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Highly efficient and chemoselective transfer hydrogenation of nitroarenes at room temperature over magnetically separable Fe–Ni bimetallic nanoparticles†

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A highly chemoselective catalytic transfer hydrogenation (CTH) of nitroarenes to corresponding amino derivatives is achieved with Fe–Ni bimetallic nanoparticles (Fe–Ni NP's) as the catalyst and NaBH₄ at room temperature. Their catalytic efficiency is ascribed to the presence of Ni sites on the bimetallic surface that not only hinder the surface corrosion of the iron sites but also facilitate efficient electron flow from the catalyst surface to the adsorbed nitro compounds. This facet is corroborated with reusability studies as well as surface characterization of the catalyst before and after its repetitive usage. Thus, these nanoparticles efficiently catalyze the reduction of functionalized nitroarenes to corresponding amines without use of corrosive agents like base or other additives under ambient conditions and are easily separated by a laboratory magnet in an eco-friendly manner.

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1. Introduction

Selective catalytic hydrogenation of functional nitroarenes to anilines is an industrially important process for synthesis of agrochemicals, pharmaceuticals, dyestuffs, urethanes and other industrially important products.¹⁻³ Conventionally, this reduction is carried out with Fe/HCl that requires a stoichiometric excess of reagents which eventually produces a large amount of secondary waste and therefore, is not considered an environmentally benign process. RANEY® nickel is widely used as the catalyst but has two major disadvantages: moisture sensitivity and a pyrophoric nature. Pd/C is also known to catalyze this reaction but it is more expensive and also quite sensitive to trace impurities. Besides Pd, a number of other transition metal catalysts like Pt, Ru are also reported to be efficient for this transformation. However, these methodologies require a cumbersome experimental set up like an autoclave and the process is carried out under high temperature-pressure conditions in the presence of a catalyst and H₂ gas.^{4,5} Concomitantly, this conversion is also reported to occur at room temperature with H₂ gas with a variety of catalysts⁶ as well as for other types of reactions such as alkenes, alkynes, olefins, ketones and cyclohexene with 90-100% conversion.7-9

In order to overcome these lacunas, an alternative approach is adopted wherein various hydrogen donors like hydrazine, ammonium formate, IPA and NaBH₄ are used for liquid phase catalytic transfer hydrogenation (CTH) of functional aromatics. This approach is considered to be safe, cost-effective, selective and eco-friendly. Employing this strategy, a highly chemoselective reduction of aromatic nitro compounds to the corresponding amino derivatives is achieved by a combination of copper nanoparticles and ammonium formate¹⁰ in ethylene glycol at 120 °C. On the other hand, selectivity for a Rh nanocatalyst is demonstrated for the reduction of nitroarenes with hydrazine1 monohydrate at 60 °C while a similar potentiality is exhibited by Ru⁰-nanoparticles for the transfer hydrogenation of substituted nitrobenzenes in IPA with retention of its activity for several cycles.11 A facile, simple and environment friendly hydrogen-transfer reaction over recyclable ferrite-nickel magnetic nanoparticles (Fe3O4-Ni) using glycerol as the hydrogen source affords the synthesis of aromatic amines and alcohols from nitroarenes and carbonyl compounds.12 Furthermore, ionic liquid supported Ni nanofibers are found to be highly efficient for reduction of substituted nitroarenes with NaBH4 at room temperature with >90% conversion within 2 h.13 On the other hand, oxide based heterogeneous catalysts have also been explored for CTH. For example, CeO2 nanorods exhibited excellent catalytic behaviour with high conversion and selectivity for a variety of aromatic nitro compounds using N2H4.14 Reduction of nitro derivatives to amines using IPA as a hydrogen source and KOH as a promoter is reported for a nano-catalyst MgO-ZrO2.15 Solid supported nano- and microparticles of Pd successfully convert nitroarenes to amines with various hydrogen donors.16

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[†] Electronic supplementary information (ESI) available: TEM image of Fe–Ni NP's, catalyst amount optimization, GC-MS data of CTH reactions and catalyst activity table. See DOI: 10.1039/c3ra45787g

Paper

With increasing environmental concerns, much interest has been generated towards facile, sustainable and eco-friendly processes that include easily accessible raw materials, and simplicity in designing the catalysts that are efficient as well as inexpensive. To address this issue, we have selected iron based catalysts because of their low cost, nontoxicity and environmentally benign properties. The potentiality of iron based catalysts, either in bulk or nano-form, has been explored for reductive degradation of aquatic contaminants; however, their repeated use is restricted due to surface corrosion. By virtue of forming bimetallic species with other noble or non-noble metals, it is observed that such bimetallic systems remain active over longer periods due to the presence of other metal centers which eventually lead to increased catalytic efficiency and lifespan of iron based catalysts. Keeping this view in mind, we have synthesized Fe-Ni NP's and employed them for transfer hydrogenation of nitroarenes with NaBH₄ as the hydrogen source owing to its non-flammability, easily hydrolysable nature and controlled H₂ production rate.¹⁷

2. Experimental

2.1. Chemicals

The following analytical grade chemicals were purchased from Loba Chemie, UK and used as received: iron(II) sulphate (FeS- $O_4 \cdot 7H_2O$), nickel(II) sulphate (NiSO₄ $\cdot 6H_2O$), sodium borohydride (NaBH₄). Deionized water is used throughout the experiments. All glassware and Teflon-coated magnetic stir bars are cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 100 °C.

2.2. Synthesis of Fe-Ni NP's

Fe–Ni NP's are synthesized in accordance with the procedure reported earlier.¹⁸

2.3. Characterization of nanocomposite

X-ray powder diffraction (XRD) patterns are recorded on a Phillips X'pert MPD X-ray diffractometer using Cu-K α radiation. Transmission electron microscopic (TEM) images are obtained using a JEOL electron microscope (model 1200X) while X-ray photoelectron spectroscopy (XPS) analysis is carried out on a VG Micro Tech ESCA3000 instrument using Mg-K α radiation (photo energy 1253.6 eV). Brunauer–Emmett–Teller (BET) surface area analysis is performed using the nitrogen adsorption method with surface analyzer system CHEMBET3000, Quantichrome Instruments, US. Kinetics of the transfer hydrogenation are monitored with a UV-Vis spectrometer (Lamda 25, Perkin Elmer) while the product analysis is carried out with GC-MS (Clarus 500, Perkin Elmer).

2.4. Catalytic transfer hydrogenation

General method for the catalytic transfer hydrogenation of nitroarenes is as follows: in a 50 mL three neck round bottom flask, 1.6 mmoles of nitroarene is dissolved in 10 mL of methanol followed by addition of 0.16 mmoles of Fe–Ni NP's. The entire mixture is stirred at room temperature for 5 min and then 13 mmoles of NaBH₄ dissolved in 5 mL of methanol is added drop wise with constant stirring till addition of NaBH₄ is complete. The whole reaction mixture is further stirred for the desired period of time during which the progress of the reaction is monitored with TLC. After completion of the reaction, the catalyst is separated magnetically as well as by centrifugation (3000 rpm) and the separated reaction solution is subjected to GC-MS analysis. To investigate the reusability of Fe–Ni NP's, the magnetically separated catalyst is washed successively with acetone and vacuum-dried at room temperature before further catalytic cycles.

3. Results and discussion

3.1. Characterization of Fe-Ni NP's

The XRD pattern of the Fe–Ni NP's (Fig. 1a) exhibits characteristic peaks corresponding to Fe–Ni alloy with diffraction patterns in the range of 40–65° that are assigned to (111) and (200) crystal planes of fcc (JCPDS 47-1417) as well as bcc (JCPDS 37-0474) Fe–Ni alloy.¹⁹ Additionally, the XRD peak at 40° can be ascribed to face centred cubic (fcc) of Fe–Ni alloy, which is consistent with the standard card (JCPDS card no. 38-0419). The morphology of Fe–Ni NP's (ESI; Fig. S1†) is found to be a spherical shape (20–40 nm) with surface area of 14.2 m² g⁻¹.

3.2. Catalytic activity

It has been reported earlier that nitrobenzene is reduced by iron under anaerobic conditions to aniline in aqueous medium with nitrosobenzene as an intermediate product; however, a decreased reduction rate is attributed to the precipitation of siderite on the iron surface that inhibits further reduction processes.20 Although, hydrogenation of nitroarenes by nickel nanoparticles and hydrogen gas is \sim 100%, such an approach is of limited use as these reactions are carried out at elevated temperatures (100 °C) that results in oxidation of the nickel surface.21 Moreover, nickel nanoparticles with isopropanol are proved to be suitable for chemoselective hydrogenation of ketones at 76 °C, however, formation of nickel oxide film on the surface of the catalyst consequently hampers its catalytic activity.22 Considering these shortcomings, we have adopted a rational approach wherein the corrosion of Fe⁰ or Ni⁰ is controlled through the formation of the bimetallic state that offers synergism on the surface and subsequently may enhance the reduction capabilities of the individual metals. In the present work, Fe-Ni NP's are employed as a heterogeneous catalyst in transfer hydrogenation of some substituted nitrobenzenes to the corresponding anilines (Table 1). Although there are several reports on the transfer hydrogenation of nitroarenes, these reactions are carried out at elevated temperatures as well as requiring higher reaction times either with noble or non-noble metals as heterogeneous catalysts.^{1,10} However, we have adopted a simple, facile and affordable route wherein Fe⁰ acts as an electron donor while Ni serves the purpose of electron shuttle thereby forming a galvanic cell on the bimetallic surface. Such a feature of the Fe-Ni bimetallic system has



already been established for reductive degradation of organic and inorganic contaminants.^{18,23}

To optimise the amount of Fe-Ni NP's required for CTH with NaBH₄, the nitrobenzene reaction is carried out at different catalyst loadings (ESI; Fig. S2[†]). It is observed that conversion is almost complete with 10 mol% which, therefore, is kept constant throughout the investigation. Table 1 illustrates the transfer hydrogenation of nitroarenes in the presence of Fe-Ni NP's carried out at room temperature with NaBH₄ as the hydrogen source. It can be seen from this table that nitrobenzene (entry 1) is completely converted to aniline ($\sim 100\%$) within 0.5 h with 100% selectivity (ESI; Fig. S3[†]). Interestingly, when either Fe⁰ or Ni⁰ nanoparticles are used for nitrobenzene reduction under identical conditions, only 50% conversion is observed with the former while reaction does not proceed using the latter catalyst (ESI Table T1[†]). To further access the rate of conversion, we have also established the kinetics of the hydrogenation of nitrobenzene catalyzed by Fe-Ni NP's in the presence of NaBH₄ (Fig. 2a). It can be seen from this figure that reduction of nitrobenzene proceeds initially with a rapid decrease of reactant concentration up to about 97% but later on it follows almost first order reaction kinetics suggesting that the reaction is almost complete within 35 min. These findings clearly suggest that the catalytic activity is indeed due to both Fe and Ni nanoparticles in a bimetallic phase through synergistic effects on the catalytic surface.

The conversion of nitroarenes to corresponding amines is completed within a short span of time (0.5–6 h) with almost 98% conversion and about 95% selectivity. The lower selectivities of entries 2 and 3 are probably due to the presence of bulky methyl while *m*-dinitrobenzene (entry 6) is converted to the mono-amine with low yield (80%) and lower selectivity (Table 1). The latter conversion may be attributed to the strong desorption tendency of the formed basic *m*-nitroaniline on the negatively charged catalytic surface. On the other hand, selectivity for nitro-reduction is found to be ~100% with almost 99% conversion for entries 7–9 implying that the catalyst possesses high selectivity towards the nitro-function. A similar facet is also observed for entry 10 where the double bond is selectively reduced and not the ester function. The plausible reason for such a facile conversion stems from the fact that the formation of metal hydride on the catalytic surface is facilitated by expulsion of hydrogen generated by borohydride in the reaction medium. Concurrently, the adsorption of nitroarene on the Fe-Ni NP's surface and simultaneous removal of a water molecule lead to formation of the nitroso compound, which subsequently combines with another molecule of hydrogen giving rise to hydroxylamine. Finally, hydroxylamine is reduced to the amine derivative in a slow reaction step with water as a byproduct (Scheme 1). It is also worth mentioning here that the turnover frequency (TOF) is 13 times higher for Fe-Ni NP's as compared to Pt-Ni bimetallic nanoparticles²⁴ used for the transfer hydrogenation of nitroarenes under identical conditions. Thus, such a faster reduction process and considerably higher TOF is probably due to the efficient flow of electrons from Fe⁰ to the adjacent Ni⁰ site on the catalytic surface as well as the synergistic effect of both Fe-Ni and NaBH4 in tandem that plausibly enhances the liquid phase reduction process at room temperature.

3.3. Reusability studies

The efficiency of Fe-Ni NP's is further evaluated for repeated use without sacrificing the catalytic activity. For this purpose, transfer hydrogenation of nitrobenzene is carried out with recovered catalyst under identical experimental conditions. These results (Fig. 3) suggest that the catalyst remains highly active up to six cycles with >99% conversion for every cycle. Moreover, the reaction rate remains almost constant for the 1st cycle $(2.31 \times 10^{-3} \text{ s}^{-1})$ up to the 6th cycle $(2.25 \times 10^{-3} \text{ s}^{-1})$. Such a behavior can be explained on the basis of several aspects: (i) methanol (solvent) induces faster methanolysis of NaBH₄ leading to rapid evolution of hydrogen²⁵ that maintains nanoparticles well dispersed/suspended throughout the reduction, (ii) a small amount of liberated H₂ expels air from the solution thereby preventing the surface corrosion of the catalyst, (iii) some amount of the liberated hydrogen also helps in retaining the zero valent state of the nanoparticles,

Table 1 Catalytic transfer hydrogenation of nitroarenes to corresponding anilines

		$Ar - NO_2 -$	$Fe-Ni(10 \text{ Mol\%}) \rightarrow Ar - NH_2$ $NaBH_4 / MeOH, R.T$			
Entry	Substrate	Product	Time	% Conversion	% Selectivity	$\mathrm{TOF}^{a} imes 10^{-4} \mathrm{(s^{-1})}$
1	NO ₂	NH ₂	35 min	99.52	100	47.62
2	NO ₂	NH ₂	4 h	88.02	92	6.94
3	NO ₂	NH ₂	5 h	90.17	94	5.56
4		NH ₂	5 h	95.57	98	5.56
5			3 h	99.37	100	9.26
6	NO ₂ NO ₂	NH ₂	6 h	80.26	95	4.63
7		NH ₂	6 h	99.79	100	4.63
8	NO ₂ Br	NH ₂	4 h	98.85	100	6.94
9		NH ₂	1 h	99.57	100	2.78
10	° C	C C	1.2 h	99.27	100	2.31
^{<i>a</i>} TOF = 7	TON/reaction time.					

(iv) formation of NaB(OCH₃)₄ during the methanolysis of NaBH₄ facilitates continuous evolution of hydrogen and (v) sodium methoxide formed during the transfer hydrogenation

reacts with $NaBH_4$ which further enhances hydrogen generation. Moreover, to ascertain that the rate of conversion is not affected by successive usage of Fe–Ni NP's, we have



Fig. 2 Time profile of nitrobenzene reduction for (a) fresh and (b) recovered Fe–Ni NP's. Inset shows magnetic separation of catalyst after completion of the reaction.



Scheme 1 Proposed mechanism for CTH of nitroarenes by Fe–Ni NP's.

established the kinetics of the hydrogenation of nitrobenzene catalyzed by recovered catalyst (Fig. 2b). It is interesting to note that catalytic activity remains almost the same even after the 6th cycle which suggests that its surface is not passivated even after exposure to several chemical treatments. Thus, all these factors contribute towards prevention of surface corrosion of the nanoparticle surface that consequently enhances its catalytic life. Such a feature has already been observed in the degradation of a dye by Fe–Ni NP's stored for 1 year; an orange G wherein it is observed that the reduction capacity is retained even after exposure to light and moisture.²⁶ Hence, it can be argued that this bimetallic system is also efficient towards transfer hydrogenation of



Fig. 3 Reusability of Fe-Ni NP's for chemoselective reduction of nitrobenzene.

nitroarenes with high selectivity under simple laboratory conditions.

These facts are further corroborated by the evaluation of the catalyst surface properties of Fe-Ni NP's before and after the transfer hydrogenation reduction of nitrobenzene. Techniques employed for this assessment include (i) XRD that assists in differentiating crystalline phases of Fe-Ni NP's and (ii) surface analysis by XPS which identifies the nature of the chemical species present on the surface of the Fe-Ni NP's before and after CTH. XRD analysis of these nanoparticles after the 6th cycle (Fig. 1b) indicates that there is no appreciable change in the pattern although the intensities of peaks are somewhat reduced. It is probably due to the successive exposure of these planes to the chemical environment that may lead to slight disturbances in the lattice structure. On the other hand, XPS analysis of nanoparticles after the last cycle was carried out for the iron and oxygen regions (Fig. 4) to examine the extent of surface corrosion that occurred on the nanoparticle surface. It can be seen that the nature and peak positions at 710, 712.4 and 715.3 eV for the iron region (Fig. 4a) remain almost identical with a slight change in their intensity pattern. Surprisingly, the amount of Fe(II) formed on the surface has increased by about 7% after the 6th cycle implying that some part of the liberated hydrogen from NaBH₄ has also been utilized for the reduction of surface Fe(III) species. Such a surface phenomenon observed for Fe-Ni NP's, therefore, suggests that the surface corrosion is appreciably inhibited due to the presence of a reducing atmosphere during the entire course of the reaction. Moreover, these characteristics are also reflected in the oxygen region where the peaks at 530, 531.4 and 532.6 eV remain unchanged (Fig. 4b) even after the successive use of Fe-Ni NP's without much alteration in their intensities. Thus, it may be argued that almost 99% conversion of nitrobenzene to aniline with 100% selectivity is predominantly due to the existence of an anaerobic environment throughout six cycles and this approach may be regarded as a necessary feature for sustainable development in



the field of catalytic transfer hydrogenation of organics without sacrificing the catalytic efficiency.

rates and significantly enhance the catalytic activity of Fe–Ni NP's.

3.4. Proposed mechanism

It is well known that metallic particles, either monometallic or multimetallic, being electronically conducting solids, strongly catalyze redox reactions. The proposed mechanism for the reduction of nitroarenes by borohydride in the presence of Fe-Ni NP's is illustrated in Scheme 1. The catalytic hydrogenation promoted by a H-donor proceeds on the surface of the metal nanoparticles. The generation of H₂ on the catalyst surface is due to efficient methanolysis of sodium borohydride²⁵ forming metal hydrides followed by intermolecular hydrogen transfer from the nanoparticle surface to adsorbed nitroarenes on the catalyst surface. Subsequently, loss of a water molecule leads to the formation of the nitroso compound, which being highly reactive, combines with another molecule of hydrogen giving rise to stable hydroxylamine. Since the conversion of hydroxylamine to aniline through dehydroxylation is the slower and rate determining step,³ variation in the conversion time is noted from 0.5-6 h for different nitroarenes. Water being the byproduct of CTH, it is possible that the iron surface may become corroded due to adsorbed water. However, in our case, the corrosion of the iron site is inhibited due to the presence of adjacent nickel sites as well as the anaerobic environment that prevents its surface passivation. The Ni sites also promote efficient flow of electrons and subsequently increase reduction

4. Conclusions

The present investigation clearly demonstrates that nanoengineered Fe-Ni NP's indeed exhibit promising catalytic activity for transfer hydrogenation of nitroarenes under ambient conditions with almost 99% conversion having 100% selectivity. Since the iron surface is susceptible to corrosion, it may be argued that such high efficiency of the catalyst may be ascribed to synergism in Fe-Ni NP's that not only controls the iron passivation but also facilitates efficient flow of electron transfer from iron (donor) to nitroarenes (acceptor) mediated by Ni site that acts as an electron shuttle between donor and acceptor. This facet is further exemplified by their reusability potential where the catalyst surface remains active up to six cycles. To corroborate this aspect, XRD analysis of fresh and used catalysts suggests that the lattice structure remains almost the same even after repeated use. Moreover, surface properties are also not altered during the recycling process implying that the iron-corrosion process is effectively hindered due to adjacent Ni sites. It is also quite likely that some of the liberated H₂ during CTH may be consumed by the catalyst to retain its activity. This catalytic system not only efficiently catalyzes the reduction of functionalized nitroarenes to the corresponding substituted anilines but also avoids the need for an inert

atmosphere, and additional base or other additives. Thus, Fe-Ni NP's employed in the present investigation not only possess excellent catalytic activity with very high chemo-selectivity towards selective reduction of nitroarenes but they also can be magnetically separated from the reaction medium.

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