benzyl alcohol to benzaldehyde has also been successfully achieved using Au-Pd/Fe-Gr as catalyst and n-butanol as solvent, in which the conversion of \(1\) and the selectivity of \(2\) are as high as 89.1% and 87.5%, respectively.\(^{18}\)

**Scheme 4**

\[
\begin{align*}
\text{PhOH} & \xrightarrow{\text{O}_2, \text{methanol, Cat}} \text{PhCHO} + \text{PhCOOH} + \text{PhCOOEt} \\
1 & \quad 2 \quad 3 \quad 4
\end{align*}
\]

Zhang *et al.*\(^{19}\) have reported magnetically separable Pd nanoparticles grafted onto carbon-coated iron nanocrystals (Pd/Fe@C) by an impregnation method. The catalyst showed high catalytic activity towards the selective oxidation of benzyl alcohol under mild conditions in an \(O_2\) atmosphere.

Bhat *et al.*\(^{7}\) have successfully synthesized magnetic nanoparticles immobilized Schiff base complexes containing either Ni or Co as active metal species. MNP based Schiff base complex represented a promising greener approach with high catalytic activity for the oxidation of primary and secondary alcohols. Ferromagnetic interaction in the Co(II) complex enhanced the catalytic activity of the immobilized complex as compared to Ni(II) complex. The key advantages of immobilized metal catalyst include high catalytic activity, thermal stability and facile reusability (**Scheme 5**).
Polshettiwar et al.\textsuperscript{20} have reported a convenient method for the synthesis of a nano ferrite supported Pd catalyst. The nanoferrite Pd catalyzed the selective oxidation of alcohols and olefins with high turnover number (TON) and excellent selectivity. Additionally, being magnetic in nature, it eliminated the requirement of catalyst filtration after the completion of the reaction (Scheme 6).
Martins et al.\textsuperscript{21} have reported doped ferrite NPs (MnFe\textsubscript{2}O\textsubscript{4}, CoFe\textsubscript{2}O\textsubscript{4} and CuFe\textsubscript{2}O\textsubscript{4}) as efficient catalysts for the microwave-assisted oxidation of alcohols to the corresponding ketones or aldehydes in solvent-free conditions. The reaction was carried out using t-BuOOH as an oxidant at 120 °C and afforded products in the range of 81 to 94%. Besides, the catalysts could be easily isolated using an external magnet and no significant loss of activity was observed up to ten consecutive runs.

Li et al.\textsuperscript{22} have developed magnetic catalyst, CoPz(S-Bu)\textsubscript{8}/SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} via the immobilization of cobalt octkis(butylthio)porphyrazines complex (CoPz(S-Bu)\textsubscript{8}) onto silica-coated magnetic nanospheres (SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}). The synthesized catalyst was tested for the oxidation of benzyl alcohol using H\textsubscript{2}O\textsubscript{2} as oxidant. It has been reported that corresponding benzoic acids were obtained in excellent selectivity but conversion rate was poor. Although the catalytic efficiency of the synthesized catalyst was not very satisfactory from the viewpoint of conversion rate, yet its selectivity and eco-friendliness were advantageous.

Despite these recent advances, catalytic oxidation of benzyl alcohols has often suffered from several drawbacks such as low yields, poor selectivity, harsh reaction conditions, difficulty in separation of catalyst etc. Moreover, selective oxidation of alcohols becomes trickier in case of compounds containing more than one oxidizable functional groups. Also, only few magnetic heterogeneous metal catalysts have been reported in the literature, which mediates oxidation reactions in an aqueous phase. Hence, there is an immense necessitate to develop novel magnetically separable heterogeneous metal catalysts for the benzylic C-H bond oxidations. In order to overcome these drawbacks, herein we report a mild and efficient approach to oxidize a broad range of benzyl alcohols to their corresponding aldehydes in good to excellent yields under mild reaction conditions (Scheme 7).

\textbf{Scheme 7}

\[
\begin{align*}
\text{R-CH}_2\text{OH} & \xrightarrow{\text{Pd@Fe}_3\text{O}_4-\text{NH}_2/\text{Starch}} \text{R-CHO} \\
& \text{30\% H}_2\text{O}_2, \text{EtOH:H}_2\text{O (3:1)} \quad 70 ^\circ\text{C}
\end{align*}
\]
Results and discussion

Optimization of the reaction conditions

In order to optimize the reaction conditions for the selective oxidation of benzyl alcohols, oxidation of 4-methoxybenzyl alcohol into 4-methoxybenzaldehyde was chosen as the model reaction and the results are presented in Table 1 and 2. Initially, model reaction was performed in the absence of catalyst, but product formation has not been observed (entry 1, Table 1). The model reaction was then attempted using different catalysts such as Fe₃O₄-NH₂, Pd@Fe₃O₄ and Pd@Fe₃O₄-NH₂, but low yields were obtained in all these cases (entries 2-4, Table 1). Further, when the desired reaction was performed with Pd@Fe₃O₄-NH₂/Cellulose and Pd@Fe₃O₄-NH₂/Starch, quite pleasing results were obtained (entries 5 and 7, Table 1). But, it has been observed that out of Pd@Fe₃O₄-NH₂/Cellulose and Pd@Fe₃O₄-NH₂/Starch, Pd@Fe₃O₄-NH₂/Starch gave better yield and selectivity in 1.5 h (entry 7, Table 1). The high catalytic activity of Pd@Fe₃O₄-NH₂/Starch might be owing to the helical structure of the starch along with the intra-chain hydrogen bonding which stabilizes the metal nanoparticles more effectively. Further, to evaluate the effect of catalyst amount, the model reaction was attempted using variable catalyst amounts i.e. 0.05 g (1.18 mol% Pd), 0.10 g (2.36 mol% Pd), 0.15 g (3.54 mol% Pd) and 0.2 g (4.72 mol% Pd). There occurred no significant increase in the yield of desired product beyond 0.1 g of the catalyst (entry 8 and 9, Table 1). Thus, 0.1 g of Pd@Fe₃O₄-NH₂/Starch (2.36 mol% Pd) was herein chosen as the optimal amount for carrying out the desired reactions (entry 7, Table 1).

Table 1. Optimization of the reaction conditions for the oxidation of benzyl alcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Amount (g)</th>
<th>Time (h)</th>
<th>Yield  (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>-</td>
<td>10</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>Fe₃O₄-NH₂</td>
<td>0.1</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>Pd@Fe₃O₄</td>
<td>0.1</td>
<td>10</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>Pd@Fe₃O₄-NH₂</td>
<td>0.1</td>
<td>6.5</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>Pd@Fe₃O₄-NH₂/Cellulose</td>
<td>0.1</td>
<td>3.5</td>
<td>73</td>
</tr>
</tbody>
</table>
Further, in order to optimize the reaction conditions with respect to other parameters such as oxidant, solvent and temperature, the model reaction was performed under different set of conditions to achieve the best possible combination and the results are summarized in Table 2. Initially, the effect of different solvents such as CH$_2$Cl$_2$, CH$_3$CN, H$_2$O, DMF and EtOH: H$_2$O at temperatures ranging from room temperature to 100 °C was tested on the model reaction. As clearly indicated from Table 2, the poor yields were obtained with CH$_2$Cl$_2$ and DMF (entries 1-7, Table 2), whereas the yields have been much better in case of CH$_3$CN and H$_2$O (entries 8-12, Table 2). However, the best results were obtained in EtOH: H$_2$O at 70 °C (entry 15, Table 2). This may be accredited to the beneficial effect of the co-solvent which is responsible for the good solubility of the organic substrates. Moreover, when the model reaction was attempted with EtOH: H$_2$O at elevated temperature of 100 °C, there occur no noteworthy increase in the yield of the product (entry 16, Table 2). Thus, 70 °C was the optimum temperature for carrying out the desired reaction in EtOH: H$_2$O. Next, the effect of different oxidants such as O$_2$, H$_2$O$_2$ and TBHP was examined. The results revealed that the oxidation with H$_2$O$_2$ has been found to be best in terms of time, yield and selectivity (entry 15, Table 2). Although, good results were obtained with TBHP as well, yet, it has led to decrease in selectivity of the product formation (entry 14, Table 2). Further, the oxidation with O$_2$ gave the poor yields even in EtOH: H$_2$O solvent system (entry 13, Table 2).
Table 2. Optimization of different solvents, oxidants and reaction temperatures for the oxidation of benzyl alcohols\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Oxidant</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>O\textsubscript{2}</td>
<td>RT</td>
<td>3</td>
<td>Traces</td>
</tr>
<tr>
<td>2</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>O\textsubscript{2}</td>
<td>40</td>
<td>3</td>
<td>Traces</td>
</tr>
<tr>
<td>3</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>TBHP</td>
<td>40</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>H\textsubscript{2}O\textsubscript{2}</td>
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<td>5</td>
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<td>O\textsubscript{2}</td>
<td>80</td>
<td>2.5</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>CH\textsubscript{3}CN</td>
<td>TBHP</td>
<td>80</td>
<td>3</td>
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<tr>
<td>10</td>
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<td>60</td>
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<tr>
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<tr>
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<td>H\textsubscript{2}O</td>
<td>H\textsubscript{2}O\textsubscript{2}</td>
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<td>70</td>
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<tr>
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<td>EtOH:H\textsubscript{2}O (3:1)</td>
<td>O\textsubscript{2}</td>
<td>70</td>
<td>1.5</td>
<td>45</td>
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<tr>
<td>14</td>
<td>EtOH:H\textsubscript{2}O (3:1)</td>
<td>TBHP</td>
<td>70</td>
<td>1.5</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>EtOH:H\textsubscript{2}O (3:1)</td>
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<td>70</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>16</td>
<td>EtOH:H\textsubscript{2}O (3:1)</td>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>100</td>
<td>1.5</td>
<td>91</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 4-methoxybenzyl alcohol (1 mmol), Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch (0.1 g, 2.36 mol\% Pd), Solvent (8 mL).

\textsuperscript{b}Column chromatography yields.
After the optimization of the reaction conditions, scope of the reported protocol was evaluated for a wide range of substrates and the results are presented in **Table 3**.

**Table 3.** Oxidation of benzyl alcohols using Pd@Fe$_3$O$_4$-NH$_2$/Starch in EtOH: H$_2$O mixture at 70 °C$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH</td>
<td>CHO</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
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<td>1.5</td>
<td>90</td>
</tr>
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<td>3</td>
<td>OH</td>
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<td>1.25</td>
<td>95</td>
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<td>4</td>
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<td>CHO</td>
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</tr>
<tr>
<td>9</td>
<td>OH</td>
<td>CHO</td>
<td>1</td>
<td>93</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: benzyl alcohol (1 mmol), H$_2$O$_2$ (1.5 mmol), Pd@Fe$_3$O$_4$-NH$_2$/Starch (0.1 g, 2.36 mol% Pd), EtOH: H$_2$O (3:1, 8 mL) at 70 °C.

$^b$Column chromatography yields.
**Recyclability and heterogeneity**

To test the recyclability of the catalyst, a series of six consecutive runs (entry 1, Table 3) were carried out using Pd@Fe₃O₄-NH₂/Starch as catalyst under the selected conditions. The results are presented in Fig. 1. The catalyst was recovered via external magnet and reused for further reactions. It is important to mention that amount of reactants required to carry out the new reaction was adjusted according to the amount of catalyst recovered from previous run. It has been observed that catalyst could be recycled upto five consecutive runs without any significant loss of activity. The ICP-AES study of the used Pd@Fe₃O₄-NH₂/Starch after 5th run indicated the presence of 2.92 wt% Pd, which inferred that a very small amount of the Pd metal was leached from the catalyst (fresh catalyst contains 3.0 wt% Pd). Further, to rule out the possibility of leaching of Pd(0) NPs from the support, hot filtration test was performed. The reaction in case of entry 1, Table 3 has been carried out using Pd@Fe₃O₄-NH₂/Starch, until the conversion was 45% (0.65 h) and afterthat, catalyst was filtered off at the reaction temperature. The liquid phase so obtained was then transferred to another flask and allowed to react, but no further considerable conversion was observed. So, we conclude that there is no significant leaching of Pd(0) NPs from the surface of the Pd@Fe₃O₄-NH₂/Starch, thus deciphered the heterogeneous nature of the catalyst.

![Graph showing recyclability of Pd@Fe₃O₄-NH₂/Starch.](image)

**Fig. 1** Recyclability of Pd@Fe₃O₄-NH₂/Starch. Reaction conditions: benzyl alcohol (1 mmol), 30% H₂O₂ (1.5 mmol), Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) and ethanol:water (3:1.8 mL) at 70 °C for 1.5 h.
Proposed mechanism

To confirm whether the selective oxidation of benzylic alcohols involves a radical mechanism or not, a radical-trapping agent, TEMPO (a radical scavenger) was used. The reaction in case of entry 1, Table 3 has been carried out until the conversion was 44% (0.6 h), then TEMPO (1 mmol) was added to the reaction mixture and then it was further allowed to proceed up to 1.5 h. It has been found that no further reaction was observed, which indicated that the selective oxidation of benzyl alcohols most likely occurred via radical mechanism (Scheme 8).

Scheme 8

A plausible reaction mechanism for the Pd@Fe₃O₄-NH₂/Starch catalyzed selective oxidation of substituted benzyl alcohols via free radical pathway has been proposed.

Fig. 2 Proposed mechanism for the Pd@Fe₃O₄-NH₂/Starch catalyzed selective oxidation of benzyl alcohol.
Initially, Pd(0) on reaction with H$_2$O$_2$ form hydrogen peroxide palladium(II) complex (I)\textsuperscript{24} and first type of radical H·. Consequently, H· reacts with benzyl alcohol to generate benzyl radical (II). Finally, the hydrogen peroxide palladium(II) complex (I) reacts with benzyl radical (II) to form the desired product (III) and Pd(0) is regenerated back (Fig. 2).

**Conclusion**

In conclusion, a simple, efficient, cost-effective and environment-friendly procedure has been developed for the selective oxidation of diversely substituted benzyl alcohols into corresponding aldehydes using Pd@Fe$_3$O$_4$-NH$_2$/Starch (0.1 g, 2.36 mol% Pd) as magnetically recoverable heterogeneous catalyst. The catalyst can be easily recovered using external magnet and reused up to five times without any significant deterioration in its catalytic activity. The salient features of the reported methodology embrace operational simplicity, easy recyclability, a cleaner reaction profile, which lead to short reaction time and high yields, thus adding a credit towards the development of greener methodologies for organic synthesis.
Experimental

General procedure for the Pd@Fe₃O₄-NH₂/Starch catalyzed selective oxidation of benzyl alcohols

The mixture of benzyl alcohol (1 mmol), Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) and 30% H₂O₂ (0.34 mL, 1.5 mmol) in EtOH: H₂O (3:1, 8 mL) was stirred at 70 °C for an appropriate time. After completion of the reaction (monitored by TLC), the catalyst was separated via an external magnet. The resulting solution was extracted with ethyl acetate (2 × 10 mL), washed with brine (30 mL) and dried over anhyd. Na₂SO₄. Finally, the product was obtained after removal of the solvent under reduced pressure and passing through column of silica gel and elution with EtOAc–pet. ether. The recovered catalyst was washed with EtOAc (3 ×15 mL) followed by double distilled water (3 × 15 mL). It was dried and then reused for the subsequent reactions.

The structures of the products were confirmed by ¹H and ¹³C NMR, mass spectral data and comparison with authentic samples obtained commercially or prepared according to the literature methods.
Spectral data of the compounds listed in Table 3

Benzaldehyde (entry 1)

\[
\begin{array}{c}
\text{CHO} \\
\text{C} \quad \text{H} \quad \text{O}
\end{array}
\]

Liquid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 7.48-7.52\) (m, 2H, ArH), 7.58-7.62 (m, 1H, ArH), 7.85-7.87 (d, 2H, J=8 Hz, ArH), 9.99 (s, 1H, CHO); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta 128.4, 129, 129.7, 130, 134.5, 171, 192.5\); MS (ESI): 106 (M\textsuperscript{+}).

4-Methoxybenzaldehyde (entry 2)

\[
\begin{array}{c}
\text{MeO} \\
\text{CHO} \\
\text{Me} \\
\text{C} \quad \text{H} \quad \text{O}
\end{array}
\]

Liquid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 3.69\) (s, 3H, OCH\textsubscript{3}), 6.82-6.84 (d, 2H, J=8 Hz, ArH), 7.65-7.67 (d, 2H, J=8 Hz, ArH), 9.71 (s, 1H, CHO); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta 55.3, 114.4, 130, 131.8, 164.8, 190.7\); MS (ESI): 136 (M\textsuperscript{+}).

4-Methylbenzaldehyde (entry 3)

\[
\begin{array}{c}
\text{Me} \\
\text{CHO} \\
\text{Me} \\
\text{C} \quad \text{H} \quad \text{O}
\end{array}
\]

Liquid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 2.36\) (s, 3H, CH\textsubscript{3}), 7.30-7.32 (d, 2H, J=8 Hz, ArH), 7.75-7.77 (d, 2H, J=8 Hz, ArH), 9.89 (s, 1H, CHO); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta 21.1, 129.6, 130.3, 133.2, 146.2, 191.9\); MS (ESI): 120 (M\textsuperscript{+}).

4-Chlorobenzaldehyde (entry 4)

\[
\begin{array}{c}
\text{Cl} \\
\text{CHO} \\
\text{C} \quad \text{H} \quad \text{O}
\end{array}
\]

Solid, M.pt. 50-51 °C (Lit. M.pt. 50-52 °C)\textsuperscript{35}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta 7.52-7.54\) (d, 2H, J=8 Hz, ArH), 7.83-7.85 (d, 2H, J=8 Hz, ArH), 10.00 (s, 1H, CHO); \textsuperscript{13}C NMR
(CDCl₃, 100 MHz): δ 129.6, 130.9, 134.7, 141, 190.9; MS (ESI): 139 (M-1), 141 (M+1).

2-Methoxybenzaldehyde (entry 5)

![Chemical structure of 2-Methoxybenzaldehyde]

Liquid. ¹H NMR (CDCl₃, 400 MHz): δ 3.96 (s, 3H, OCH₃), 7.01-7.08 (m, 2H, ArH), 7.57-7.61 (m, 1H, ArH), 7.85-7.87 (d, 1H, J=8 Hz, ArH), 10.50 (s, 1H, CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 55.7, 111.5, 120.7, 128.7, 135.9, 162, 189.9; MS (ESI): 135 (M-1), 137 (M+1).

2-Chlorobenzaldehyde (entry 6)

![Chemical structure of 2-Chlorobenzaldehyde]

Liquid. ¹H NMR (CDCl₃, 400 MHz): δ 7.18 (s, 1H, ArH), 7.25 (s, 2H, ArH), 7.31 (s, 1H, ArH), 10.02 (s, 1H, CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 127.2, 129.2, 130.9, 135.1, 189.6; MS (ESI): 140 (M⁺), 142 (M+2).

2-Nitrobenzaldehyde (entry 7)

![Chemical structure of 2-Nitrobenzaldehyde]

Brown solid, M.pt. 42-44 °C (Lit. M.pt. 46-47 °C).¹H NMR (CDCl₃, 400 MHz): δ 7.51-7.53 (d, 1H, J=8 Hz, ArH), 7.69-7.73 (m, 1H, ArH), 7.76-7.78 (d, 1H, J=8 Hz, ArH), 8.13-8.15 (d, 1H, J=8 Hz, ArH), 12.12 (s, 1H, CHO); ¹³C NMR (CDCl₃, 100 MHz): δ 125.2, 128.9, 130.2, 133.9, 189.7; MS (ESI): 152 (M⁺).
3-Chlorobenzaldehyde (entry 8)

![Chemical structure of 3-Chlorobenzaldehyde]

Liquid. $^1$$H$ NMR (CDCl$_3$, 400 MHz): $\delta$ 7.41-7.51 (m, 1H, ArH), 7.52-7.54 (m, 1H, ArH), 7.69-7.71 (m, 1H, ArH), 7.72-7.77 (m, 1H, ArH), 9.91 (s, 1H, CHO); $^{13}$$C$ NMR (CDCl$_3$, 100 MHz): $\delta$ 127.9, 130.3, 134.3, 137.9, 190.8; MS (ESI): 140 (M$^+$), 142 (M+2)

Cinnamaldehyde (entry 9)

![Chemical structure of Cinnamaldehyde]

Liquid. $^1$$H$ NMR (CDCl$_3$, 400 MHz): $\delta$ 6.71-6.77 (m, 1H, CH), 7.21-7.35 (m, 2H, ArH), 7.41-7.51 (m, 3H, ArH), 7.57-7.59 (m, 1H, CH), 9.69-9.71 (d, 1H, J=8 Hz, CHO); $^{13}$$C$ NMR (CDCl$_3$, 100 MHz): $\delta$ 126.6, 126.9, 128.2, 129.1, 131.29, 133.9, 152.9, 194; MS (ESI): 132 (M$^+$).
REFERENCES


66-67,72-73

62-65,68-71,74-81
2.3 Pd@Fe$_3$O$_4$-NH$_2$/Starch as a sustainable catalyst for the hydrogenation of nitroarenes under mild conditions

Catalytic hydrogenation is one of the most noteworthy and commonly used transformations in organic synthesis$^1$. Selective hydrogenation of organic substrates such as nitroarenes to their corresponding amines is of utmost interest in organic chemistry due to their wide spectrum of applications$^2$. Functionalized amines are important feedstock for the synthesis of biologically important organic compounds such as pesticides, dyes, pharmaceuticals, antioxidants, polymers, agrochemicals and drugs$^3$. Moreover, they constitutes fundamental part of numerous important natural products such as the commercially available amino group containing drugs, rifamycin and actinomycin$^4,5$.

Earlier approaches for the reduction of nitroarenes

Reduction of nitroarenes is of immense importance as the amino compounds act as important feedstock for the synthesis of valuable organic compounds. Amino compounds are generally formed by the reduction of nitriles,$^6$ or imines$^7$, reductive amination of carbonyl compounds$^8$, hydroamination of olefins,$^9$ and decarboxylation of carbamic acids.$^{10}$ But, the best approach to synthesize industrially and biologically important aryl amines is the hydrogenation of nitro compounds. Most commonly developed protocols for the hydrogenation of nitroarenes involve the use of stoichiometric chemical reagents, such as NaBH$_4$, LiAlH$_4$, or the use of corrosive acetic acid, which possesses severe limitations both economically and environmentally.$^{10-11}$ Moreover, the selective reduction of nitroarenes containing other competitively reducible or degradable functional groups is also a challenging task in the field of synthetic organic chemistry. Another limitation associated with the reduction of nitroarenes is that it often stops at an intermediate stage, leading to hydrazines, hydroxylamines, and azoarenes as side products.$^{12}$ Numerous catalytic methods have been reported in the literature for the selective reduction of nitroarenes, but these methodologies suffer from many limitations.$^{13}$ Though, a variety of catalytic hydrogenation methods have been reported using different transition metal catalysts$^{14-17}$, but their inadequate availability and high cost increased the overall
expenditure. This has led the researchers to search for more economical, greener and environmentally acceptable alternatives.

Gamble et al.\textsuperscript{18} have reported an proficient method for the reduction of nitroarenes to their corresponding aryl amines using ultrasonication technique. It has been proved that iron powder was superior to stannous chloride for the reduction of nitroarenes, even in the presence of sensitive functional groups. High yield of the desired aryl amines was obtained in relatively short reaction times (Scheme 1).

**Scheme 1**

\[
\begin{array}{c}
\text{MeO} \quad \text{NO}_2 \quad \text{Fe or SnCl}_2 \\
\text{Sonication, 30 °C} \quad 1-2 \text{ h}
\end{array}
\rightarrow
\begin{array}{c}
\text{MeO} \quad \text{NH}_2
\end{array}
\]

Rai et al.\textsuperscript{19} reported the reduction of nitroarenes to the corresponding aromatic amines by stannous chloride in the presence of ionic liquid using sonication technique (Scheme 2).

**Scheme 2**

\[
\begin{array}{c}
\text{NO}_2 \quad \text{R} \quad \text{SnCl}_2.2\text{H}_2\text{O} \\
\text{Ionic liquid, Sonication} \quad \text{r.t., 10-15 min}
\end{array}
\rightarrow
\begin{array}{c}
\text{NH}_2 \quad \text{R}
\end{array}
\]

Noble metal NPs own fascinating physicochemical properties and their catalytic activities have been broadly explored in recent years. However, these NPs shows agglomeration due to their high surface energy which eventually diminish their catalytic activity. Further, industrial applications of these NPs are also limited due to their high cost and poor recoverability from the reaction mixture. These problems are generally overcome by immobilizing noble metal NPs of specific shapes and sizes on different solid supports. Some of the examples of supported noble metal NPs catalyzed hydrogenation of nitroarenes are cited below:

The reduction of nitroarenes to their corresponding aromatic amines using heterogeneous catalyst, silica-grafted polyethylene glycol in the presence of zinc powder has been reported by Reza et al.\textsuperscript{20}
The fibrous nano-silica immobilized Ni@Au core-shell nanoparticles has been employed for the reduction of 2-nitroaniline and 4-nitrophenol by Ma et al.\textsuperscript{21} (Scheme 3). The catalyst showed excellent activity and selectivity for the reduction of nitroarenes.

Scheme 3

![Scheme 3 Diagram]

Giri et al.\textsuperscript{22} have reported the synthesis of silver nanocomposites (AgNCs) by adsorption onto an electron-rich polypyrrole-mercaptoacetic acid (PPy-MAA) composite. AgNCs showed enhanced activity for the reduction of substituted nitroarenes in water.

Highly dispersed AgPd nanoparticles supported on reduced graphene oxide were used for the catalytic hydrogenation of nitroarenes to their corresponding aromatic amines using formic acid and ammonium formate as hydrogen source at room temperature.\textsuperscript{23} It was reported that the synergetic interaction between well dispersed AgPd nanoparticles and RGO support were accountable for the impressive catalytic performance of the reported catalyst.

An efficient and novel synthesis of cellulose-supported palladium nanoparticles, Pd/Cell-C\textsubscript{4}F\textsubscript{9} was reported by Li et al.\textsuperscript{24} The catalyst showed excellent activity and selectivity for the hydrogenation of various nitroarenes to arylamines at room-temperature under hydrogen atmosphere in the absence of any additives. Besides, high chemoselectivity was also obtained in the hydrogenation of substituted nitroarenes containing multiple reducible groups.

Among the different solid supports used for the immobilization of noble metal NPs, magnetic support has been gaining much attention due to their unique properties.
Magnetite nanoparticles (MNPs) have played a dual role, such as acting both catalysts as well as magnetic support for active catalyst species. These are easy to recover from the reaction medium via external magnet. The combination of these types of materials can further improve activity and dispersibility of noble metal NPs.

Graphene-Fe₃O₄ nanocomposite (G-Fe₃O₄) was used as an efficient catalyst for the reduction of nitroarenes to corresponding aromatic amines with hydrazine hydrate. Further, G-Fe₃O₄ catalyst can be easily recovered and reused five times without any significant loss of the catalytic activity.

The synthesized Ag/Fe₂O₃-rGO nanocomposite was used as magnetically recoverable catalyst for room-temperature chemoselective reduction of aromatic nitro groups to the corresponding amines. This catalytic method has showed various advantages such as elimination of homogeneous catalysts, high yields, simple and easy separation and recycling of the catalyst. Moreover, the catalyst showed true heterogeneity as its effectiveness remains almost same even after five cycles of reuse.

A palygorskite (clay mineral) based magnetic bimetallic catalyst, Pal@Fe₃O₄@PdRu was employed for the hydrogenation of nitroarenes and organic dyes by Jia et al. The reported catalyst also showed good recyclability in the hydrogenation of several other nitroarenes and azo dyes.

Movahed et al. have reported the synthesis of palladium nanoparticles immobilized on Fe₃O₄@nitrogen doped carbon (N-C) core-shell (C-S) and yolk-shell (Y-S) nanostructures. Pd NPs grafted on Fe₃O₄@N-C@C-S and Y-S nanostructures were used for the reduction of nitroarenes to corresponding aromatic amines. The reported catalysts showed excellent activity for the reduction of nitroarenes and products were obtained in good yields. Furthermore, it was shown that the yolk-shell nanostructure showed higher catalytic efficiency than the core-shell based catalyst.

The air and moisture stable nano magnetic catalyst, MNPs@SB-Pd was used for the reduction of nitroarenes by Kandathil et al. The key advantages of the reported protocol were short reaction time, use of green medium, high yield of products, eco-friendly and cost-effective catalyst. Further, the catalyst was easily separated from the reaction
mixture via external magnet and could be reused for ten consecutive cycles without any significant loss of catalytic efficiency.

In order to carry out such industrially significant reactions under mild and environment-friendly conditions, there is an imperative need to develop appropriate catalysts for the reduction of nitro compounds to the corresponding amines under mild, cost-effective and green conditions. Herein, we report the reduction of a variety of nitroarenes in the presence of Pd@Fe₃O₄-NH₂/Starch as a catalyst and molecular hydrogen as reducing agent using EtOH:H₂O as reaction medium. The products were obtained in good to excellent yields at room temperature (Scheme 4).

**Scheme 4**

![Scheme 4](image)

**Results and discussion**

**Optimization of the reaction conditions**

Different experiments were performed in order to obtain suitable reaction conditions to carry out the reduction of nitroarenes smoothly. To optimize the reaction condition for the hydrogenation of nitroarenes, we have selected 4-methylnitrobenzene as the model substrate. The model reaction was tested using variable catalyst amounts i.e. 0.05 g (1.18 mol% Pd), 0.10 g (2.36 mol% Pd), 0.15 g (3.54 mol% Pd), 0.2 g (4.72 mol% Pd) and best results were achieved with 0.1 g (2.36 mol% Pd) of the catalyst. Therefore, 0.1 g of Pd@Fe₃O₄-NH₂/Starch (2.36 mol% Pd) was herein selected as the optimal amount for carrying out the hydrogenation of nitroarenes (Table 1).
Table 1. Optimization of the reaction conditions for the selective reduction of nitroarenes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Amount (g)</th>
<th>Time (min)</th>
<th>Yield\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch</td>
<td>0.05</td>
<td>20</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch</td>
<td>0.1</td>
<td>13</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch</td>
<td>0.15</td>
<td>13</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch</td>
<td>0.2</td>
<td>13</td>
<td>97</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 4-methylnitrobenzene (1 mmol), molecular H\textsubscript{2} (balloon), EtOH: H\textsubscript{2}O (3:1, 8 mL) at room temperature.

\textsuperscript{b}Column Chromatography yields.

Further optimization of the model reaction was done with respect to different solvents and the results are given in Table 2. It has been found that nature of the solvent affected the conversion rate of the reduction reaction. The model reaction was tested with different solvents such as CH\textsubscript{2}Cl\textsubscript{2}, MeOH, EtOH, H\textsubscript{2}O and EtOH:H\textsubscript{2}O, but the best results were obtained with ethanol:water (3:1) solvent system in terms of time and yield (entry 5, Table 2). This may be accredited to the synergistic effect of the co-solvent which results in good solubility of the organic substrate. Thus, screening of different solvent systems using Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch as an efficient and novel catalyst showed that water:ethanol mixture (3:1) as the most suitable solvent to carry out the reduction of nitroarenes smoothly.

Table 2 Effect of different solvents on the Pd@Fe\textsubscript{3}O\textsubscript{4}-NH\textsubscript{2}/Starch catalyzed hydrogenation of nitroarenes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Yield\textsuperscript{b} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>25</td>
<td>72</td>
</tr>
</tbody>
</table>
To check the compatibility of the reaction in the presence of other functional groups, we examined an array of synthetically valuable aromatic nitroarenes using Pd@Fe₃O₄-NH₂/Starch under the optimized reaction conditions (Table 3). Wide range of nitro substituted aromatic compounds was reduced to corresponding amines under hydrogen atmosphere at room temperature. It is noteworthy to mention that the azoxy, azo and hydrazo compounds as the usual side products of reduction of nitroarenes were not observed in this method. Further, no dehalogenated product was obtained during the hydrogenation of halogen substituted nitroarenes (entries 2, 6 and 7, Table 4).

Table 3. Reduction of nitroarenes using Pd@Fe₃O₄-NH₂/Starch in the presence of molecular hydrogen in EtOH: H₂O solvent system at room temperaturëa

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
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<td><img src="image2.png" alt="Product Image" /></td>
<td>15</td>
<td>90</td>
</tr>
<tr>
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<td><img src="image4.png" alt="Product Image" /></td>
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<tr>
<td>3</td>
<td><img src="image5.png" alt="Substrate Image" /></td>
<td><img src="image6.png" alt="Product Image" /></td>
<td>10</td>
<td>95</td>
</tr>
</tbody>
</table>

aReaction conditions: 4-methylnitrobenzene (1 mmol), Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) using molecular H₂ (balloon) in solvent (5 mL) at room temperature.

bColumn chromatographic yields.
Recyclability and heterogeneity

Recyclability of the synthesized Pd@Fe$_3$O$_4$-NH$_2$/Starch for the hydrogenation of nitroarenes was checked by performing different experiments. For this purpose, a fresh reaction was performed in case of entry 4, Table 3 using Pd@Fe$_3$O$_4$-NH$_2$/Starch as novel catalyst. After completion of the reaction, catalyst was separated using magnet, washed with chloroform (2 $\times$ 15 mL) and deionized water (2 $\times$ 15 mL) to remove any physisorbed material and dried under vacuum. Then a new reaction was tested with the used catalyst. Amount of the reactant taken for further run was calculated according to the amount of catalyst recovered from the previous run. An extremely small decrease in the activity of the synthesized catalyst was observed up to five runs (Fig. 1). Further, to reveal the heterogeneity of the synthesized catalyst, a reaction in case of entry 4, Table 3 was carried out until the conversion was 45% (5 min). After that, the reaction was

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Conditions</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>NO$_2$Me NH$_2$</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>NO$_2$COOH NH$_2$</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>NO$_2$Cl Cl</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>NO$_2$Br Br</td>
<td>15</td>
</tr>
</tbody>
</table>

aReaction conditions: nitroarene (1 mmol), Pd@Fe$_3$O$_4$-NH$_2$/Starch (0.1 g, 2.36 mol% Pd), EtOH: H$_2$O (3:1, 8 mL) using molecular hydrogen at room temperature.

bColumn chromatography yields.
stopped and the catalyst was filtered off from the reaction mixture. The liquid phase was transferred to another flask and again allowed to react, but no further considerable conversion was observed. This proved the heterogeneous nature of the catalyst.

![Graph showing recyclability of Pd@Fe₃O₄-NH₂/Starch](image)

**Fig. 1** Recyclability of Pd@Fe₃O₄-NH₂/Starch. Reaction conditions: 4-methyl-nitrobenzene (1 mmol), molecular H₂ (balloon), ethanol:water (3:1, 8 mL) at room temperature for 13 minutes.

**Proposed Mechanism**

A plausible reaction mechanism has been proposed for the reduction of nitroarenes to aromatic amines in the presence of Pd@Fe₃O₄-NH₂/Starch involving phenylhydroxylamine as the intermediate (**Fig. 2**). Initially, nitroarene gets anchored on the surface of hydrogenated catalyst I and abstract hydrogen atoms from the catalyst surface leaving water as by-product and itself get reduced to nitrosobenzene intermediate II. The nitrosobenzene II, so formed undergoes rapid hydrogen transfer from the catalyst to the N=O double bond to form ArNH-OH or hydroxyl amine intermediate III, which on abstracting one more molecule of hydrogen from the hydrogenated Pd(0) NPs gives final amine product (IV) and Pd(0) NPs are regenerated back.
Fig. 2 Proposed mechanism for the hydrogenation of nitroarenes to aromatic amines using H\(_2\) in the presence of Pd@Fe\(_3\)O\(_4\)-NH\(_2\)/Starch.

**Conclusion**

In conclusion, we have reported an efficient and green catalytic method for the reduction of nitroarenes in the presence of Pd@Fe\(_3\)O\(_4\)-NH\(_2\)/Starch using environmentally-benign molecular hydrogen at room temperature under mild reaction conditions. Wide range of substituted nitroarenes were successfully reduced to corresponding amines and afforded desired products in good to excellent yields. Moreover, the usual side products of hydrogenation of nitroarenes such as azoxy, azo and hydrazo compounds were not observed in this method. The simplicity of the proposed method, easy workup procedure, recyclability of the catalyst and excellent yields of aminoarenes makes it an environmentally acceptable and greener alternative for the hydrogenation of nitroarenes.
Experimental

General procedure for the Pd@Fe₃O₄-NH₂/Starch catalyzed reduction of nitroarenes

To a mixture of nitroarene (1 mmol) and Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) in a round bottom flask (25 mL), EtOH: H₂O (3:1, 8 mL) was added, and the reaction mixture was stirred at room temperature under H₂ atmosphere (H₂ balloon) for a suitable time. The catalyst was separated using external magnet after completion of the reaction (monitored by TLC) and the supernatant was diluted with ethyl acetate. The organic layer was washed with brine solution (3 × 15 mL) and dried over anhydrous Na₂SO₄. Finally, the desired product was obtained after removal of the solvent under reduced pressure, followed by passing through column of silica gel and elution with EtOAc-pet. ether (2:98). The recovered catalyst was washed with deionized water (3 × 20 mL) followed by chloroform (3 × 20 mL), dried under vacuum and reused for the subsequent reactions.

The structures of the products were confirmed by ¹H NMR, ¹³C NMR and mass spectral data and comparison with authentic samples prepared according to the literature methods.
Spectral data of products listed in Table 3

Aniline (entry 1)

Yellow liquid. $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta$ 3.98 (bs, 2H, NH$_2$, exchangeable with D$_2$O), 6.78-6.80 (d, 2H, J=8 Hz, ArH), 6.96-6.98 (d, 1H, J=8 Hz, ArH), 7.21-7.23 (d, 2H, J=8 Hz, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 122.3, 124.8, 131.5, 141.3; MS (ESI): 93 (M$^+$).

4-Chloroaniline (entry 2)

Pale yellow solid, M.pt. 68-69 °C (Lit. M.pt. 69.5 °C). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta$ 3.76 (bs, 2H, NH$_2$, exchangeable with D$_2$O), 6.50-6.52 (d, 2H, J=8 Hz, ArH), 7.06-7.08 (d, 2H, J=8 Hz, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 116.1, 120.4, 128.9, 147.1; MS (ESI): 127 (M$^+$), 129 (M+2).

4-Methoxyaniline (entry 3)

Brown solid, M.pt. 56-58 °C (Lit. M.pt. 59 °C). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta$ 3.44 (bs, 2H, NH$_2$, exchangeable with D$_2$O), 3.77 (s, 3H, OCH$_3$), 6.66-6.68 (d, 2H, J=8 Hz, ArH), 6.76-6.78 (d, 2H, J=8 Hz, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 55.7, 114.8, 116.4, 139.9, 152.8; MS (ESI): 123 (M$^+$).
4-Methylaniline (entry 4)

Pale yellow solid, M.pt. 42-44 °C (Lit. M.pt. 44 °C)\textsuperscript{30}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 2.28 (s, 3H, CH\textsubscript{3}), 3.49 (bs, 2H, NH\textsubscript{2}, exchangeable with D\textsubscript{2}O), 6.64-6.66 (d, 2H, J=8 Hz, ArH), 7.00-7.02 (d, 2H, J=8 Hz, ArH); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 20.5, 115.3, 127.8, 129.7, 143.8; MS (ESI): 107 (M\textsuperscript{+}).

4-Aminobenzoic acid (entry 5)

White solid, M.pt. 184-186 °C (Lit. M.pt. 187 °C)\textsuperscript{30}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 5.87 (bs, 2H, NH\textsubscript{2}, exchangeable with D\textsubscript{2}O), 6.54-6.56 (d, 2H, J=8 Hz, ArH), 7.61-7.63 (d, 2H, J=8 Hz, ArH), 11.96 (bs, 1H, COOH); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 113, 117.3, 131.6, 153.6, 167.9; MS (ESI): 138 (M+1).

3-Chloroaniline (entry 6)

Brown liquid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 3.77 (bs, 2H, NH\textsubscript{2}, exchangeable with D\textsubscript{2}O), 6.56-6.57 (d, 1H, J=4 Hz, ArH), 6.69 (s, 1H, ArH), 6.77-6.79 (d, 1H, J=8 Hz, ArH), 7.09-7.13 (m, 1H, ArH); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 113.5, 114.9, 118.5, 130.6, 134.9, 147.9; MS (ESI): 127 (M\textsuperscript{+}), 129 (M+2).
4-Bromoaniline (entry 7)

Brown solid, M.pt. 59-61 °C (Lit. M.pt. 62 °C)\textsuperscript{30}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 3.69 (bs, 2H, NH\textsubscript{2}, exchangeable with D\textsubscript{2}O), 6.57-6.60 (d, 2H, J=8 Hz, ArH), 7.25-7.27 (d, 2H, J=8 Hz, ArH); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 110.3, 116.9, 138.5, 145.2; MS (ESI): 170 (M\textsuperscript{+}), 172 (M+2).
REFERENCES


2.4 Pd@Fe$_3$O$_4$-NH$_2$/Starch as a magnetically recoverable catalyst for the one-pot reductive amination of aldehydes with nitroarenes under mild conditions

Synthesis of functionalized amines is one of the most significant organic transformations as amines are constructive intermediates for the synthesis of numerous functional materials$^1$. Many biologically active and pharmaceutically pertinent compounds contain amines and their derivatives in their skeletal framework.$^2$ These compounds possess extensive applications as intermediates for pharmaceuticals and agrochemicals,$^3$ solvents, textile additives, raw materials for resins, disinfectants, corrosion inhibitors$^4$, rubber stabilisers, and in the manufacture of detergents and plastics. Further, these have also played vital role in chemotherapeutics of numerous diseases$^5$ and are requisite building blocks in pesticides$^6$ and colour pigments$^7$. Compounds like polyfluoro- and perfluoroamines play important role in medicinal chemistry and biochemistry$^8$, and also gain special attention as they behave as an excellent fluorinating agents for alcohols, diols and haloalcohols.$^9$ Some biologically important amines are given in the Fig. 1. Compounds 1 and 2 exhibit significant anticancer activity against PC-3 cell lines, indicating the selective inhibition of PC-3 cells.$^{10}$ Ephedrine (3), epinephrine (4)$^{11}$ and novocaine (5) are biologically active functionalized amines. Ciprofloxacin (6) is a fluoroquinolone antibacterial agent. Lamisil (7, terbinafine) is a very effective tropical antifungal agent, whereas anileridine (8) is an opioid analgesic. Chlorpheniramine (9) is an antihistamine drug, usually used in pharmaceutical preparations for symptomatic relief of common cold and allergic diseases. It is one of the most frequently used antihistamines in small-animal veterinary practice.$^{12}$ Chlorpromazine (10, CPZ) is a renowned antipsychotic drug, widely used to treat symptoms of psychotic depression, schizophrenia and organic psychoses. Clomipramine (11, trademarked as an afranil) is a tricyclic antidepressant (TCA) drug used for the treatment of chronic pain,$^{13}$ panic disorder,$^{14}$ obsessive compulsive disorder (OCD).
Earlier approaches for the reductive amination of carbonyl compounds

Earlier, amines were synthesized by the reduction of nitrogen containing functional groups, alkylation of ammonia and Buchwald-Hartwig couplings in the presence of stoichiometric amounts of reducing agents, such as formates, borohydrides and silanes. But these methods endure numerous drawbacks such as formation of side products, use of excess amount of inorganic bases and inorganic salts as wastes. Moreover, consumption of aniline creates another problem as it get readily oxidized by autoxidation under the reaction conditions. Recently, domino reductive amination using nitroarenes is particularly very attractive as it does not require preliminary reduction of nitroarenes.
avoids separation of intermediates and purification steps, and minimizes waste production, thus, fulfilling one of the requirements of green chemistry. In the reductive amination, the selection of reducing agent plays significant role in the success of the reaction. A more useful method is to utilize molecular hydrogen as a reducing agent in the presence of a catalyst, as it is the most atom-economical and environmentally benign method, particularly in large-scale reactions. Some of the recently reported methods for the reductive amination of carbonyl compounds are presented below:

A soluble transition metal complex $\{[\text{Rh}(\text{cod})\text{Cl}]_2\}$ has been used for the reductive amination of carbonyl compounds using aqueous ammonia as amine source along with water-soluble phosphine and ammonium acetate by Beller et al.\textsuperscript{15} (Scheme 1). Synthesis of primary amines were also achieved for the first time using a bimetallic catalyst based on Rh/Ir.

**Scheme 1**

\[
\begin{align*}
\text{CHO} + \text{NH}_3 & \xrightarrow{[\text{Rh}(\text{cod})\text{Cl}]_2\text{ TPPTS}} \text{CH}_2\text{NH}_2 + \text{CH}_2\text{OH} \\
\text{H}_2\text{O}, \text{THF}, 135^\circ\text{C} & \text{65 bar H}_2, 2 \text{ h}
\end{align*}
\]

Silica chloride has been employed as an active, inexpensive and recyclable catalyst for the reductive amination of aldehydes and ketones using sodium borohydride as reducing agent at room temperature by Alinezhad et al.\textsuperscript{16} (Scheme 2). The reductive amination of carbonyl compounds worked smoothly even with aliphatic, aromatic, cyclic and acyclic carbonyl compounds. Besides, substituted functionalized amines were obtained as single regioisomers in good to excellent yields.

**Scheme 2**

\[
\begin{align*}
\text{R}_1\text{=O} + \text{H-N}_3 & \xrightarrow{\text{SiCl}_4\text{ NaBH}_4, \text{THF}} \text{R}_1\text{N}_3 \\
\text{r.t.}
\end{align*}
\]

Greener protocol for the synthesis of substituted amines by direct reductive amination of carbonyl compounds with different amines in aqueous media was reported by Patil et
The reported Fe@Pd/C catalyst showed excellent activity for the direct reductive amination reaction in aqueous medium (Scheme 3).

Scheme 3

![Scheme 3 Image]

An effective process mediated by Pd/C/Fe mixture for the reductive amination of aldehydes was successfully reported by Ma et al. Here, water serves as a solvent as well as a terminal hydrogen source in the presence of CO₂. This methodology would broaden the application of CO₂ as a reaction medium and promoter in greener chemical processes (Scheme 4).

Scheme 4

![Scheme 4 Image]

Novel and highly efficient graphene supported NiPd alloy nanoparticles (G-NiPd) have been developed to carry out reductive amination of aldehydes using ammonia borane in a water/methanol mixture under ambient conditions (Scheme 5). The desired products were obtained up to 99% yields in 6 h.
In the variety of methods reported for the reductive amination of carbonyl compounds, anilines were used as substrates. But these procedures suffered from several limitations such as formation of side products, use of excess amount of organic and inorganic bases and most importantly, employ of aniline creates another problem as it get readily oxidized by autooxidation under the reaction conditions. Another suitable pathway for the preparation of functionalized amines is the domino reductive amination of aldehydes with nitroarenes, as it does not require prior reduction of the nitroarenes. Recently, reductive amination of carbonyl compounds by nitroarenes becomes a key method for the synthesis of functionalized amines in synthetic chemistry. Some of the reported methods are cited below:

Ramachandran et al.\textsuperscript{20} have reported ammonia borane as a versatile and efficient reagent for the reductive amination of aldehydes and ketones, providing a variety of primary, secondary, and tertiary amines in good to excellent yields in the presence of titanium isopropoxide (Scheme 6).

Scheme 6

Direct one-pot reductive amination of aldehydes with nitroarenes has been reported by Sreedhar et al.\textsuperscript{21} in a domino fashion. This methodology was found to be appropriate to
both aliphatic as well as aromatic aldehydes and a broad range of nitroarenes using molecular hydrogen as the reducing agent (Scheme 7).

Scheme 7

\[
\begin{align*}
\text{H} & \quad + \quad \text{O}_2\text{N} \\
\text{GA-Pd nanoparticles} & \quad \text{H}_2 \text{atm., MeOH, r.t.} \\
\text{H} & \quad + \quad \text{N}
\end{align*}
\]

Pd/Fe\textsubscript{3}O\textsubscript{4} NPs have been synthesized by a simple and clean synthetic method using E. stracheyi Boiss root extract as the natural source of reducing and stabilizing agent. The nanocatalyst was reported as a competent, magnetically recoverable and recyclable catalyst for the one-pot reductive amination of aldehydes by Nasrollahzadeh et al.\textsuperscript{22} (Scheme 8).

Scheme 8

\[
\begin{align*}
\text{R'CHO} & \quad + \quad \text{RNO}_2 \\
\text{Pd/Fe}_3\text{O}_4 \text{NPs} & \quad \text{EtOH, H}_2, \text{r.t.} \\
\text{R-NH-R'} & \quad \text{Pd/Fe}_3\text{O}_4 \text{NPs}
\end{align*}
\]

Pd immobilized on magnetic support has been developed for the one-pot reductive amination of carbonyl compounds with nitroarenes under mild conditions. This procedure was used to synthesize a diverse range of amines in good to excellent yields. Besides, the catalyst exhibited high activity even after eight cycles.\textsuperscript{23}

Zhou et al.\textsuperscript{24} have reported palladium catalyzed reductive amination of carbonyl compounds with nitroarenes mediated by diboronic acid using water as a hydrogen source. A series of functionalized amines containing various reducible functional groups were synthesized in good to excellent yields.

Zhou et al.\textsuperscript{25} have reported the one-pot reductive amination of carbonyl compounds with nitroarenes using nitrogen-doped carbon supported cobalt nanoparticles and obtained structurally diverse functionalized amines with high yields.
Considering the enormous importance of functionalized amines, our foremost focus was to develop a simple and greener approach for the reductive amination reaction using Pd@Fe₃O₄-NH₂/Starch as a magnetically recoverable catalyst under hydrogen atmosphere. Thus, simple, competent and environment-friendly protocol has been developed for the one-pot synthesis of functionalized amines via reductive amination of carbonyl compounds with nitroarenes in the presence of Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) as a magnetically recoverable catalyst and molecular hydrogen as source of hydrogen at room temperature (Scheme 9).

**Scheme 9**

![Chemical Structure](image)

**Results and discussion**

**Optimization of the reaction conditions**

Current research was intended to use initial reactants, nitroarenes and alcohols, which are the precursors of amines and aldehydes, for the reductive amination reaction. For this purpose, reductive amination of benzyl alcohol with nitrobenzene was tested using Pd@Fe₃O₄-NH₂/Starch as catalyst in the presence of molecular hydrogen at room temperature. It was found that the reaction was sluggish, yield was very low (33%) and moreover, side products were also formed. Then, another possibility was tested for the synthesis of functionalized amines by the reductive amination of aldehydes with nitroarenes in the presence of molecular hydrogen at room temperature and pleasing results were obtained.

Primarily, reductive amination of benzaldehyde with nitrobenzene in the presence of Pd@Fe₃O₄-NH₂/Starch (0.1 g), molecular H₂ and ethanol at room temperature was tested to check the applicability of this method. Fascinatingly, N-benzylaniline was obtained in good yield (82%) in just 3.5 h. After that, we studied the effect of the different solvents
on reductive amination of benzaldehyde with nitrobenzene. Solvents such as CH$_2$Cl$_2$, H$_2$O and MeOH were tried, but low yields were obtained (entries 1-3, Table 1). However, when we tested the reaction with EtOH, quite satisfactory results were obtained i.e. 82% yield in 3.5 h (entry 4, Table 1). But the best results were obtained with organic/aqueous co-solvent system (EtOH:H$_2$O; 3:1) in terms of yield and time, which may be due to the synergetic effect of the co-solvent (entry 5, Table 1).

**Table 1.** Effect of solvents on the Pd@Fe$_3$O$_4$-NH$_2$/Starch catalyzed reductive amination using molecular hydrogen at room temperature$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CH$_2$Cl$_2$</td>
<td>6.5</td>
<td>52</td>
</tr>
<tr>
<td>2.</td>
<td>H$_2$O</td>
<td>5</td>
<td>69</td>
</tr>
<tr>
<td>3.</td>
<td>MeOH</td>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>4.</td>
<td>EtOH</td>
<td>3.5</td>
<td>82</td>
</tr>
<tr>
<td>5.</td>
<td>EtOH/ H$_2$O (3:1)</td>
<td>2</td>
<td>93</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: benzaldehyde (1 mmol), nitrobenzene (1 mmol), Pd@Fe$_3$O$_4$-NH$_2$/Starch (0.1 g, 2.36 mol% Pd), solvent (5 mL) under H$_2$ atmosphere at room temperature.

$^b$Column chromatography yields.

After optimization of the reaction conditions, we then studied the general applicability of this procedure for the synthesis of functionally diverse secondary amines and results are summarized in Table 2. As shown in Table 2, a variety of substituted aldehydes bearing either electron-donating or electron-withdrawing groups undergoes reduction smoothly under mild conditions. Different functional groups such as chloro, bromo, methyl and methoxy at para position in arylaldehyde were tolerated fairly well and afforded the desired products in good to excellent yields (entries 2-5, Table 2). Further, diversely substituted nitroarenes such as 4-chloronitrobenzene and 4-methylnitrobenzene were also successfully employed to gave the corresponding functionalized amines in good to excellent yields (entries 6-8, Table 2). In the case of ketones, cyclohexanone underwent
reductive amination successfully with nitrobenzene to give \( N \)-cyclohexylbenzenamine in 83% yield (entry 9, Table 2). The reaction of furfural with nitrobenzene also gave the desired secondary amine product with 85% yield (entry 10, Table 2). Thus, the presence of electron-withdrawing or electron donating substituents on the aromatic ring did not affect the course of the reaction. The reactions are clean and highly selective for the synthesis of secondary amines.

**Table 2.** Synthesis of functionalized amines from aldehydes and nitroarenes at room temperature using Pd@Fe\(_3\)O\(_4\)-NH\(_2\)/Starch\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Product 1" /></td>
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<td>2</td>
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<td>1.5</td>
<td>95</td>
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<td>4</td>
<td><img src="image4" alt="Product 4" /></td>
<td>1.2</td>
<td>93</td>
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<tr>
<td>5</td>
<td><img src="image5" alt="Product 5" /></td>
<td>1.3</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Product 6" /></td>
<td>2</td>
<td>91</td>
</tr>
</tbody>
</table>
Reactivity

The reusability of the synthesized catalyst for the reductive amination of carbonyl compounds was also checked by various experiments carried out in case of entry 2, Table 2 using Pd@Fe₃O₄-NH₂/Starch. After completion of the reaction, catalyst was separated via external magnet, washed with deionized water (2 × 15 mL) and chloroform (2 × 15 mL) to remove any physically adsorbed material and dried under vacuum. Then a fresh reaction was attempted with the used catalyst. A very small decrease in the activity of the reported catalyst was observed up to five runs (Fig. 2), and hence the catalyst could be used at least five times without any change in activity. It is pertinent to mention that amount of reactants after every run was adjusted according to the amount of catalyst recovered from the previous run.
Fig. 2 Recyclability graph of Pd@Fe₃O₄-NH₂/Starch. Reaction conditions: nitrobenzene (1 mmol), 4-chlorobenzaldehyde (1 mmol), Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd), EtOH:H₂O (3:1, 8 mL) using molecular hydrogen at room temperature.

Proposed mechanism

The reaction mechanism for the reductive amination of aldehydes with nitroarenes in the presence of Pd@Fe₃O₄-NH₂/Starch has been presented in Fig. 3. Firstly, nitrobenzene gets adsorbed on the surface of hydrogenated Pd(0) nanoparticles and forms nitrosobenzene intermediate II along with the generation of water molecule. Intermediate II formed insitu on reaction with another H₂ molecule forms intermediate III which on abstracting hydrogen molecule from hydrogenated Pd(0) NPs form amine IV. The insitu generated amine IV, on reaction with aldehyde gave imine V which on further hydrogenation from hydrogenated Pd(0) NPs (I) resulted in N-alkylamine VI as product, and Pd(0) NPs was regenerated back.
Fig. 3. Plausible mechanism for the Pd@Fe₃O₄-NH₂/Starch catalyzed reductive amination of aldehydes with nitroarenes.

Conclusion

We have developed an efficient, sustainable and magnetically separable catalyst, Pd@Fe₃O₄-NH₂/Starch for the reductive amination of carbonyl compounds. The synthesized catalyst showed excellent catalytic activity for the reductive amination of carbonyl compounds with nitroarenes. It has been observed that presence of different functional groups such as chloro, bromo, methyl and methoxy in arylaldehyde were tolerated fairly well and the desired products were obtained in good to excellent yields. This methodology is clean and highly selective for the synthesis of secondary amines in high yields. Moreover, the reported catalyst was magnetic in nature, avoids the tedious process of separation and was also recyclable up to five runs.
Experimental

General procedure for the Pd@Fe₃O₄-NH₂/Starch catalyzed reductive amination of aldehydes with nitroarenes

Aldehyde (1 mmol), nitroarene (1 mmol), Pd@Fe₃O₄-NH₂/Starch (0.1 g, 2.36 mol% Pd) and EtOH: H₂O (3:1, 8 mL) were added in a round bottom flask (25 mL), and the reaction mixture was stirred at room temperature under H₂ atmosphere (balloon) for the appropriate time. After completion of the reaction (monitored by TLC), the catalyst was separated via magnet and the supernatant was diluted with ethyl acetate and washed with brine solution, dried over anhyd. Na₂SO₄ and concentrated under reduced pressure. The desired product was obtained after passing the residue through column of silica gel and elution with EtOAc-pet. ether (2:98). The recovered catalyst was washed with chloroform (3 × 15 mL) followed by deionized water (3 × 15 mL), dried under vacuum and used for the subsequent reactions.

The structures of the products were confirmed by ¹H NMR, ¹³C NMR and mass spectral data, and comparison with authentic samples prepared according to the literature methods.
Spectral data of products listed in Table 2

**N-Benzylaniline (entry 1)**

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): δ 4.09 (bs, 1H, NH, exchangeable with D$_2$O), 4.38 (s, 2H, CH$_2$), 6.69-6.71 (d, 2H, J=8 Hz, ArH), 6.77-6.80 (t, 1H, J=8 Hz, ArH), 7.22-7.26 (t, 2H, J=8 Hz, ArH), 7.40-7.45 (m, 5H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 48.3, 113.1, 117.6, 127.5, 128.6, 129.3, 139.5, 148.2; MS (ESI): 183 (M$^+$), 91 (M-92).

**N-(4-Chlorobenzyl)aniline (entry 2)**

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): δ 4.34 (s, 2H, CH$_2$), 4.37 (bs, 1H, NH, exchangeable with D$_2$O), 6.64-6.66 (d, 2H, J=8 Hz, ArH), 6.75-6.87 (m, 1H, ArH), 7.19-7.23 (t, 2H, J=8 Hz, ArH), 7.29-7.34 (m, 4H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 47.7, 112.8, 117.9, 128.7, 129.3, 133.1, 137.9, 147.7; MS (ESI): 217 (M$^+$), 219 (M+2).

**N-(4-Bromobenzyl)aniline (entry 3)**

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): δ 4.35 (bs, 1H, NH, exchangeable with D$_2$O), 4.70 (s, 2H, CH$_2$), 7.23-7.30 (m, 3H, ArH), 7.41-7.45 (t, 2H, J=8 Hz, ArH), 7.63-7.65 (d, 2H, J=8 Hz, ArH), 7.79-7.81 (d, 2H, J=8 Hz, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 45.8, 121, 126.1, 129.3, 129.9, 132.4, 135.3, 151.5, 159.5; MS (ESI): 261.03 (M$^+$), 263.01 (M+2).
**N-(4-Methylbenzyl)aniline (entry 4)**

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.39 (s, 3H, CH$_3$), 3.79 (bs, 1H, NH, exchangeable with D$_2$O), 4.34 (s, 2H, CH$_2$), 6.57-6.59 (d, 2H, J=8 Hz, ArH), 6.78-6.80 (d, 2H, J=8 Hz, ArH), 7.03-7.17 (m, 5H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 26.7, 46.7, 115.7, 118.5, 128.4, 130.5, 133.5, 137, 140.7, 147.2; MS (ESI): 197 (M$^+$).

**N-(4-Methoxybenzyl)aniline (entry 5)**

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 3.84 (s, 3H, OCH$_3$), 4.38 (s, 2H, CH$_2$), 4.80 (bs, 1H, NH, exchangeable with D$_2$O), 6.58-6.60 (d, 2H, J=8 Hz, ArH), 6.92-6.94 (d, 2H, ArH), 7.27-7.29 (d, 3H, J=8 Hz, ArH), 8.10-8.12 (d, 2H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 29.7, 47.3, 54.6, 111.2, 114.4, 126.4, 128.9, 153.1, 159.8; MS (ESI): 213 (M$^+$).

**N-(4-Methoxybenzyl)-4-chloroaniline (entry 6)**

Solid, M.pt. 77-78 °C (Lit. M.pt. 78 °C). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 3.91 (s, 3H, OCH$_3$), 3.97 (bs, 1H, NH, exchangeable with D$_2$O), 4.64 (s, 2H, CH$_2$), 7.00-7.02 (d, 2H, J=8 Hz, ArH), 7.13-7.15 (d, 2H, J=8 Hz, ArH), 7.34-7.36 (d, 2H, J=8 Hz, ArH), 7.84-7.86 (d, 2H, J=8Hz, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 48.5, 54.2, 113.8, 115.3, 128.9, 129.5, 130, 134.7, 145, 159.5; MS (ESI): 247 (M$^+$), 249 (M+2).
**N-(4-Methylbenzyl)-4-chloroaniline (entry 7)**

![Chemical Structure](image1)

Solid, M.pt. 72-73 °C (Lit. M.pt. 71-73 °C)\(^{26}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 2.37 (s, 3H, CH\(_3\)), 4.05 (bs, 1H, NH, exchangeable with D\(_2\)O), 4.28 (s, 2H, CH\(_2\)), 6.56-6.58 (d, 2H, J=8 Hz, ArH), 7.12-7.14 (d, 2H, J=8 Hz, ArH), 7.17-7.19 (d, 2H, J=8 Hz, ArH), 7.25-7.29 (m, 2H, ArH); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 21.1, 48.1, 113.9, 122.2, 127.4, 129, 129.3, 135.8, 137, 146.9; MS (ESI): 231 (M-1), 233 (M+1).

**N-(4-Chlorobenzyl)-4-methylaniline (entry 8)**

![Chemical Structure](image2)

Solid, M.pt. 69-71 °C (Lit. M.pt. 70-72)\(^{26}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 2.34 (s, 3H, CH\(_3\)), 3.99 (bs, 1H, NH, exchangeable with D\(_2\)O), 4.02 (s, 2H, CH\(_2\)), 6.65-6.67 (d, 2H, J=8 Hz, ArH), 6.75-6.77 (d, 2H, J=8 Hz, ArH), 7.05-7.06 (d, 2H, J=8 Hz, ArH), 7.16-7.19 (t, 2H, J=8 Hz, ArH); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 23.5, 47.6, 111.9, 117.9, 125.6, 128.4, 131.4, 136.1, 146.5; MS (ESI): 232 (M\(^+\)), 234 (M+2).

**N-Cyclohexylbenzenamine (entry 9)**

![Chemical Structure](image3)

Solid, M.pt. 78-80 °C (Lit. M.pt. 79-81 °C)\(^2\). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 0.86-0.91 (m, CH\(_2\), 4H), 1.88-1.91 (m, 2H, CH\(_2\)), 2.35-2.39 (m, 4H, CH\(_2\)), 3.16-3.21 (m, 1H, CH\(_2\)), 3.52 (bs, 1H, NH, exchangeable with D\(_2\)O), 6.71-6.73 (d, 2H, J=8 Hz, ArH), 6.77-6.81 (t,
1H, ArH), 7.17-7.21 (t, 2H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 22.7, 25, 27, 29.7, 30.2, 31.4, 38.4, 42, 112.7, 115.1, 117.2, 118.5, 129.2, 129.3, 146.3; MS (ESI): 175 (M$^+$).

N-[(Furan-2-yl)methyl]benzenamine (entry 10)

Liquid. $^1$H NMR (CDCl$_3$, 400 MHz): δ 4.15 (bs, 1H, NH, exchangeable with D$_2$O), 4.25 (s, 2H, CH$_2$), 6.22-6.23 (m, 2H, ArH), 6.54-6.56 (d, 2H, J=8 Hz, ArH), 6.67-7.02 (m, 1H, furyl CH), 7.14-7.18 (m, 2H, furyl CH), 7.23-7.29 (m, 1H, ArH); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 37.8, 110.8, 112.3, 114.2, 118.2, 129.1, 141.6, 147.8, 151.8; MS (ESI): 173 (M$^+$).
REFERENCES


