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Keywords (separated by '-')	Hematite - Pd - Heterogeneous - Nitroarenes - Synergistic effect
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## Enhanced catalytic activity of natural hematite-supported ppm levels of Pd in nitroarenes reduction

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### Abstract

In this work, Pd NPs supported on amine-modified natural hematite have been prepared and characterized. Using this simple catalyst, nitroaromatic compounds as a major cause of industrial pollution were reduced to corresponding amines with ppm levels of Pd in the presence of designer surfactant TPGS-750-M and NaBH<sub>4</sub> at room temperature in aqueous media. Synergistic effect between hematite and Pd is responsible for the observed enhanced catalytic activity. This catalyst was recycled for at least four times with a small decrease in the activity.

**Keywords** Hematite · Pd · Heterogeneous · Nitroarenes · Synergistic effect

### Introduction

Iron is one of the naturally occurring abundant elements in the Earth's crust which is considered as important energy sources for biogeochemical and geochemical processes such as nitrogen fixation, oxygen delivery, and photosynthesis. On the other hand, sorption of toxic elements such as arsenic, antimony, and phosphorus on iron (oxy)hydroxides is vital as it offers a means of controlling the mobility, toxicity, and availability of these elements in natural environments [1–4]. Hematite, one of the most abundant natural minerals on Earth's surface, is mined as the main ore of iron in the Fe<sub>2</sub>O<sub>3</sub> form [5]. On the other side, the worldwide use of nitroaromatic compounds, known as major industrial pollutants, in

manufacturing explosives, pesticides, dyes, pharmaceuticals, and plastics gives rise to the huge discharge into the environment [6, 7]. One of the efficient methods for the removal of nitro compounds is the reduction of them to the corresponding amines, which are versatile precursors in organic synthesis as well as in the preparation of various compounds such as pharmaceuticals and agrochemicals [8–11]. In recent years, catalytic hydrogenation of nitroaromatic compounds employing different noble transition metals such as Pd [12–14] and Au [15–22] was investigated well. Moreover, cheap alternative metals such as Fe [23–32], Zn [33–38], and Sn [39, 40] have been widely used for reduction of nitro group. However, these reactions often require stoichiometric (or super stoichiometric) amounts of metals and/or harsh reaction conditions. Recently, a great deal of attention has been paid to use of bimetallic catalysts in different organic reactions. It is expected that synergistic electronic effect in bimetallic catalysts enhances their catalytic activity compared to the corresponding monometallic systems [41, 42]. In this way, using ppm levels of precious transition metals such as Pd in the presence of abundant metals and studying their synergistic effect in the reduction of nitroarenes are a key objective of sustainable chemistry [43, 44]. Lately, synergistic effects of Fe nanoparticles doped with ppm levels of Pd- or Pd/Ni-catalyzed reduction of aromatic nitro compounds were studied under homogeneous conditions at room temperature [45–47]. In this work, we endeavored to carry out further study into the reduction of nitroarenes, using hematite-supported Pd NPs as green heterogeneous

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56 catalyst under enhanced catalytic activity and recoverable  
57 conditions.

## 58 Experimental

### 59 Materials and methods

60 All materials were purchased from Sigma-Aldrich, Acros  
61 and Merck Millipore. Reactions were monitored by gas  
62 chromatography (GC) using Varian CP 3800 and thin-layer  
63 chromatography (TLC) using Merck silica gel 60F254 glass  
64 plate with 0.25 mm thickness. Hematite was purchased from  
65 Daneshmand chemical trading co (Iran). Column chroma-  
66 tography was carried out on silica gel 60 Merck (230–240  
67 mesh) in a 2-cm-diameter column.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR  
68 spectra were recorded at 400 MHz and 100 MHz, respec-  
69 tively, on a Bruker Avance HD apparatus in  $d_6$ -DMSO and  
70  $\text{CDCl}_3$ . Chemical shifts are given on the  $\delta$ -scale in ppm,  
71 and residual solvent peaks were used as internal stand-  
72 ards. X-ray diffraction (XRD) patterns were recorded using  
73 Philips X'Pert Pro instrument. The TEM and SEM images  
74 were captured with EOL JEM-2010 and JEOL JSM 840,  
75 respectively. FTIR study of samples was performed using  
76 FTIR spectrophotometer (Bruker vector 22 spectrophotom-  
77 eter, Germany) by preparing their KBr pellets from 400 to  
78  $4000\text{ cm}^{-1}$ . The weight loss of samples was measured using  
79 thermogravimetry (NETZSCH STA 409) under an  $\text{O}_2$  flow  
80 rate of  $20\text{ mL min}^{-1}$  with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$   
81 from 30 to  $800\text{ }^\circ\text{C}$ . Energy-dispersive X-ray analysis (EDX)  
82 results were obtained using Carl Zeiss Sigma instrument.

### 83 General procedure for catalytic reduction of nitro 84 compounds using hematite and ppm levels of Pd

85 Nitroarene (0.4 mmol),  $\text{NaBH}_4$  (1.6 mmol, 60.5 mg), hema-  
86 tite (100 mg), Pd (ppm levels in 1.65 mL) and  $\text{H}_2\text{O}/\text{THF}$   
87 (1.5:0.15 mL) were added to a 5-mL flask, and the reaction  
88 was stirred for appropriate reaction time at room tempera-  
89 ture. The progress of the reactions was monitored by GC  
90 analysis. After completion of the reaction, the crude prod-  
91 uct was extracted with ethyl acetate ( $3 \times 5\text{ mL}$ ) and purified  
92 using column or plate chromatography.

### 93 Procedure for the preparation of Hematite@ $\text{NH}_2$

94 To a 50-mL flask, hematite (2 g) and dry toluene (20 mL)  
95 were added and the mixture was sonicated for 10 min at  
96 room temperature. Then, (3-aminopropyl) triethoxysi-  
97 lane (10 mmol, 2.3 mL) was added slowly under an argon  
98 atmosphere and the resulting mixture was stirred at  $110\text{ }^\circ\text{C}$   
99 for 24 h. Afterward, the reaction mixture was cooled down  
100 to room temperature, the obtained solid was separated

with centrifugation and it was washed with ethyl acetate  
( $2 \times 15\text{ mL}$ ) and dried in the oven at  $80\text{ }^\circ\text{C}$ .

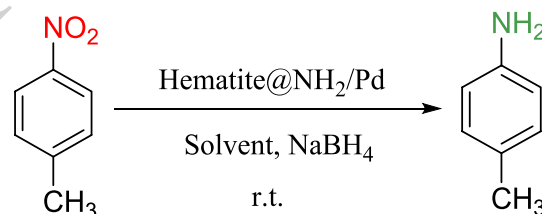
### Procedure for the preparation of Hematite@ $\text{NH}_2/\text{Pd}$

Hematite@ $\text{NH}_2$  (1 g) was sonicated in water (10 mL) for  
15 min. Then, a solution of  $\text{Pd}(\text{OAc})_2$  (0.0093 mmol, 2 mg)  
in 2 mL  $\text{H}_2\text{O}/\text{THF}$  (1:1) was added and then solution of  
 $\text{NaBH}_4$  (0.08 mmol, 3 mg) in  $\text{H}_2\text{O}$  (1 mL) was added slowly  
and the mixture was stirred for 24 h at room temperature  
under argon atmosphere. The resulting solid was separated  
with centrifugation, washed with water ( $3 \times 10\text{ mL}$ ) and eth-  
anol ( $3 \times 10\text{ mL}$ ) and dried in an oven at  $60\text{ }^\circ\text{C}$ . The loading  
of Pd on the obtained material was determined by atomic  
absorption spectroscopy (AAS) and inductively coupled  
plasma mass spectrometry (ICP) to be  $0.001\text{ mmol g}^{-1}$ .

### General procedure for the catalytic reduction of nitro compounds using Hematite@ $\text{NH}_2/\text{Pd}$ as the catalyst

To a 5-mL flask, nitroarene (0.4 mmol),  $\text{NaBH}_4$  (1.6 mmol,  
60.5 mg), Hematite@ $\text{NH}_2/\text{Pd}$  (100 mg, 0.01 mol% of Pd,

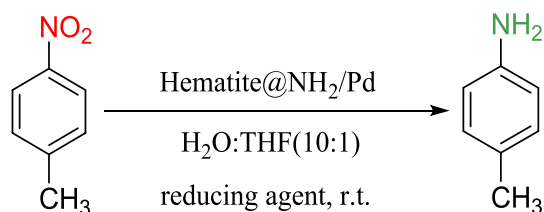
Table 1 Reduction of 4-nitrotoluene using Hematite@ $\text{NH}_2/\text{Pd}$  in dif-  
ferent solvents



Entry	Solvent	Yield (%) <sup>[a]</sup>
1	Ethyl acetate	76
2	1,4-Dioxane	5
3	$\text{H}_2\text{O}/\text{THF}$	97
4	PEG200	21
5	DMF	6
6	THF	5
7	Ethanol	71
8	Toluene	3
9	Acetone	67
10	DMSO	7
11	Dichloromethane	8
12	$\text{H}_2\text{O}/\text{Ethanol}$ (10:1)	65
13	$\text{H}_2\text{O}$	58

Reaction condition: nitroarene (0.4 mmol), Hematite@ $\text{NH}_2/\text{Pd}$  (100 mg, 0.01 mol% of Pd, 6 ppm in 1.65 mL solvent), solvent (1.65 mL),  $\text{NaBH}_4$  (4 eq) at room temperature

<sup>a</sup>GC yields, octadecane was used as an internal standard

**Table 2** Reduction of 4-nitrotoluene using Hematite@NH<sub>2</sub>/Pd in different reducing agents

Entry	Reductant	Time (h)	Yield (%) <sup>a</sup>
1	Ammonium formate	4	3
2	Formic acid	4	6
3	Isopropyl alcohol	4	2
4	Hydrazine	4	4
5	Glycerol	4	5
6	Sodium borohydride	1	97

Reaction conditions: 4-nitroarene (0.4 mmol), Hematite@NH<sub>2</sub>/Pd (100 mg, 0.01 mol% of Pd, 6 ppm in 1.65 mL solvent), H<sub>2</sub>O: THF (10:1, 1.65 mL), reducing (4 eq) at room temperature

<sup>a</sup>GC yields, octadecane was used as an internal standard

6 ppm in 1.65 mL solvent), and 2 wt% TPGS-750-M in H<sub>2</sub>O/THF (1.5:0.15 mL) were added and the reaction was stirred for an appropriate reaction time at room temperature. The progress of the reactions was monitored by GC or TLC. After completion of the reaction, the crude product was extracted by ethyl acetate (3 × 5 mL) and purified using column or plate chromatography.

### Typical procedure for the one-pot synthesis of acetaminophen

4-Nitrophenol (0.4 mmol), NaBH<sub>4</sub> (1.6 mmol, 60.5 mg), Hematite@NH<sub>2</sub>/Pd (100 mg 0.038 mol% of Pd, 25 ppm in 1.65 mL solvent), and 2 wt% TPGS-750-M in H<sub>2</sub>O/THF (1.5:0.15 mL) were added to a 5-mL flask and the reaction was stirred at room temperature. After 30 min, acetic anhydride (0.76 mmol, 0.08 mL) was added and the reaction was stirred at 120 °C for 1 h. Subsequently, the crude product was extracted with ethyl acetate (3 × 5 mL) and purified using column chromatography affording acetaminophen in 78% isolated yield.

## Results and discussion

In order to prepare hematite-supported Pd, we did different experiments to find approximate minimum amount of Pd in the catalyst. Initially, we studied reduction of 4-nitrotoluene in the presence of different amounts of hematite and ppm

levels of Pd. Results indicated that using 150 mg of hematite in the presence of 2 ppm Pd, 68% 4-aminotoluene was obtained (Table 1, ESI). By increasing Pd contents to 3 ppm and using 150 mg of hematite, 81% yield was achieved (Table 2, ESI). Using 4 ppm of Pd and 100 mg of hematite, 97% yield was also obtained during 1 h (Table 3, ESI). It should be noted that in the absence of hematite and using 2,3 and 4 ppm of Pd, reaction proceeded very slowly and low yields were obtained. Furthermore, the reaction gave very poor yields in the absence of Pd using different amounts of hematite (Table 4, ESI). Therefore, 4 ppm of Pd and 100 mg of hematite was found as optimum amounts for the reduction of 4-nitrotoluene. In the next step, we functionalized hematite with an amine group (Hematite@NH<sub>2</sub>), via reaction of hematite with (3-aminopropyl) triethoxysilane under reflux toluene (Scheme 1).

FTIR spectrum of Hematite@NH<sub>2</sub> showed the -CH<sub>2</sub> stretching and -CH<sub>2</sub> bending vibrations at 2897 cm<sup>-1</sup> and 1435–1473 cm<sup>-1</sup>, respectively. Bending vibrations of N-H in NH<sub>2</sub> group were also observed at 1532 cm<sup>-1</sup> (Fig. 1). FTIR spectrum of the Hematite@NH<sub>2</sub>/Pd is very similar to Hematite@NH<sub>2</sub>, and a low amount of Pd did not affect the structure [48–50] (Scheme 2).

The X-ray diffraction (XRD) spectrum of natural hematite was in agreement with the standard data given in its JCPDS card (33-0664) [51, 52] (Fig. 1). However, due to low concentration of Pd, related pattern of Pd was not observed in the XRD of Hematite@NH<sub>2</sub>/Pd. It should be noted that functionalization of hematite with amine group did not affect the hematite, and its structure was preserved (Fig. 2).

Thermogravimetric analysis (TGA) of Hematite@NH<sub>2</sub> was achieved in the temperature range 20 to 800 °C under air flow. The TG spectra showed a small weight loss between 20 and 160 °C, which could be related to the desorption of water and solvents. Furthermore, the samples displayed a major second weight loss of 5.23% at 300–800 °C, which was correlated to the presence of organic group of (3-aminopropyl) triethoxysilane with calculated loading of 0.9 mmol g<sup>-1</sup> (Fig. 3).

Hematite@NH<sub>2</sub> was then treated with Pd(OAc)<sub>2</sub> and NaBH<sub>4</sub> to afford Hematite@NH<sub>2</sub>/Pd with 0.001 mmol g<sup>-1</sup> Pd loading. It should be noted that due to very low level of Pd, it was hard to characterize Pd species of hematite-NH<sub>2</sub>@Pd. FTIR spectra of Hematite@NH<sub>2</sub> and Hematite@NH<sub>2</sub>/Pd were also recorded. Comparison of the Hematite@NH<sub>2</sub>/Pd and Hematite@NH<sub>2</sub> indicated the similar spectra that confirmed the structure of catalyst (Fig. 2). Scanning electron microscopy (SEM) images of Hematite@NH<sub>2</sub>/Pd showed the presence of uniform hematite sheets (Fig. 4). Moreover, transmission electron microscopy (TEM) images of Hematite@NH<sub>2</sub>/Pd showed clay sheets as well as small nanoparticles of Pd (Fig. 5).

195 Energy-dispersive X-ray spectroscopy (EDX) spectrum of  
196 the Hematite@NH<sub>2</sub>/Pd confirmed the presence of different  
197 elements such as Fe, Mg, Ni, Si, Cu, N, C, and O as well as  
198 Pd species (Fig. 6).

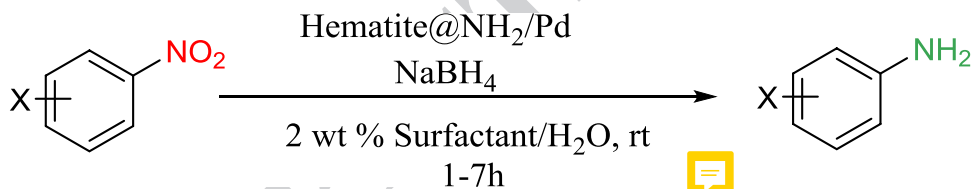
199 After characterization of Hematite@NH<sub>2</sub>/Pd, we investi-  
200 gated the effect of different solvents and reducing agents on  
201 the efficiency of Hematite@NH<sub>2</sub>/Pd (100 mg 0.01 mol% of  
202 Pd, 6 ppm in 1.65 mL solvent) in the reduction of 4-nitro-  
203 toluene as model reaction (Tables 1 and 2). For this purpose,  
204 the model reaction was studied in different solvents such as  
205 ethyl acetate, 1,4-dioxane, H<sub>2</sub>O/THF, PEG200, DMF, THF,  
206 toluene, EtOH, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, and H<sub>2</sub>O at room tempera-  
207 ture. Results indicated that 97% of the desired product was  
208 achieved in H<sub>2</sub>O/THF while lower yields were obtained  
209 in other solvents. Generally, these results indicate higher  
210 activity of catalyst in polar solvents compared to nonpolar  
211 solvents.

212 We also studied effect of other reducing agents such as  
213 ammonium formate, formic acid, isopropyl alcohol, hydra-  
214 zine, and glycerol on the reduction of 4-nitrotoluene. How-  
215 ever, results showed the formation of desired product in  
216 lower yields than using NaBH<sub>4</sub>.

217 We also investigated the effect of different types of sur-  
218 factants on the reduction of three different nitroarenes in  
219 the presence of Hematite@NH<sub>2</sub>/Pd. Results indicated higher  
220 efficiency of TPGS-750-M than span 80, SDS, and CTAB  
221 (Table 3).

222 Having optimized conditions in hand, we investigated the  
223 reduction reaction of variety of amines using 100 mg Hema-  
224 tite@NH<sub>2</sub>/Pd, NaBH<sub>4</sub> (4 eq), 1.5 mL H<sub>2</sub>O, 0.15 mL THF,  
225 and 2 wt% TPGS-750-M. Results of this study indicated  
226 that using Hematite@NH<sub>2</sub>/Pd as heterogeneous catalyst, a  
227 variety of nitro compounds were reduced to corresponding  
228 amines giving high-to-excellent yields at room temperature  
229 (Table 4). It is worth mentioning that in nitroarenes-con-  
230 taining carbonyl group, both carbonyl and nitro groups were  
231 reduced to alcohol and amine, respectively (Table 4, entries  
232 21–23, 26). Reduction of 2-nitropyridine as a heterocyclic  
233 nitro compound was proceeded well and afforded corre-  
234 sponding product in 91% yield (Table 4, entry 27). Reduc-  
235 tion of higher molecular weight and pharmaceutically active  
236 nitro compounds under optimized reaction conditions was  
237 proceeded slowly. Therefore, we prepared a catalyst with  
238 higher loading of Pd and used 100 mg (0.038 mol% of Pd,

**Table 3** The effect of different surfactants on the reduction of nitroarenes under optimized conditions



Surfactant

Surfactant	Time	Yield (%) <sup>a</sup>	Time (h)	Yield (%) <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
–						
SDS	1 h	67	7	64	3	61
Span 80	1 h	69	7	66	3	63
CTAB	1 h	65	7	57	3	59
TPGS-750-M	1 h	83	7	85	3	80
TPGS-750-M/THF <sup>c</sup>	50 min	97	6	90	2.5	91
H <sub>2</sub> O	1 h	58	7	53	3	50

Reaction condition: Hematite@NH<sub>2</sub>/Pd (100 mg, 0.01 mol% of Pd, 6 ppm in 1.65 mL solvent), nitroarene (0.4 mmol), 2 wt% surfactant/H<sub>2</sub>O (1.5 mL), NaBH<sub>4</sub> (1.6 mmol) at room temperature

<sup>a</sup>GC yields, octadecane was used as an internal standard

<sup>b</sup>Yields are isolated

<sup>c</sup>THF (0.15 mL)

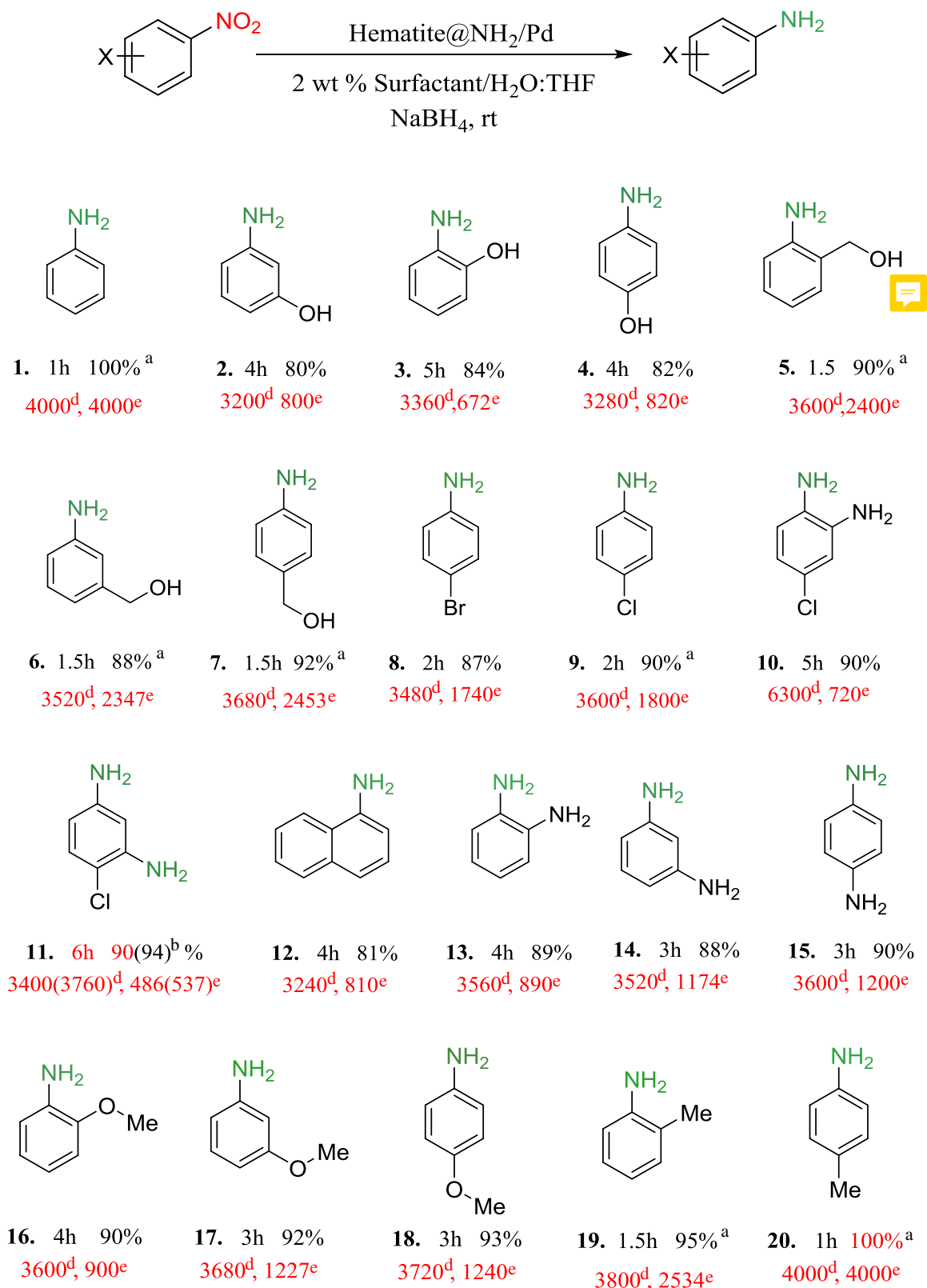
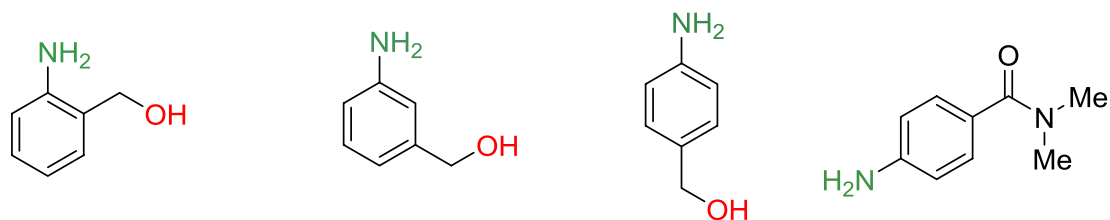
**Table 4** Reduction of structurally different nitroarenes using Hematite@NH<sub>2</sub>/Pd at room temperature



Table 4 (continued)

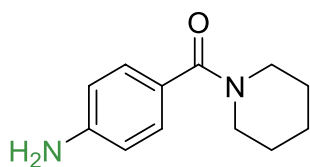


21. 5h 80(91)<sup>b</sup> %  
3200(3640)<sup>d</sup>, 640(728)<sup>e</sup>

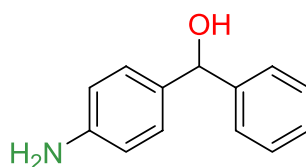
22. 5h 85(94)<sup>b</sup> %  
3400(3760)<sup>d</sup>, 680(752)<sup>e</sup>

23. 5h 87(95)<sup>b</sup> %  
3480(3800)<sup>d</sup>, 696(760)<sup>e</sup>

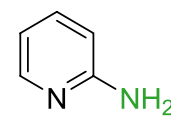
24. 3h 94%  
3760<sup>d</sup>, 1253<sup>e</sup>



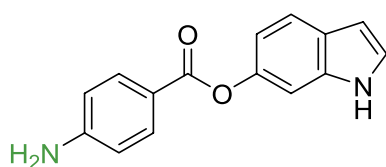
25. 3h 87%  
3480<sup>d</sup>, 1160<sup>e</sup>



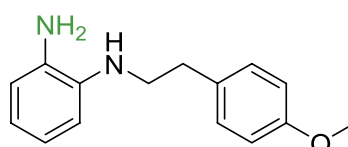
26. 5h 80(89)<sup>b</sup> %  
3200(3560)<sup>d</sup>, 640(712)<sup>e</sup>



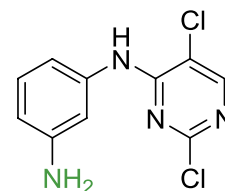
27. 3h 91%  
3640<sup>d</sup>, 1214<sup>e</sup>



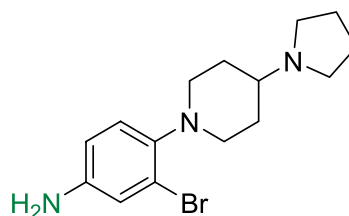
28. 20h 85%<sup>c</sup>  
2236<sup>d</sup>, 112<sup>e</sup>



29. 16h 80%<sup>c</sup>  
2105<sup>d</sup>, 132<sup>e</sup>



30. 23h 90%<sup>c</sup>  
2368<sup>d</sup>, 103<sup>e</sup>



31. 22h 81%<sup>c</sup>  
2132<sup>d</sup>, 97<sup>e</sup>

Reaction conditions:  $\text{TPGS-750-M}/\text{H}_2\text{O}/\text{Pd}@\text{NH}_2$  (100 mg, 0.01 mol% of Pd, 6 ppm in 1.65 mL solvent), nitroarene (0.4 mmol), 2 wt% TPGS-750-M/ $\text{H}_2\text{O}$  (1.5 mL) and THF (0.15 mL),  $\text{NaBH}_4$  (1.6 mmol) at room temperature

Yields are isolated

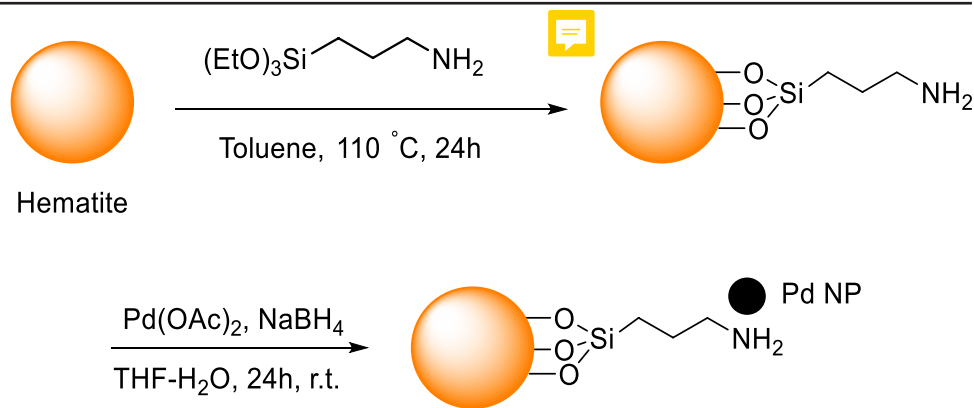
<sup>a</sup>Yields determined GC yields, octadecane was used as an internal standard

<sup>b</sup> $\text{NaBH}_4$  (3.2 mmol)

<sup>c</sup>Nitroarene (0.2 mmol),  $\text{NaBH}_4$  (0.8 mmol), catalyst (100 mg, 0.038 mol% of Pd, 25 ppm in 1.65 mL), 2 wt% TPGS-750-M/ $\text{H}_2\text{O}$  (1.2 mL) and THF (0.5 mL)

<sup>d</sup>[TON] values [(mol product/mol catalyst)]

<sup>e</sup>[TOF] values [(mol product/mol catalyst)/time of reaction (h)]

**Scheme 1** Preparation of Hematite@NH<sub>2</sub>

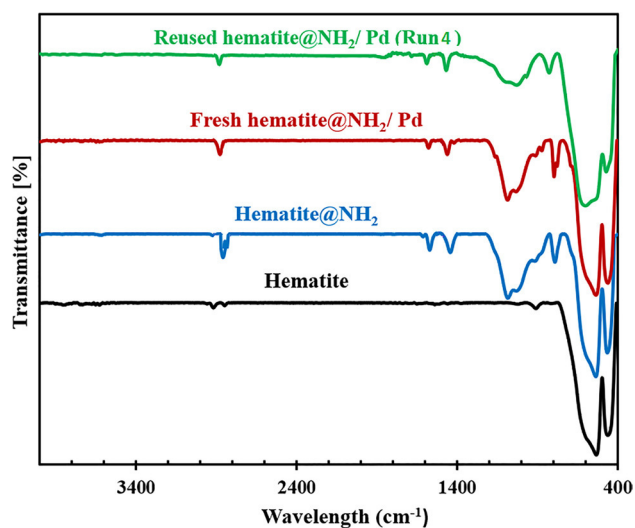
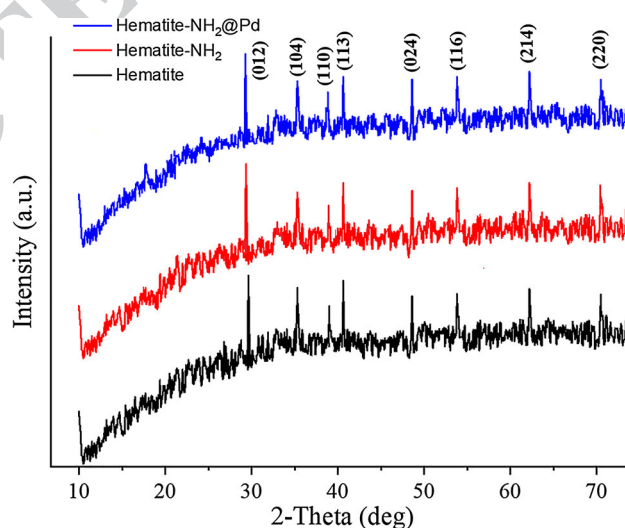
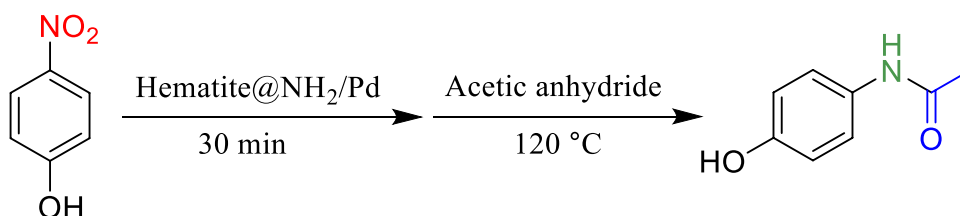
239 25 ppm in 1.65 mL) of this catalyst for the reduction. Under  
 240 this condition, reactions proceeded well, and corresponding  
 241 amines were produced in 80–90% isolated yields (Table 4,  
 242 entries 28–31).

243 Figure 1 ESI represents reduction of 5-chloro-2-nitroanilide (orange color) to 4-chloro-*o*-phenylenediamine (gray color) under optimized reaction condition.

246 As the reduction of nitrophenols was performed quan-  
 247 titatively, we carried out a one-pot reduction/amidation

248 sequence of 4-nitrophenol with acetic anhydride. As  
 249 depicted in Scheme 1, the one-pot conversion of 4-nitrophenol to acetaminophen adduct was performed efficiently  
 250 and afforded product in 78% isolated yield (Scheme 1, Fig. 2  
 251 ESI).

252 Recycling ability of the Hematite@NH<sub>2</sub>/Pd was studied  
 253 in the reduction of 4-nitrotoluene. Results indicated that the  
 254 catalyst was successfully recovered and reused for four conse-  
 255 cutive runs with a small decrease in the activity. Using  
 256

**Fig. 1** FTIR spectrum of Hematite, Hematite@NH<sub>2</sub>, fresh Hematite@NH<sub>2</sub>/Pd, and reused Hematite@NH<sub>2</sub>/Pd**Fig. 2** Compared XRD pattern of natural Hematite (black), Hematite@NH<sub>2</sub> (red), and Hematite@NH<sub>2</sub>/Pd (blue)**Scheme 2** One-pot preparation of acetaminophen

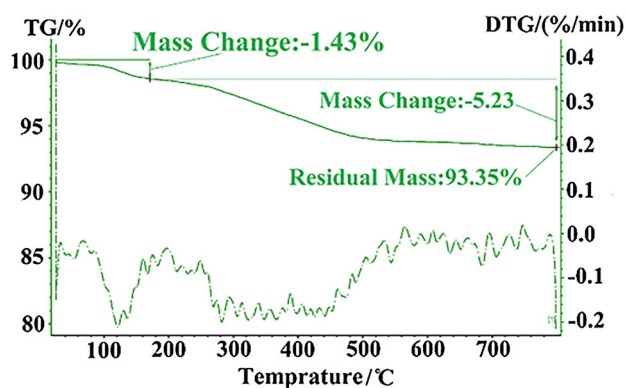


Fig. 3 Thermogravimetric analysis (TGA) of Hematite@NH<sub>2</sub>

257 ICP analysis leaching of Pd after the fourth run was studied  
 258 indicating 11% leaching of Pd species. However, in the fifth  
 259 run, the obtained yield was decreased to 71% (Fig. 7). TEM  
 260 images of the reused catalyst after five runs showed preser-  
 261 vation of the structure and very similar pattern to the fresh  
 262 catalyst (Fig. 8).

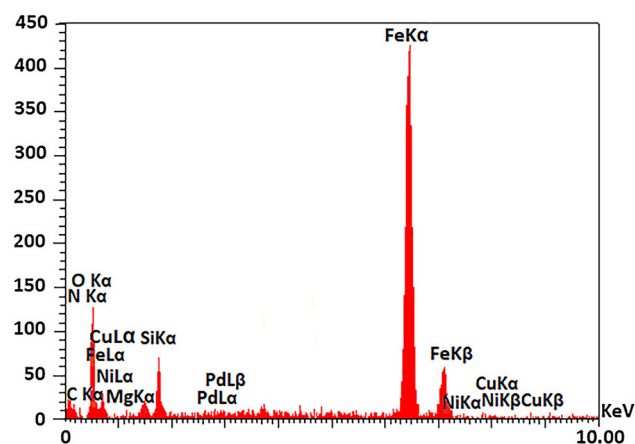


Fig. 6 EDS spectra of Hematite@NH<sub>2</sub>/Pd

263 Also, the structure of reused catalyst after four runs was  
 264 studied by FTIR and EDX analyses (Figs. 2 and 9). Results  
 265 showed that catalyst structure was preserved, and very simi-  
 266 lar patterns to fresh catalyst were obtained.

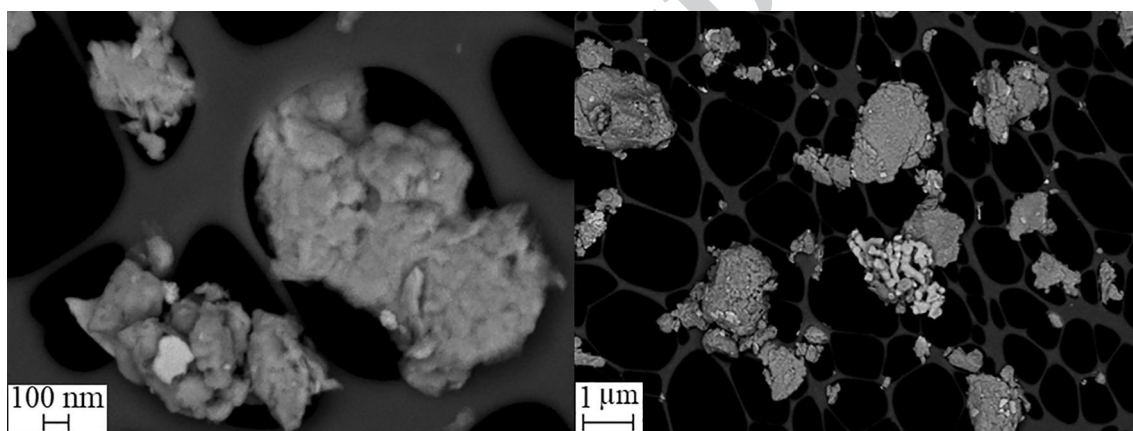
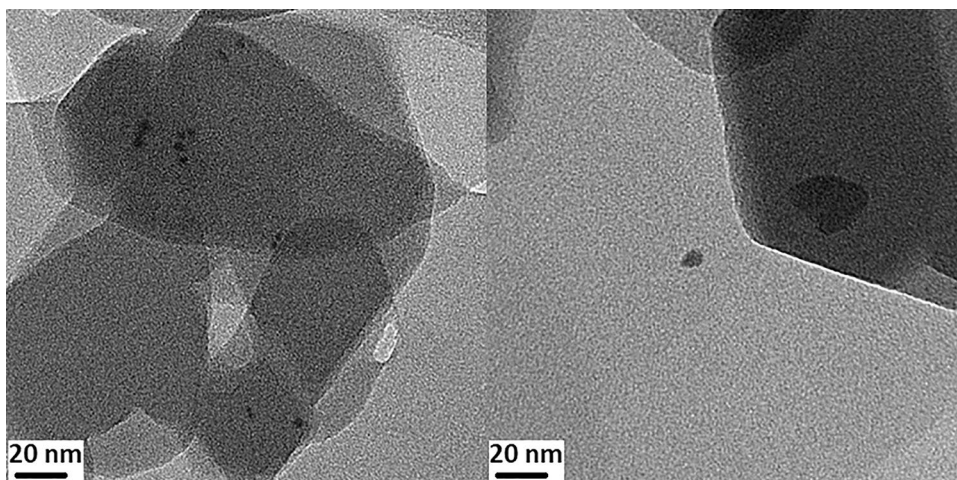


Fig. 4 SEM images of Hematite@NH<sub>2</sub>/Pd in different magnifications

Fig. 5 TEM images of Hema-  
 titite@NH<sub>2</sub>/Pd



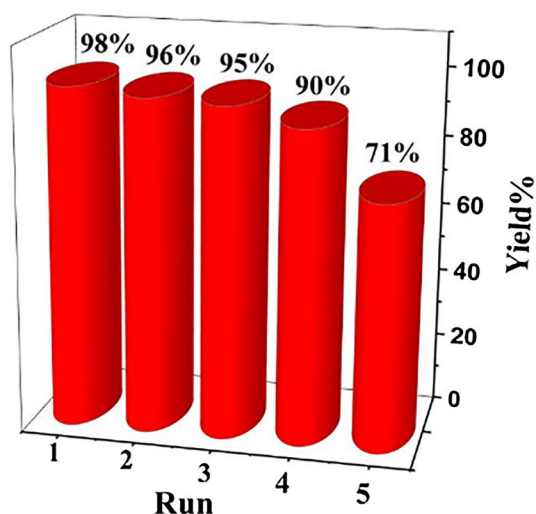


Fig. 7 Recycling of the catalyst (Hematite@NH<sub>2</sub>/Pd) for the reduction of 4-nitrotoluene

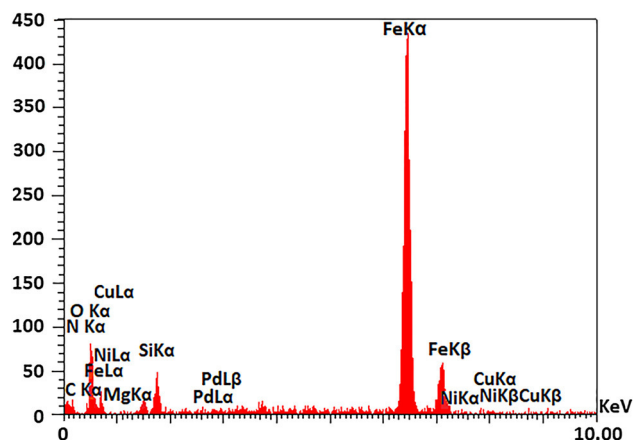


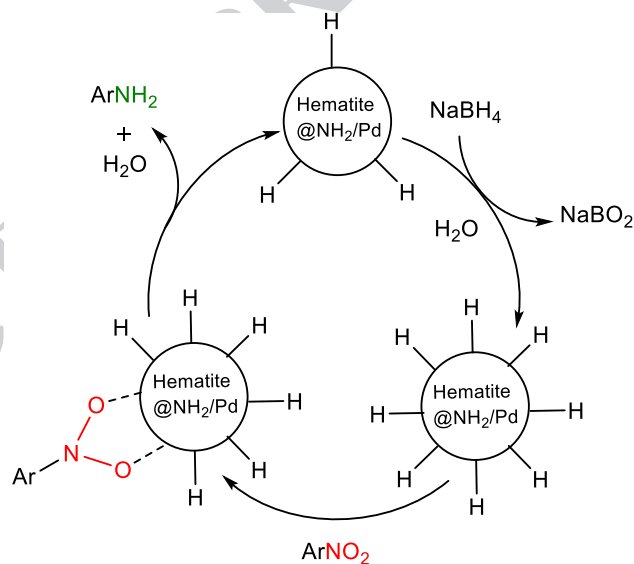
Fig. 9 EDS spectra of Hematite@NH<sub>2</sub>/Pd

267 According to the common analogies, the proposed mechanism for the reduction of nitroarenes is the same as the  
 268 known mechanism for the Pd-catalyzed nitroarenes reduction. Briefly, produced H<sub>2</sub> from the reaction of NaBH<sub>4</sub> and  
 269 H<sub>2</sub>O was absorbed on the catalyst; then, physically absorbed nitro group on the catalyst was reduced to corresponding  
 270 amine (Scheme 3) [53–55].  
 271  
 272

273  
 274 Comparison activity of Hematite@NH<sub>2</sub>/Pd with some palladium catalysts in the reduction of nitrobenzene confirmed higher TOF of the presented catalyst (Table 5).  
 275  
 276

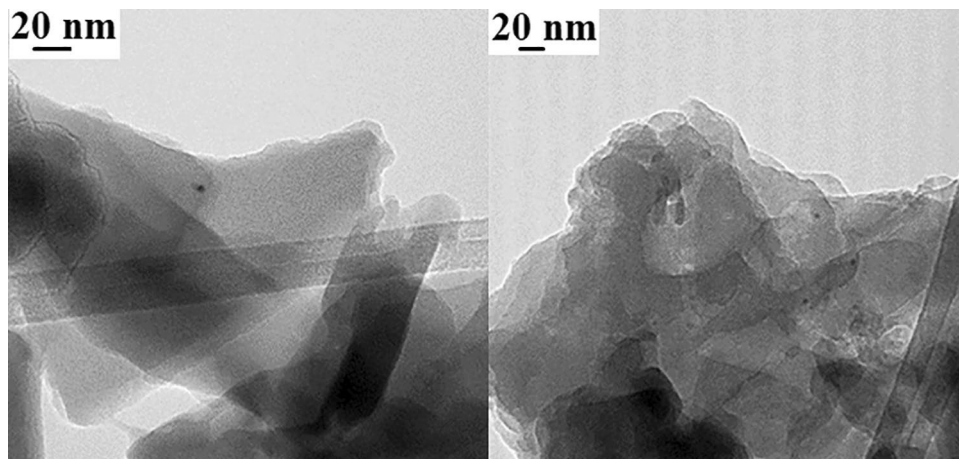
## 277 Conclusion

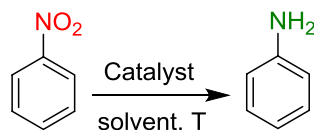
278 In conclusion, we used natural hematite for stabilization of ppm Pd NPs for the first time. Using this clay composite as a heterogeneous and recyclable catalyst, variety of  
 279  
 280



Scheme 3 Mechanism of the catalytic reduction of nitroarene with Hematite@NH<sub>2</sub>/Pd

Fig. 8 TEM images of reused catalyst after five runs



**Table 5** Comparison of the catalytic activity of Hematite@NH<sub>2</sub>/Pd NPs with that of other Pd catalysts in the nitro reduction reaction

Catalyst	T (°C), t (h)	Solvent	Yield (%)	TOF (h <sup>-1</sup> )
Pd cNPs/C@Fe <sub>3</sub> O <sub>4</sub> [56]	70, 1	EtOH	99>	270
Pd@CQD@Fe <sub>3</sub> O <sub>4</sub> [57]	r.t, 2	H <sub>2</sub> O:EtOH	96	<600
APSNP [58]	r.t, 2	EtOH	100	50
PdNP@PPh <sub>2</sub> -PEGPIILP [59]	25, 1.5	H <sub>2</sub> O	100	<142
NHC-Pd@GO [60]	r.t, 0.16	MeOH:H <sub>2</sub> O (1:1)	95	1604
Pd/CNS [61]	160, 0.16	H <sub>2</sub> O	100	38
PdNPs/4MePy [62]	180, 1	H <sub>2</sub> O:EtOH (1:30)	80	571
Fe <sub>3</sub> O <sub>4</sub> @sepiolite-Pd <sup>2+</sup> [63]	70, 0.83	EtOH:H <sub>2</sub> O (3:1)	82	1600
Pd(II)Pc [64]	100, 12	EtOH	98	8
Fe <sub>2</sub> O <sub>3</sub> @HAP-Pd [65]	60, 3	EtOH	100	6
Pd-pol [66]	r.t, 6	H <sub>2</sub> O	96	1000
Hematite@NH <sub>2</sub> /Pd	r.t, 1	H <sub>2</sub> O:THF (10:1)	100	4000

281 nitroarenes were reduced to corresponding amines at room  
 282 temperature. Synergetic effect between hematite and ppm  
 283 levels of Pd plays an important role in the reactivity of the  
 284 catalyst.

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