



Activated Mont K10-Carbon supported Fe₂O₃: A versatile catalyst for hydration of nitriles to amides and reduction of nitro compounds to amines in aqueous media

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Abstract. The iron oxide was successfully supported on activated clay/carbon through an experimentally viable protocol for both hydrations of nitrile to amide and reduction of nitro compounds to amines. The as-prepared catalyst has been extensively characterised by XPS, SEM-EDX, TEM, TGA, BET surface area measurements and powdered X-ray diffraction (PXRD). A wide variety of substrates could be converted to the desired products with good to excellent yields by using water as a green solvent for both the reactions. The catalyst was recyclable and reusable up to six consecutive cycles without compromising its catalytic proficiency.

Keywords. Mont K-10; iron oxide; hydration; reduction; versatility.

1. Introduction

The hydration of nitriles into corresponding amides is one of the most widely studied transformations, whose applications lie at the core of organic synthesis as well as the chemical industry as excellent intermediates and raw materials. The amides are important starting materials for production of detergents, drug stabilisers, lubricants, intermediates in peptide and protein synthesis.^{1–5} Nitrile hydration can be considered as one of the simplest methods for the preparation of primary amides.⁶ However, it is very difficult to stop the reaction at amide products without further hydrolysis to carboxylic acids. Use of concentrated acid or base can lower the rate of hydration of amides to carboxylic acids.^{7,8} Therefore, in contemporary times, the selective hydration of nitriles to amides under mild reaction condition is of high strategic challenge both in industry and academia. A large number of transition metal catalysts such as Ru,⁹ Pt,¹⁰ Pd,¹¹ Au,¹² have been frequently used for the nitrile hydration with various methodologies. Of course, most of these protocols were homogeneous in nature, as a result, the relatively

short lifetime of catalyst could not tolerate the harsh conditions (high pressure and temperature), difficulty in separating the catalyst and product and expenditure of the catalyst limits the use of homogeneously catalysed reactions.

Similarly, reduction of nitroarenes into amines have received significant attention due to their importance as intermediates in agrochemicals, pharmaceuticals, dyestuffs, pigments and fine chemical industries.^{13–19} Traditionally, reduction of nitro compounds is carried out with Fe/HCl which is accompanied by a large amount of secondary wastes which is not sustainable from environmental perspectives. A number of protocols with good recyclability were reported so far for the transformation of nitro compounds using H₂ or other reducing agents. However, these methodologies suffer from time selectivity problem and the formation of toxic by-products or impurities. In recent years, a lot of works have already been performed in the field of nitro reduction employing precious metals like Pd, Pt, Ru, etc.,^{20–22} but their moisture sensitivity and limited availability still appeal to develop a new protocol that might induce an efficient reduction of nitro compounds into corresponding amines using earth-

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abundant, low-cost metals like Fe, Ni, Cu, Co, etc., in greener reaction condition.

It is noteworthy that given the growing awareness of greener approach to reduce pollution in synthetic processes, heterogeneous catalytic systems have received prime importance among researchers in addition to easy recovery, low catalyst loading and excellent retrievability.¹¹ To achieve sufficient reactivity as well as non-leaching of metal species from the support, the selection of solid support is one of the most important criteria in a heterogeneous system.²³ Earlier reports of the heterogeneous systems such as potassium fluoride doped Al₂O₃,²⁴ phosphates,²⁵ alumina,²⁶ silica-supported manganese oxides²⁷ have significant advancements, however, in some cases reuse of the catalysts were found not easy and turn over number of the protocols were low. Montmorillonite K-10 is a type of acidic stratified silicate mineral, a three-layered structure with two-dimensional silicate sheets that are separated by interlayer cationic species with high exchangeability for other cations, easily available, inexpensive, large surface area, environmentally benign both at industrial level and on a laboratory scale and good adsorption capacity. Particularly, the acid-treated clay catalysts have gained significant attention in different organic syntheses as a catalyst or as a support because of higher surface area, pore volume, pore diameter and higher surface acidity.^{28,29} Activated carbon is a structurally homogeneous material of high surface area and microporous structure. It is therefore widely used in various industrial processes as adsorbent, catalyst or catalyst support.³⁰⁻³² There are a couple of reports using Ru metal both in homogeneous and heterogeneous systems for hydration of nitriles to amides. The Fe belonging to the same group with Ru is one of the most abundant metals on the earth crust, inexpensive and eco-friendly,³³ nevertheless its use in catalysis is still limited. This prompted us to explore its catalytic proficiency for nitrile hydration as well as nitro reduction.

2. Experimental

2.1 Materials and methods

Montmorillonite K-10 (Sigma Aldrich), Charcoal (Merck), FeSO₄·7H₂O (SRL) Hydrazine hydrate (Merck), nitrile compounds were obtained from TCI and all the nitro compounds were obtained from Sigma Aldrich. The chemicals were used as received without any further purification or drying. Powder X-ray

diffraction patterns (PXRD) of clay/charcoal and activated Montmorillonite K-10/carbon@ Fe₂O₃ were recorded on a Bruker AXS D8 Advance. The amount of Fe loading in the catalyst was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on a Thermo Electron IRIS INTERPID II XSP DUO. ¹H NMR spectra were recorded in CDCl₃ using TMS as an internal standard on a BRUKER AVANCE II 400 MHz spectrometer. The SEM images and EDX spectra were obtained with a Quanta 200 FEG Scanning electron microscope. Specific surface areas were recorded following the BET procedure using Quantachrome Novae 2200. TEM micrographs were obtained from JEM-2100, 200 kV JEOL. Thermo Gravimetric analysis (TGA) was done in the temperature range 30 °C-800 °C at a heating rate of 20 °C/min with a Perkin Elmer, STA-8000 thermal analyzer.

2.2 Preparation of activated carbon

The charcoal (2 g) was boiled in 0.5 N HCl (50 mL) for 40-45 min. The residue was filtered off, followed by washing with distilled water for 4-5 times and dried in an oven at 100 °C for 45 min.

2.3 Preparation of activated Mont K-10/C@ Fe₂O₃ catalyst

A mixture of 0.7 g of activated clay and 0.3 g of activated charcoal was grounded in a mortar for 15 min and placed in a 100 mL beaker with 0.5 g of FeSO₄·7H₂O and allowed to stir continuously for 16 h in 50 mL ethanol at 50 °C. After that the solution was filtered off, followed by washing with ethanol for several times. The product was then dried in an oven and used as the catalyst for hydration of nitriles to amides and reduction of nitro compounds to amines.

2.4 General procedure for hydration of nitrile to amide compounds

In a 50 mL round-bottomed flask nitriles (1.0 mmol), catalyst (25 mg, 0.05 mol% Fe), KOH (1 mmol) and water (5 mL) were mixed and allowed to react for the required amount of time at temperature 60 °C with constant stirring. The progress of the reaction was monitored with thin layer chromatography (TLC). After completion of the reaction, the catalyst was removed from the reaction mixture by simple filtration. The resulting mixture was extracted from the

filtrate by using water and ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4 . After evaporation of the solvent under reduced pressure using a rotary evaporator, the residue was purified by column chromatography (silica gel, ethyl acetate: hexane 1:1) as eluent to get the desired products. For recycling experiments, the catalyst was washed several times after each cycle with water and diethyl ether. After overnight drying at 110°C , the recovered catalyst was subjected to successive runs under identical reaction conditions.

2.5 General procedure for the reduction of nitro compounds

In a typical reduction protocol, a mixture of nitroarene (1 mmol), catalyst (15 mg, 0.03 mol% Fe), $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (2 mL) and H_2O (5 mL) was added in a 50 mL round-bottomed flask at temperature 60°C with constant stirring for the required amount of time. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was centrifuged and the catalyst was separated by filtration. The residue was extracted from the filtrate using water-ethyl acetate mixture (1:1) followed by washing with brine and drying over anhydrous Na_2SO_4 . The residue was purified by column chromatography using silica gel (60-120 mesh) with ethyl acetate/hexane as eluent to obtain the required products. For recycling experiments, the catalyst was washed with water and diethyl ether for several times after each cycle. After overnight drying at 110°C , the recovered catalyst was subjected to successive runs under identical reaction conditions.

3. Results and Discussion

3.1 Characterisation of the materials

The powder X-ray diffraction patterns ($2\theta = 5^\circ\text{--}80^\circ$) of activated clay-carbon and activated clay/carbon@ Fe_2O_3 have been demonstrated in Figure 1. The peaks at 8.1° (001), 19.8° (003), 20.8° (110), and 26.6° (004) are ascribed to Mont K-10 [Figure 1(a)]. The clear diffraction peaks at 23.6° , 34.0° , 35.5° , 40.4° , 43.5° , 49.5° , 54.2° , 57.8° , 61.7° , 63.4° , 72° and 75.4° corresponding to (012), (104), (110), (113), (202), (024), (116), (122), (214), (300), (101) and (220) planes [Figure 1(b)] could be clearly indexed with the hematite phase ($\alpha\text{-Fe}_2\text{O}_3$) of iron oxide and are reasonably close to the reported literature of Fe_2O_3 .^{34,35} In the XRD pattern (c), the peaks of both Mont K10

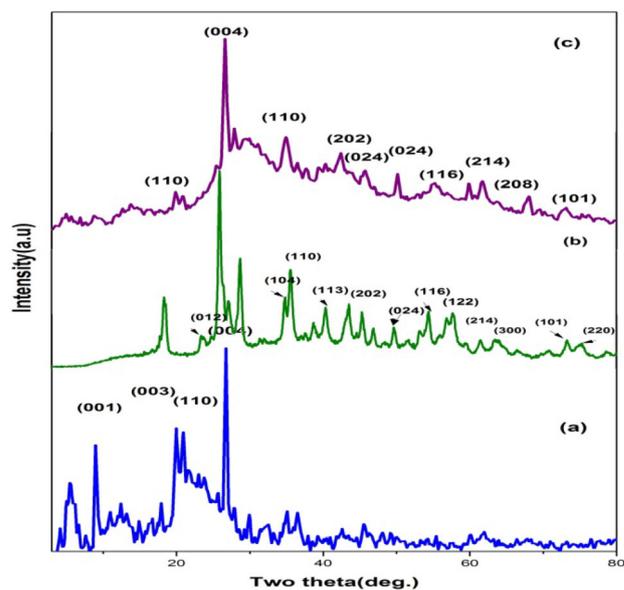


Figure 1. XRD patterns of (a) activated clay/ carbon (b) Fe_2O_3 and (c) activated clay/carbon@ Fe_2O_3 .

and Fe_2O_3 could be seen although some peaks of Fe_2O_3 are not significant in the composite which might be due to low loading of Fe_2O_3 in the clay/C composite. Moreover, the XRD pattern of the reused catalyst almost corresponds to the fresh catalyst (Figure S1, Supplementary Information).

The XPS survey spectrum [Figure 2(a)] of the activated clay/carbon@ Fe_2O_3 catalyst confirmed the presence of Fe, O, Al, Si and C in the catalyst. The Al 2p XPS spectrum [Figure 2(b)] showed a peak at 75.2 eV could be assigned to the binding energy of Al^{3+} in Al-OH.³⁶ The Si 2p contains distinctive curve centre at 103.6 eV (Si-O-Si) [Figure 2(c)]. The spectrum of C 1s region of the activated clay/carbon@ Fe_2O_3 catalyst showed multiple absorption peaks [Figure 2(d)], might be due to the presence of C-C (284.7 eV), C-OH (285.7 eV), and C=O (288.5 eV) functional groups. The C-C peak is mainly arising from the activated carbon, whereas the other two species (C-OH and C=O) are due to partially dehydrated residues, whose presence greatly affect the surface properties of the clay/carbon@ Fe_2O_3 catalyst.^{20,36} The $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ peaks at 711.10 eV and 725.40 eV were accompanied by two satellite peaks at around 716.7 eV and 733.6 eV, respectively, were characteristic of hematite ($\alpha\text{-Fe}_2\text{O}_3$).^{37,38} The O 1s spectrum exhibited a peak at 532.8 eV (Figure 2e) with a shift of ~ 2 eV towards higher binding energy, revealing the presence of lattice oxygen in Fe_2O_3 .

The BET analysis of activated clay/carbon and activated clay/carbon@ Fe_2O_3 provides key

information regarding change occurring over the surface of the catalyst. The N_2 adsorption-desorption isotherm measured at 77K of clay/C shows type IV isotherm (in accordance to the IUPAC classification) with one clear H3-type hysteresis loop from $P/P_0 \sim 0.6$ to 0.9, is characteristics of mesoporous materials [Figure 3(a)]. After insertion of metal oxide into the support, the specific surface area (S_{BET}) and pore volume were found to be $93.69 \text{ m}^2 \text{ g}^{-1}$ and 0.013 cm^3

g^{-1} , respectively. These values are comparatively smaller than the support material, which strongly suggest deposition of Fe_2O_3 over the support (Table S1, Supplementary Information). Moreover, clay/C @ Fe_2O_3 shows an intermediate shape between types II and IV (Figure 3b).^{22,39,40}

Scanning electron microscope (SEM) image [Figure S2 (a), Supplementary Information] of activated clay/carbon shows a flake-like structure which became

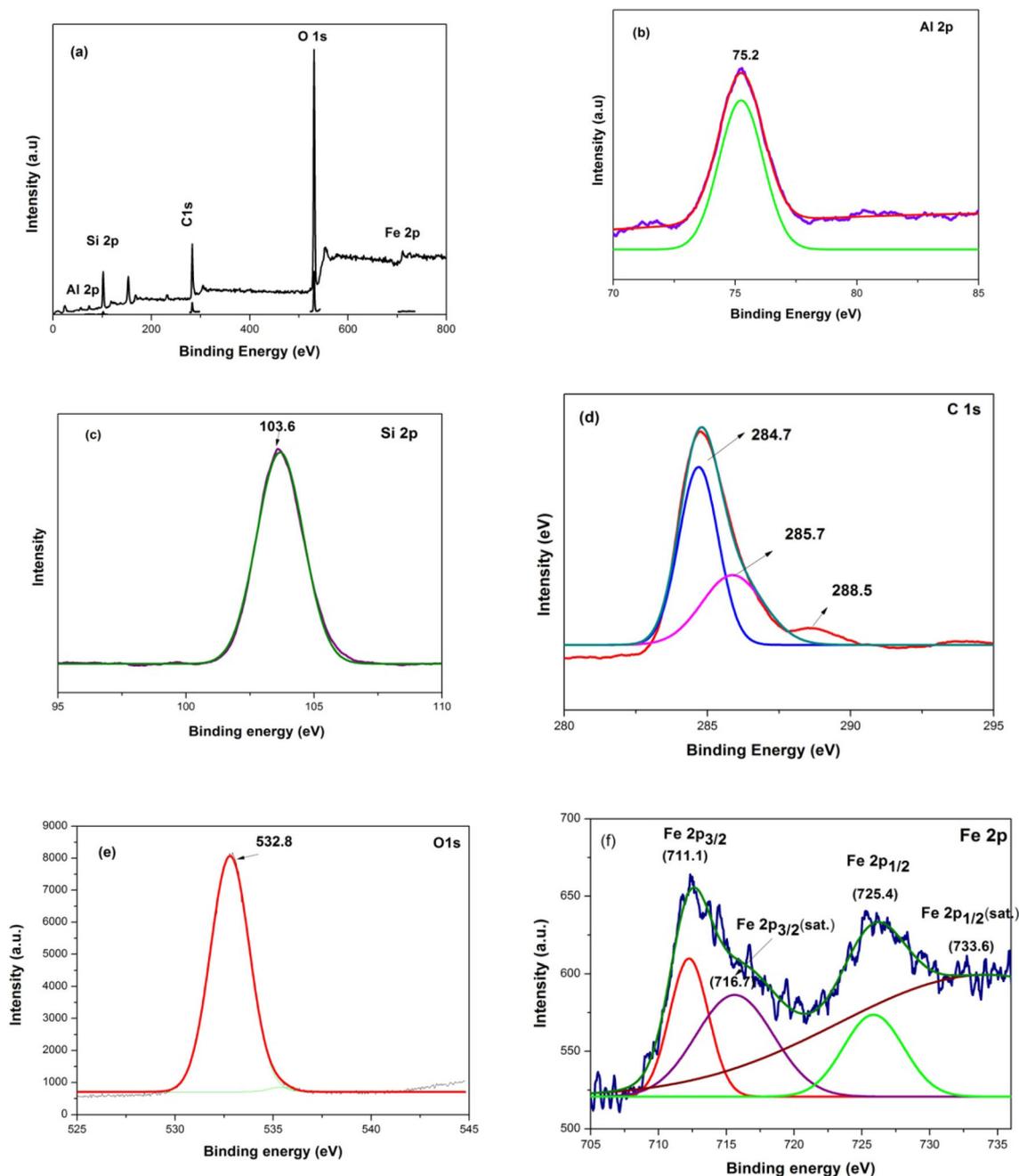


Figure 2. (a) Deconvoluted high-resolution XPS survey spectrum of clay/carbon@ Fe_2O_3 and corresponding core level spectra of (b) Al 2p (c) Si 2p (d) C 1s (e) O1s level and (f) Fe 2p.

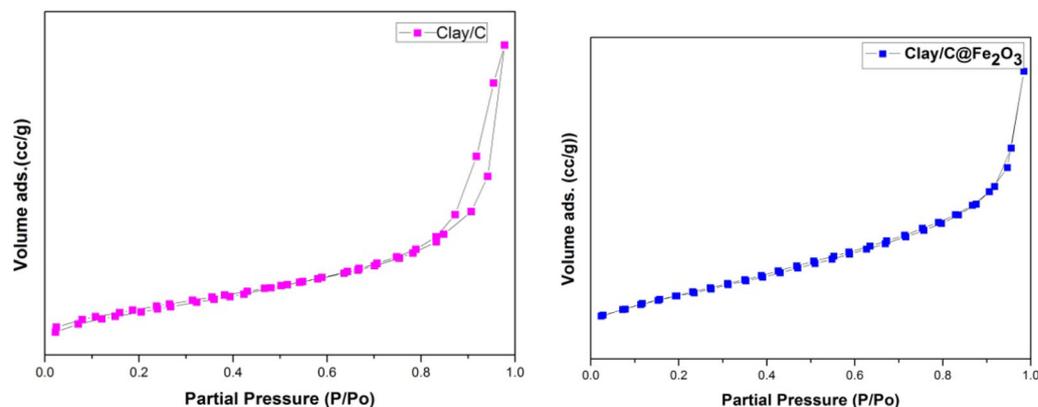


Figure 3. N₂ adsorption-desorption isotherm of (a) clay/carbon (b) clay/carbon@ Fe₂O₃.

more prominent after the impregnation of iron oxide over the surface [Figure S2 (b), Supplementary Information]. The SEM-EDX analysis confirmed the presence of iron along with the other elements of clay [Figure S2 (c) & (d), Supplementary Information]. The SAED pattern of the support and the catalyst suggest the amorphous nature of the materials (in the inset of Figure S3 (i) & (ii), Supplementary Information). Moreover, the TEM images of the fresh and recovered catalyst after the 6th cycle showed that the morphology of the catalyst almost remained the same [Figure S3 (ii) & (iii), Supplementary Information]. The thermogravimetric analysis under nitrogen has been carried out to know the thermal stability and degradation pattern of the catalyst (Figure S4, Supplementary Information). There is a weight loss of 5%, which might be attributed to the loss of surface and interlayer water. A 10% weight loss at 444 °C could be due to dehydration of residual interlayer water and complete oxidation of activated carbon. Above 450 °C there is a 29% weight loss which might be due to dehydroxylation of interlayered structure.^{20,41}

The optimization of reaction conditions for activated clay/carbon@ Fe₂O₃ catalysed nitrile hydration is outlined in Table 1. To carry out optimization studies we have chosen benzonitrile as the model substrate. Our investigations showed that on increasing the amount of catalyst from 5 mg (0.01 mol% Fe) to 25 mg (0.05 mol% Fe) the yield of the product increases (Table 1, entries 1-5). The catalyst showed excellent catalytic activity with 25 mg catalyst (0.05 mol% Fe) (Table 1, entry 5). Moreover, the progress of the reaction gets slowed down on decreasing the temperature (Table 1, entry 7). The reaction did not occur with mild bases like K₂CO₃, Na₂CO₃ (Table 1, entries 8 & 9) and without base (Table 1, entry 10), whereas with the strong

Table 1. Optimization of reaction conditions for nitrile hydration reaction catalysed by clay/C@ Fe₂O₃^a.

Entry	Catalyst ;mg (mol% Fe)	Yield ^b (%)
1	5 (0.01)	20
2	10 (0.02)	31
3	15 (0.03)	38
4	20 (0.04)	48
5	25 (0.05)	81
6	30(0.06)	81
7 ^c	25 (0.05)	44
8 ^d	25 (0.05)	-
9 ^e	25 (0.05)	-
10 ^f	25 (0.05)	-
11 ^g	25 (0.05)	-
12 ^h	-	-
13 ⁱ	25 (0.05)	12
14 ^j	25 (0.05)	19
15 ^k	25 (0.05)	29
16 ^l	25 (0.05)	48
17 ^m	25 (0.05)	61
18 ⁿ	25 (0.05)	26

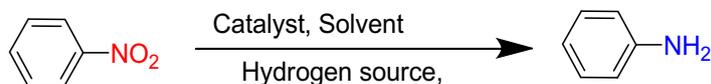
^aReaction conditions: Benzonitrile (1 mmol), catalyst (5-25 mg, 0.01-0.05 mol% Fe), time (4 h) water (5 mL) KOH (1 mmol) temp: 60 °C, ^bisolated yield, ^croom temperature (28 °C), ^dK₂CO₃ (1 mmol), ^eNa₂CO₃ (1 mmol), ^fno base, ^gno H₂O, ^hno catalyst, ⁱactivated clay, ^jactivated carbon, ^kactivated clay/carbon, ^lactivated clay@ Fe₂O₃, ^mactivated carbon@ Fe₂O₃ ⁿFe₂O₃, Bold indicates optimized condition.

base KOH in aqueous solution gave excellent conversion. Therefore, the choice of the base is critical to the reaction. The nucleophilic OH⁻ ion generated

Table 2. Substrate scope for nitrile hydration catalysed by clay/charcoal@ Fe₂O₃^a

Entry	Substrate	Product	Time (h)	Yield(%) ^b	TON	TOF
1			4	81	1620	405
2			3	87	1740	580
3			3	91	1820	606
4			2	92	1840	920
5			2	94	1880	940
6			4	88	1760	440
7			4	90	1800	450
8			6	-	-	-
9			6	-	-	-
10			6	-	-	-

^aReaction conditions: Nitrile (1 mmol), H₂O (5 mL), KOH (1 mmol), activated clay/charcoal@ Fe₂O₃ (25 mg, 0.05 mol% of Fe) at 60 °C in air, TON = mole of product/mole of Fe, TOF= TON/time, ^bIsolated yields.

Table 3. Optimization of reaction conditions for clay/charcoal@ Fe₂O₃ catalyzed nitro group reduction reactions ^a.

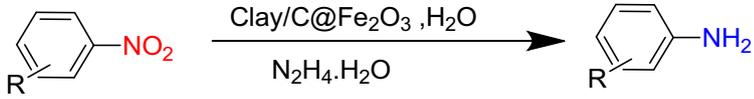
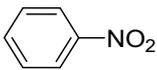
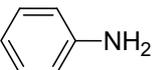
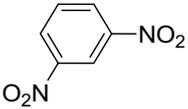
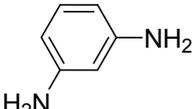
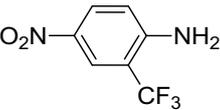
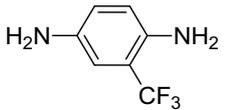
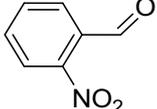
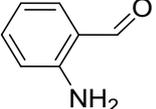
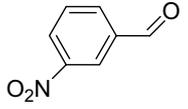
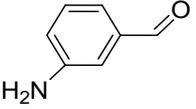
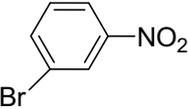
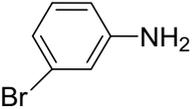
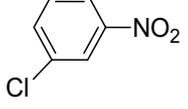
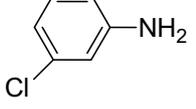
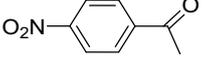
Entry	Solvent	Catalyst; mg (mol% of Fe)	Yield ^b (%)
1	CH ₃ CN	5 (0.01)	32
2	CH ₃ CN	10 (0.02)	44
3	CH ₃ CN	15 (0.03)	66
4	H₂O	15 (0.03)	86
5	C ₂ H ₅ OH	15(0.03)	58
6	H ₂ O	-	-
7	Toluene	15(0.03)	-
8	-	15 (0.03)	-
9	H ₂ O	-	-
10 ^c	H ₂ O	15 (0.03)	-
11 ^d	H ₂ O	15 (0.03)	26
12 ^e	H ₂ O	15 (0.03)	43
13 ^f	H ₂ O	15 (0.03)	67
14	H ₂ O	20 (0.04)	63
15 ^g	H ₂ O	15 (0.03)	-
16 ^h	H ₂ O	15 (0.03)	-
17 ⁱ	H ₂ O	15 (0.03)	34

^aReaction conditions: Nitrobenzene (1 mmol), N₂H₄.H₂O (2 mL), solvent (5 mL), temp (50 °C), ^bisolated yield, ^cno reducing agent, ^dactivated clay/C, ^eactivated clay@ Fe₂O₃, ^factivated carbon@ Fe₂O₃, ^gNaBH₄ (0.1 M, 2 mL) instead of N₂H₄.H₂O, ^h2-propanol instead of N₂H₄.H₂O, ⁱFe₂O₃, Bold indicates optimized condition.

from the strong base KOH in aqueous solution may easily attack the C-atom of nitrile and thereby accelerate the reaction rate towards product formation. The reaction did not proceed without water also (Table 1, entry 11). Notably, without catalyst, there is no reaction (Table 1, entry 12) and whereas, with clay (Table 1, entry 13), activated carbon (Table 1, entry 14) and activated clay/C (Table 1, entry 15) gave poor yields which clearly indicated the importance of iron oxide in addition to activated clay/C as a catalyst for this transformation. The scope of the catalyst was explored for various nitriles including aromatic and heterocyclic compounds using the optimized conditions (Table 2). The electron-withdrawing substituents such as -Br, -Cl, -CF₃, -NO₂ (Table 2; entry 2, 3, 6 and 7) gave the products with excellent yields because electron-withdrawing groups make the nitrile carbon susceptible to nucleophilic attack by an activated water molecule.¹ Furthermore, heteroaromatic nitriles could be efficiently hydrated to the corresponding amides (Table 2, entries 4 and 5). However, electron-donating groups such as -NH₂ and -CH₃ (Table 2, entries 8 and 9) did not give any

product. To explore the versatility of the catalyst its catalytic activity was also investigated for the reduction of nitro compounds to the corresponding amines. A set of reactions were performed taking nitrobenzene as a model substrate to optimize the reaction conditions. A variety of solvents such as CH₃CN, H₂O, C₂H₅OH, and toluene were screened, which showed H₂O was efficient to generate the highest product yield. However, water being environmentally benign was chosen to perform further reactions. In a heterogeneous system, catalyst loading plays an important role and found that 0.03 mol% Fe is sufficient for the reaction to occur extensively. Without the catalyst the reaction was ended with no product formation (Table 3, entry 9), while with the neat support there was a very poor conversion of reactant (Table 3, entry 11), enumerating the significance of iron oxide in the support as a catalyst. The reaction performed efficiently with N₂H₄.H₂O as a hydrogen source which produces water and nitrogen gas as the only by products.^{42,43} The reduction reaction was not proceeding in the absence of hydrogen source (Table 3, entry 10). However, other

Table 4. Substrate scope of clay/charcoal@ Fe₂O₃ catalyzed nitro group reductions^a.

						
Entry	Substrate	Product	Time (h)	Yield(%) ^b	TON	TOF
1			3	86	2866	955
2 ^c			4	81	2700	675
3 ^c			2	92	3066	1533
4			3	93	3100	1033
5			2.5	91	3033	1213
6			4	89	2966	741
7			3	82	2733	911
8			3	82	2733	911
9			4	80	2666	666
10			3	92	3066	1022
11	CH ₃ NO ₂	CH ₃ NH ₂	-	-	-	-

^aReaction conditions: Nitroarene (1 mmol), H₂O (5 mL), N₂H₄.H₂O (2 mL), activated clay/carbon @ Fe₂O₃ (15 mg, 0.03 mol% of Fe) at 50 °C in air, ^bIsolated Yield, ^cN₂H₄.H₂O (4 mL)

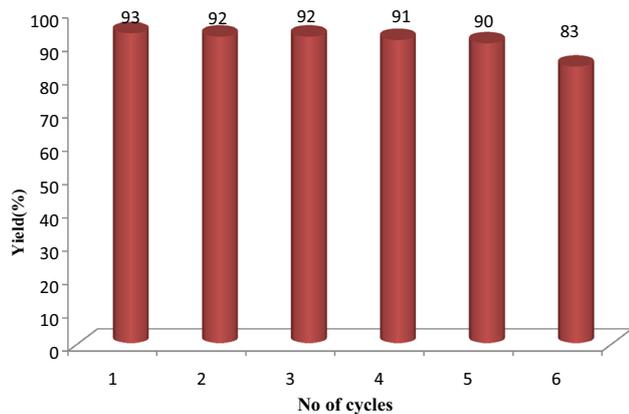


Figure 4. Reusability test of clay/C@ Fe₂O₃ catalyst for the reduction of a nitro compound to amine.

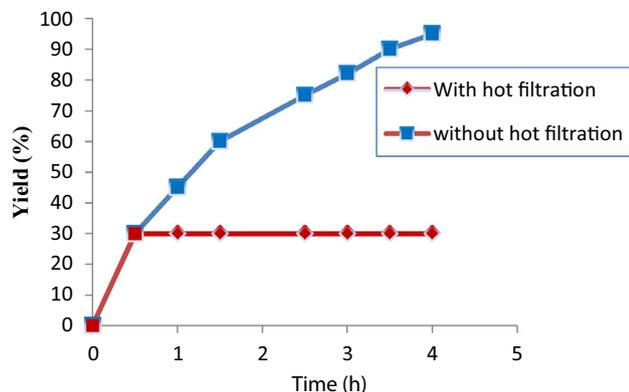
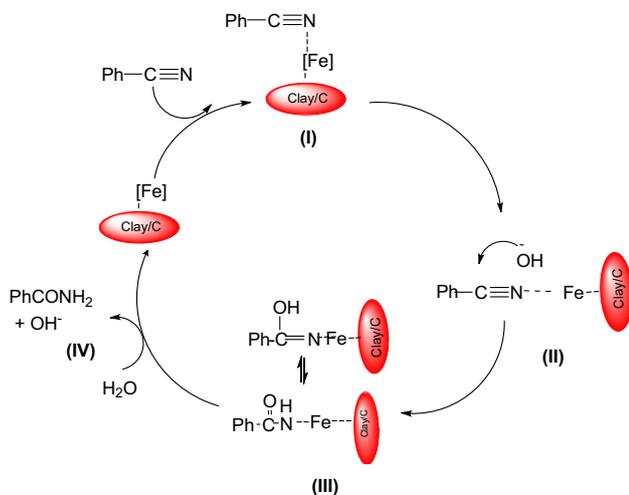
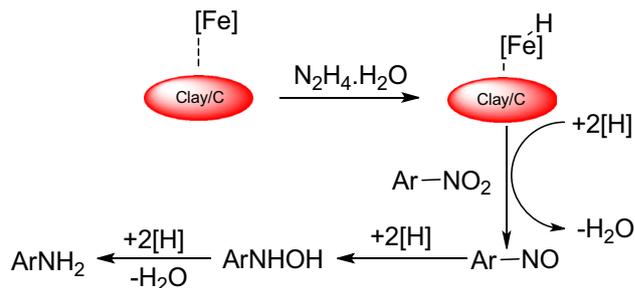


Figure 5. Activity of the catalyst for the reduction of nitro compound to amine with hot filtration and without hot filtration.



Scheme 1. Plausible mechanism for activated clay/C@ Fe₂O₃ catalyzed hydration of nitriles.



Scheme 2. Plausible reaction mechanism for activated clay/C@ Fe₂O₃ catalyzed reduction of nitro compounds.

hydrogen sources like NaBH₄ and 2-propanol (Table 3, entries 15 and 16) did not give the desired product.

The scope and generality of this transformation were explored with a variety of substrates (Table 4). The reaction of nitrobenzene under optimized conditions produced aniline with 86% isolated yield after 3 h (Table 4, entry 1). 1, 3-dinitrobenzene and 1, 4-dinitrobenzene were also reduced to 1, 3-phenylene diamine and 1, 4-phenylene diamine respectively by using an excess of hydrazine hydrate (Table 4, entries 2 and 3). The electron-withdrawing substituents like cyano, 4-nitro (trifluoromethyl) aniline gave the corresponding products with enhanced isolated yields (Table 4, entries 4 and 5). It was very interesting to observe that in the case of *o*- and *m*-nitrobenzaldehyde the catalyst, activated clay/C@ Fe₂O₃ selectively reduced the nitro group keeping intact formyl moiety (Table 4, entries 6 and 7). Identically, while *m*-bromonitrobenzene and *m*-chloronitrobenzene reduced to their corresponding products without dehalogenation (Table 4, entries 8 and 9) while the reduction of *p*-nitroacetophenone to *p*-aminoacetophenone occurred selectively and smoothly with 92% isolated yields (Table 4, entry 10).

3.2 Reusability

For heterogeneous systems, catalyst durability and ease of reusability are very important factors. To clarify the issue, a set of experiments for nitro reduction were conducted by using 4-nitrobenzonitrile as a model substrate under identical reaction conditions (Figure 4). After completion of the reaction, the product was extracted using ethyl acetate. The catalyst was recovered by simple centrifugation, washed with distilled water for 2-3 times, followed by drying. The catalyst was reused for subsequent runs up to 6th cycle

without major loss in its activity. Moreover, to examine any catalyst leaching we have carried out ICP-AES analysis of the reused catalyst obtained after the 6th cycle and found 0.028 mol% Fe content in the reused catalyst, indicating non-significant leaching of the catalyst during repeated cycles.

3.3 Heterogeneity of the catalyst

The heterogeneity of the catalyst was established by hot filtration test. The reduction reaction was performed by using 4-nitrobenzotrile as substrate under optimized reaction conditions (Figure 5). The catalyst was filtered off from the reaction mixture under hot condition (at 60 °C) after 30 min and the reaction was allowed to continue with the filtrate for another 3 h. The % conversion, as analysed by GC showed constancy at 30%. This result revealed no significant leaching of Fe. A parallel reaction without hot filtration of the catalyst for the same amount of time showed 95% conversion in GC.

A possible base catalysed hydration mechanism is proposed in Scheme 1. Initially, co-ordination of benzonitrile to the Fe-atom of the catalyst may result in increased electrophilicity of the nitrile carbon (Intermediate I), which upon addition of OH⁻ ion obtained from KOH in aqueous solution might lead to an intermediate (III). Finally, the abstraction of a proton from water may produce the corresponding amide as a product (IV).^{44,45}

A plausible reaction mechanism for the reduction of aromatic nitro compounds to corresponding amines using clay/C@ Fe₂O₃ catalyst with N₂H₄.H₂O as hydrogen source is shown in Scheme 2.⁴⁶ The catalyst would react with hydrazine hydrate resulting in the formation of FeH and proceeds to generate hydrogen in presence of heat. Due to the presence of the hydrogenation process, the nitro compound is reduced to a nitroso compound which proceeds to generate hydroxylamine and finally gives rise to an amine.

3.4 Comparison with other reported systems

Synthesis of benzamide and aniline compounds using diverse heterogeneous catalytic systems has been summarized in Table 5. It provides a comparative catalytic performance of clay/C@ Fe₂O₃ over related catalytic systems reported earlier. From Table 5 it is clear that present protocol is more efficient with respect to various factors such as temperature, catalyst

Table 5. Comparison of catalytic performance of the present catalyst for hydration of nitriles and reduction of nitro compounds with other reported systems.

Entry	Catalyst	Reaction conditions	Yield(%)	TON	TOF	References
1	Hydrotalcite-clay supported nickel nanoparticles	H ₂ O, 120 °C, 10-24 h	85	17	1.7	¹
2	Fe ₃ O ₄ @ SiO ₂ -NHC-Cu(II) (Cu: 6 mol%)	H ₂ O, 110 °C, 6 h	92	153	25.5	⁸
3	Ru/chitin (2.3 mol% Ru)	H ₂ O, 120 °C under a N ₂ atmosphere	87	378	18.9	²³
4	AgHAP (0.03 mol%)	H ₂ O, 140 °C, 6 h	94	3133	1044	⁴⁷
5	Activated Clay/C@ Fe ₂ O ₃ (25 mg, 0.05 mol % Fe)	H ₂ O, KOH, 60 °C, 4 h	75-90	1620	405	Present work
Comparison of catalytic activity of reduction of nitrobenzene to aniline						
1	FePc/FeSO ₄ ·7H ₂ O (0.5 mol %)	H ₂ O:EtOH; N ₂ H ₄ .H ₂ O, 7 h	99	990	99	⁴⁸
2	MNPs@PIL@AuNPs (1 mol%)	NaBH ₄ (10 eq.) N ₂ .H ₂ O, r.t	96	960	96	⁴⁹
3	Fe ₃ O ₄ @PAMAM/Ni(0)-b-PEG (1mol % Ni)	H ₂ O (3 mL), 1mmol NaBH ₄ , 40 °C, 2 h	91	910	455	⁵⁰
4	Activated clay/C@ Fe ₂ O ₃ (15 mg; 0.03 mol% Fe)	H ₂ O, N ₂ H ₄ .H ₂ O, 60 °C, 3h	86	2866	955	Present work

amount, turn over number and turn over frequency when compared with other reported systems.

4. Conclusions

In summary, we have successfully developed an eco-friendly, recyclable, versatile catalyst for hydration of nitriles to amides and reduction of nitro compounds as well. Both types of organic transformations have generated satisfactory isolated yields of the products. The easy catalyst preparation, simple reaction setup, low metal loading, use of a green solvent (water) are some distinct advantages of the present catalytic system. The catalyst can be recycled up to 6th cycle without significant loss of catalytic performance.

Supplementary Information (SI)

The XRD of the reused catalyst, SEM and TEM images, TGA curve of the synthesized catalyst and spectral data of the products are given at www.ias.ac.in/chemsci.

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