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Regio- and Chemoselective Reduction of Nitroarenes and Carbonyl Compounds over Recyclable Magnetic Ferrite−Nickel Nanoparticles (Fe_3O_4−Ni) by Using Glycerol as a Hydrogen Source

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Functionalized magnetic nanoparticles (MNPs) have emerged as viable alternatives to conventional materials, not just for heterogeneous,[1] but also for homogenous catalysis[2] because they offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration. A variety of catalytic systems involving metal-supported MNPs have been devised and used in synthetic organic reactions.[3] For example, immobilized palladium complexes with N-heterocyclic carbene ligands (NHC-Pd complexes) on the surface of ferrite-MNPs were used for palladium cross-coupling reactions.[2d] A more demanding protocol for the preparation of palladium nanoparticles supported on phosphate-functionalized MNPs was reported by Yinghuai and co-workers with success on Suzuki- and Heck coupling reactions.[4] Xia et al., used a magnetically separable Pd/Fe_3O_4 catalyst for a carbonylative Sonogashira coupling reaction.[5] Free nano-γ-Fe_2O_3 have been shown to be active, stable, and highly selective catalysts for various oxidations with high turnover number (TON) and excellent selectivity.[3c,6a,b] Reduction of organic substrates such as nitro, azido, and carbonyl compounds is of the utmost importance in organic synthesis.[6c] This is a fundamental process with a variety of applications in pharmaceutical industries and in the synthesis of biologically significant compounds.[6d] There have been a number of reports on hydrogenation reactions using noble metal catalysts,[7] however these catalysts present as a major drawback its high cost. Recently remarkable economic non-toxic and effective iron nanoparticles catalysts were reported for specific reduction.[8] Recently, glycerol has gained increasing attention as an alternative sustainable solvent for catalytic and non-catalytic organic transformations[9] because of its unique combination of physical and chemical properties, such as polarity, low toxicity, high boiling point, and biodegradability.[10] Very recently, glycerol has also been used in transfer hydrogenation reactions.[11] The reduction of nitro as well as carbonyl compounds[12] with hydrogen-transfer reagents is a much safer and more benign process than reactions involving molecular hydrogen, metal hydrides, or soluble metals. Varma and Manorama already addressed this issue by using palladium or nickel on dopamine-terminated surface of Fe_3O_4 for hydrogenation reactions.[3f,13] The complexes of the second- or third-row transition metals, such as Rh,[14] Ru,[15] Ir,[16] and Pt[17] are among the most efficient catalysts devised. Much less attention has been devoted to the hydrogen-transfer reduction of carbonyl compounds using inexpensive metals. In continuation of our efforts to develop protocols for green raw materials[18] and heterogeneous catalysis for hydrogen-transfer reactions and nano-catalysis,[19] we propose to use glycerol as hydrogen donor as well as solvent in the reduction of nitro and carbonyl compounds using a new, efficient, recyclable, and inexpensive ferrite-nickel magnetic-nanoparticles (Fe_3O_4-Ni MNPs). This protocol avoids multistep processes and linkers[20] between the metal and ferrites rendering the present protocol cost-effective.

Fe_3O_4-Ni MNPs were prepared by the simple wet impregnation method followed by chemical reduction[5,19g,h,21] (Scheme 1) and characterized by X-ray diffraction (XRD), inductive coupled plasma-atomic emission spectroscopy

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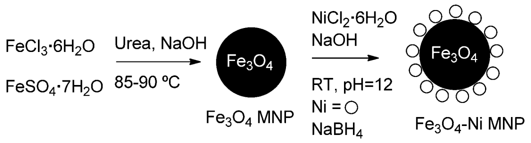


Scheme 1. Synthesis of Ferrite (Fe_3O_4) and Fe_3O_4–Ni MNPs.

(ICP-AES), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), field-emission gun scanning electron microscope and electron dispersive spectrometry (FEG-SEM-EDS).

The crystallite size of the Fe_3O_4-Ni MNPs (determined by the Debye Scherrer equation) was found to be 16 nm, which is in agreement with the result obtained from the TEM. Although signals of Ni were not detected in the XRD spectrum of Fe_3O_4-Ni, the weight percentage of Ni was determined to be 9.92 % by ICP-AES analysis. FEG-SEM and EDS analysis also confirm the ratio 10:90 (Ni/ferrite). The TEM images of Fe_3O_4–Ni shows uniform-sized magnetic nanoparticles and showing somewhat spherical morphology with an average size range of 15–30 nm (Figure 1). The presence of Ni on the surface of ferrite was confirmed with time of flight secondary ion mass spectrometry (TOF-SIMS), which is the most surface sensitive (<1 nm) and widely used technique for surface characterization. We used VG TOF-SIMS[22] instrument in static mode with primary ions (Ga^+) beam at impact energy of 10 keV. The positive ions spectrum of intact surface in the m/z range 0–100 is shown in Figure 2a, with diagnostic ions of ferrite observed at $m/z=$ 56, 57, and 73 corresponding to $^{56}Fe^+$, $^{56}FeH^+$, and $^{56}FeOH^+$, respectively (Figure 2). We also observed the positive ions at $m/z=58$ and 60, corresponding to the two main isotopes of nickel, which indicate the presence of nickel at the surface of ferrite structure. This fact was also confirmed by pre-sputtering the sample with primary ion beam in DC mode followed by analysis in pulse mode, the spectrum is shown in Figure 2b. Notably, the spectrum is dominated by $^{56}Fe^+$, and there is relatively weak intensity of $^{58}Ni^+$ indicating that, its presence was limited to the surface of ferrite which was sputtered out in pre-sputtering process before the spectrum was acquired.

The surface composition of the powder was determined from the characteristic XPS peak intensities of Ni, Fe, O and C, that is, Ni 2p, Fe $2p_{3/2}$, O 1 s and C 1 s, respectively. Oxygen appears to be the most abundant element in the powder (49 %) followed by carbon (33 %), nickel (11 %), and iron (7 %). The characteristic peak of nickel (Ni 2p) is presented in Figure 3. The main contributions of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks are at 854.2 and 872.5 eV, respectively. From the peak position and its asymmetry (in the case of Ni $2p_{3/2}$), as well as the position and the intensity of the shake-up satellites, we undoubtedly conclude that nickel is present as NiO.[23] The Fe_3O_4-Ni MNPs were explored as catalysts in the reduction of aromatic nitro compounds (**1**) using glycerol as the solvent and hydrogen donor (Scheme 2, Table 1).

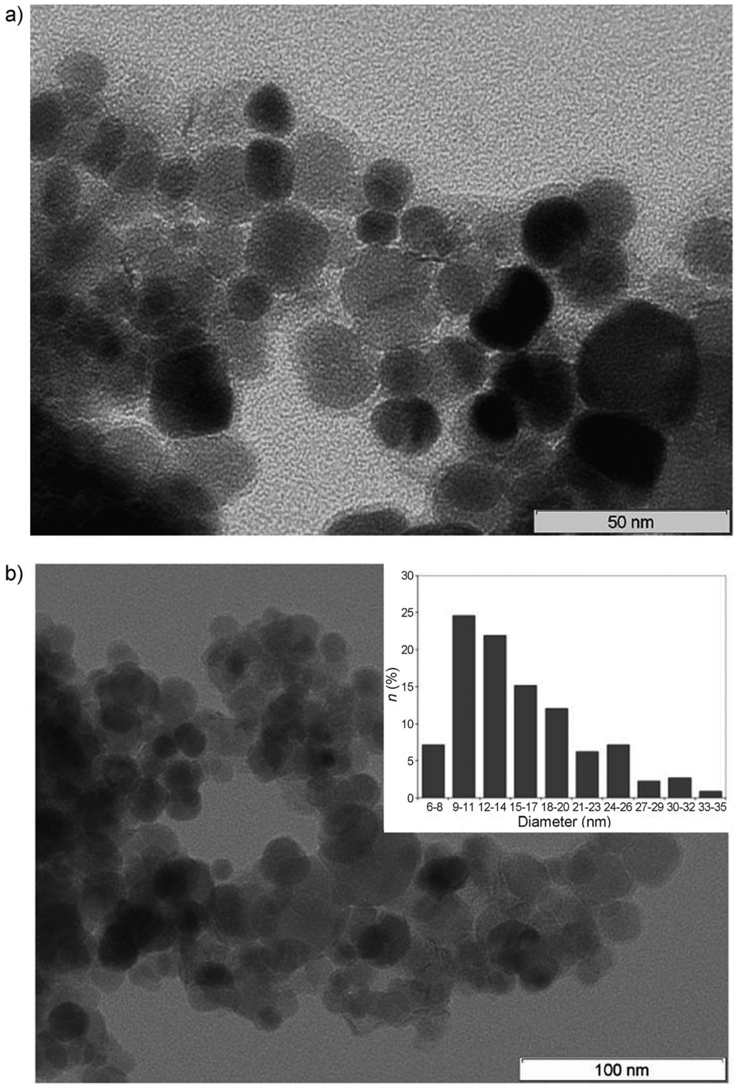
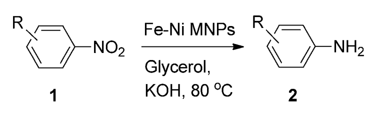


Figure 1. TEM images of Fe_3O_4–Ni MNPs at different magnifications a) 50nm; b) 100nm showing particle size distribution; the corresponding histogram is superimposed onto image (b) (see the Supporting Information).



Scheme 2. Fe_3O_4-Ni-catalyzed reduction of nitro arenes.

The catalytic performance of Fe_3O_4–Ni MNPs was initially tested for the reduction of 4-methoxy nitrobenzene allowing 4-methoxyaniline (**2e**) to be obtained in excellent yield (94 %). After optimization of the reaction conditions (see the Supporting Information), the catalytic activity of Fe_3O_4-Ni MNPs with other nitro substrates was further explored (Table 1). Probably due to steric constraint, the catalytic performance of Fe_3O_4–Ni MNPs was slightly decreased with *ortho*-substituted nitro compounds but not significantly (Table 1, entries 2 vs. 5, and 3 vs. 12) Interestingly, electron-

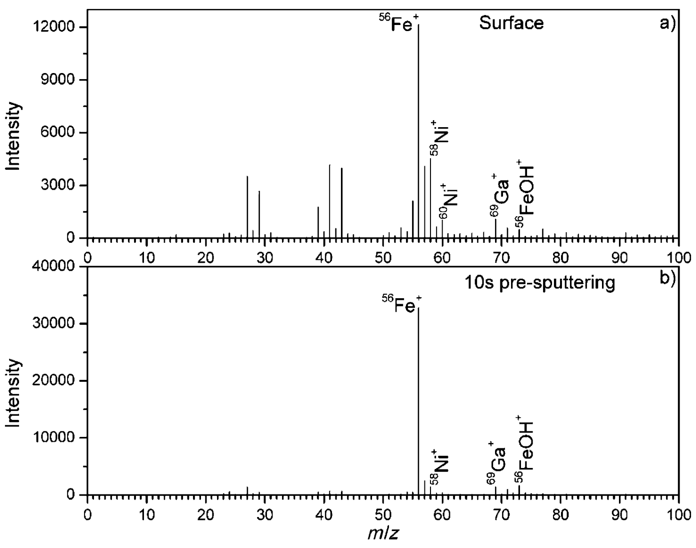


Figure 2. TOF-SIMS positive ion spectra (a) intact surface spectrum, (b) after pre-sputtering for 10 seconds in continues mode with Ga^+ ion beam at same impact energy of 10 keV.

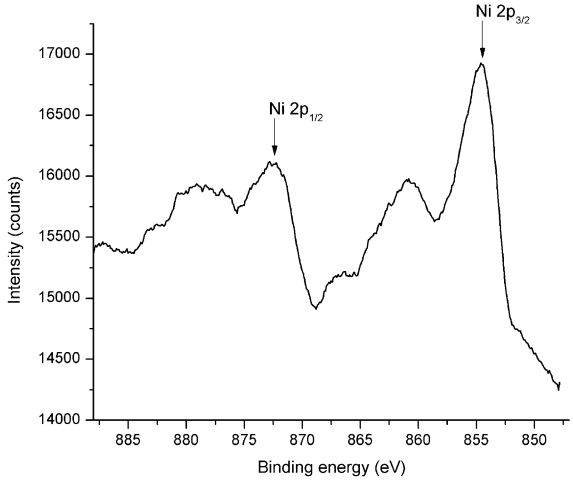


Figure 3. Ni 2p XPS line taken in FAT 22 mode with the energy step of 0.1 eV and acquisition time window of 24 s.

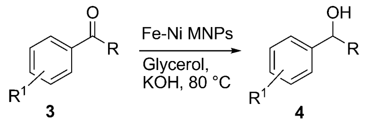
Table 1. Reduction of nitro arenes over Fe_3O_4–Ni MNPs.[a]

Entry	R	Compound	t [h]	Yield [%][b]
1	H	**2a**	3	94, 98[c]
2	2-OMe	**2b**	3.5	86
3	2-Me	**2c**	3	86
4	3-OMe	**2d**	3.5	92
5	4-OMe	**2e**	3	94
6	2-Cl	**2f**	4	85
7	4-Br	**2g**	3.5	93
8	3-Br	**2h**	4	87
9	3-Cl	**2i**	4	89
10	4-F	**2j**	4	87
11	2,5-dichloro	**2k**	4	87
12	3-Me	**2l**	3	92
13	4-OH	**2m**	3.5	88
14	2-NH_2	**2n**	3	91
15	2,3(-C_4H_4-)	**2o**	4	84
16	3-NO_2	**2p**	3	93
17	4-CN	**2q**	2.5	92
18	4-$COOC_2H_5$	**2r**	2.5	94
19	4-$COCH_3$	**2s**	2.5	93

[a] Reaction conditions: Nitroarene (1 mmol), KOH (2 mmol), 80 °C, glycerol (3 mL), 50 mg of catalyst (8.85 mmol% Ni). [b] Isolated product yield. [c] GC yield.

donating as well as -withdrawing groups such as -Cl, -F, -Br, and -OMe did not have a significant influence on the reaction (Table 1, entries 5, 7, 9, and 10). Interestingly, by using Fe_3O_4 as catalysts for the reduction of 4-methoxy nitrobenzene, compound **2e** was obtained in very low yield (the Supporting Information). It is imperative to note that these hydrogen-transfer reactions over Fe_3O_4-Ni MNPs exhibit excellent activity and selectivity for the reduction of a series of halogenated nitro arenes to the corresponding halogenated amines, without any dehalogenation occurring (Table 1, entries 6 to 11). Fe_3O_4-Ni MNPs also show excellent regio- and chemoselectivity (Table 1, entry 16 to 19). A stronger interaction of the nitro group to the catalyst surface compared with carbonyl groups may be the reason for the chemoselective reduction of the nitro group. All the nitro arenes were reduced in excellent yields affording a single product, which minimizes the efforts to separate any unreacted starting compounds.

To broaden the scope of the application of the catalyst, the hydrogen-transfer reaction was applied to the reduction of carbonyl compounds (**3**) namely of benzaldehyde and arylketones (Scheme 3). The corresponding alcohols were obtained in good to excellent yields (Table 2). Notably, reductions of carbonyl compounds are also comparable to some existing protocols.[19a,24] Again, no dehalogenation of halo acetophenones was observed (Table 2, entries 3–5). The reaction was also extended to the reduction of cyclohexanone, resulting in cyclohexanol being obtained in excellent yield (90%). The stability of Fe_3O_4-Ni MNPs was tested by recycling and reuse of the catalyst eight times for the reduction of 4-methoxy nitrobenzene without any significant loss of



Scheme 3. Fe_3O_4-Ni-catalyzed reduction of carbonyl compounds.

Table 2. Reduction of aryl carbonyl compounds over Fe_3O_4-Ni MNPs.[a]

Entry	R^1, R	Compound	t [h]	Yield [%][b]
1	R^1=H; R=H	**4a**	2	94
2	R^1=H; R=CH_3	**4b**	2.5	91
3	R^1=2-Cl; R=CH_3	**4c**	2.5	84
4	R^1=4-Cl; R=CH_3	**4d**	2.5	92
5	R^1=4-Br; R=CH_3	**4e**	2	91

[a] Reaction conditions: Compound **3** (1 mmol), KOH (2 mmol), 80 °C, glycerol (3 mL), 50 mg of catalyst (8.85 mmol% Ni). [b] Isolated product yield.

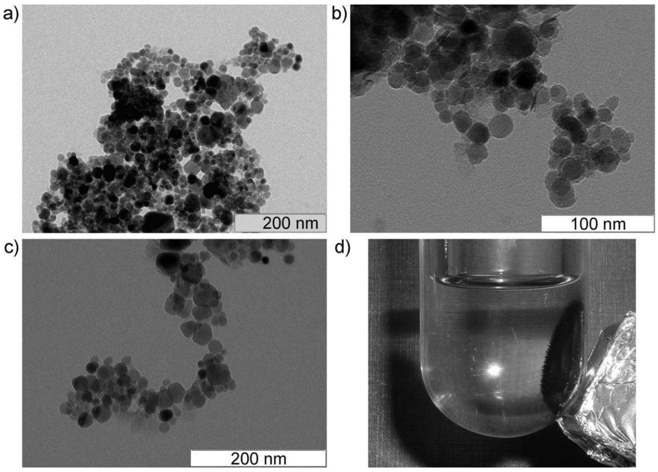


Figure 4. TEM image at 200 nm: a) before reduction of 4-methoxy nitrobenzene; b) after 8 cycles; c) after being boiled in water for 48 h; d) Ferrite-Ni MNPs separate by simple magnet.

the catalytic activity. After each cycle, Fe_3O_4-Ni MNPs were separated by using a simple magnet washed with ethanol, dried at 50 °C under vacuum and used for next cycle (Figure 4d). Also, the morphology of Fe_3O_4-Ni MNPs after eight consecutive cycles of reactions was verified by TEM. Notably, no changes in morphology of particles were observed; also, no manifest clustering tendencies could be found (Figure 4a and 4b). The Ferrite-nickel MNPs possesses excellent stability; even after heating in boiling water after 48 h the morphology remained unaltered (Figure 4c). The Ni content was found to be 9.92 % before the reaction and 9.40 % after the reusability study (8 cycles), which confirmed that only negligible leaching was observed. The yield of the reaction versus number of runs is depicted in Figure 5. Notably, the catalyst could be reused in up to eight catalytic cycles with only a slight loss of activity. To prove that the reaction is heterogeneous, a standard leaching experiment was conducted by the hot filtration method. The reaction of reduction of 4-methoxy nitrobenzene proceeded for 20 min in the presence of Fe_3O_4–Ni at 80 °C. The hot filtered reaction mixture was then stirred without catalyst for 12 h. Notably, formation of the corresponding product was not observed, even after 12 h, which indicates that no homogeneous catalyst was involved. Inductively-coupled plasma atomic emission spectra (ICP-AES) analysis of the filtrate (hot) revealed the absence of Fe and Ni species in the filtrate.

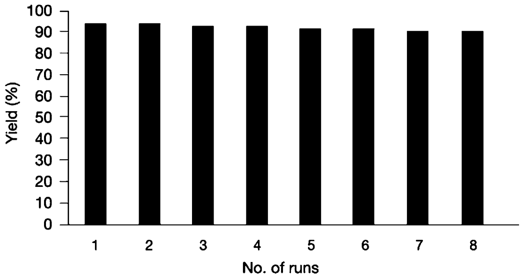


Figure 5. The recyclability test of Fe_3O_4-Ni MNPs in the reduction of 4-methoxy nitrobenzene.

In summary, we have developed a highly efficient, viable heterogeneous Fe_3O_4–Ni MNPs catalyst for hydrogen-transfer reactions by using the environmentally friendly solvent glycerol as a hydrogen donor. The Fe_3O_4–Ni MNPs catalyst was prepared by the use of inexpensive precursors, and without resource to linkers or ligands. Due to sturdy interaction between Ni and ferrite MNPs, the catalyst could be reused by recycling eight times, without any significant loss in catalytic activity and selectivity. The great advantage of the catalyst is that it is robust and magnetically recoverable, which avoids the necessity for a traditional filtration process. Further investigation, modification, and applications are under progress in our laboratory.

Experimental Section

Preparation of Ferrites/Fe_3O_4: The ferrites magnetic nanoparticle was prepared by reported procedure[19g,h] with some modifications (see the Supporting Information). The typical experimental procedure is here depicted. The $FeCl_3\cdot 6H_2O$ (5.41 g) and urea (3.6 g) were dissolved in water (200 mL) at 85 to 90 °C for 2 h. The solution turned to brown color. To the resultant reaction mixture cooled to room temperature was added $FeSO_4\cdot 7H_2O$ (2.78 g) and then 0.1 M NaOH until pH 10. The molar ratio Fe^{III} to Fe^{II} in the above system was nearly 2.00. The obtained hydroxides were treated by ultrasound in the sealed flask at 30 to 35 °C for 30 min. After ageing for 5 h, the obtained black powder of Fe_3O_4 was washed, and dried under vacuum.

Preparation of Fe_3O_4-Ni MNPs:[19g,h] Ferrite magnetic nanoparticles Fe_3O_4 (2 g) and $NiCl_2\cdot 6H_2O$ (10 wt % of nickel on ferrite) were stirred at room temperature in aqueous solution for 1 h. After impregnation, the suspension was adjusted to pH 12 by adding sodium hydroxide (0.5 M) and stirred for 10 to 12 h. The solid was washed by distilled water (5 × 10 mL). The obtained metal precursors were reduced by adding an aqueous solution of 0.2 M $NaBH_4$ dropwise under gentle stirring in an ice–water bath for 30 min until no bubbles were observed in the solution. The resulting Fe_3O_4–Ni MNPs were ultrasonicated for 10 min and then washed with distilled water and subsequently with ethanol. The synthesized Fe_3O_4–Ni MNPs were characterized by several techniques such as XRD, ICP-AES, TEM, and FEG-SEM-EDS.

General method for the reduction of nitroarenes and carbonyl compounds: Nitroarene **1** or the carbonyl compound **3** (1 mmol), glycerol (3 mL), KOH (2 mmol), and catalyst (50 mg, 8.85 mmol % Ni), were stirred at 80 °C for an appropriate time. After completion of the reaction (due to the high viscosity of glycerol a small fraction of the reaction mixture was extracted with ethyl acetate for TLC), the catalyst was separated magnetically. The resultant product was extracted with ethyl acetate from the glycerol mixture and the organic solvent evaporated in vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as the eluent.

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Keywords: green chemistry · nanoparticles · nickel · reduction · supported catalysts

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Nanoparticles

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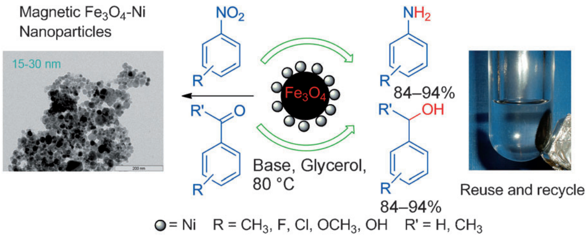
Regio- and Chemoselective Reduction of Nitroarenes and Carbonyl Compounds over Recyclable Magnetic Ferrite–Nickel Nanoparticles (Fe_3O_4–Ni) by Using Glycerol as a Hydrogen Source



Reduction by magnetic nano-Fe_3O_4-Ni: A facile, simple and environmentally friendly hydrogen-transfer reaction that takes place over recyclable ferrite-nickel magnetic nanoparticles (Fe_3O_4–Ni) by using glycerol as hydrogen source allows aromatic amines and alcohols to be synthesized from the precursor nitroarenes and carbonyl compounds (see figure).