



# Reductive cleavage of azo dyes and reduction of nitroarenes over trivalent iron incorporated hexagonal mesoporous aluminophosphate molecular sieves

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## Abstract

A novel, efficient and eco-friendly iron incorporated hexagonal mesoporous aluminophosphate (FeHMA) catalyst is put forward for the reductive cleavage of azo functions as well as for the reduction of nitroarenes, including larger molecules, by catalytic transfer hydrogenation (CTH). The results indicate that the transformations occur in elegant and rapid manner with excellent yields. Furthermore, the catalyst can easily be recovered and reused without practically affecting the yields for up to six cycles.

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## 1. Introduction

Azo dyes are extensively used in textile, printing, leather, papermaking, drug, cosmetics and food industry [1,2] and hence substantial quantities of these carcinogenic/genotoxic dyestuffs are dumped into the environment as industrial effluents [3–5]. They are known to affect microbial activities as well as microbial population sizes in sediments and water columns of aquatic habitats [6] as well as recalcitrant against bio-degradative processes [7]. Since the conventional biological treatment such as activated sludge is ineffective, more expensive treatment alternatives are often adopted [8–12]. However, elimination of azo

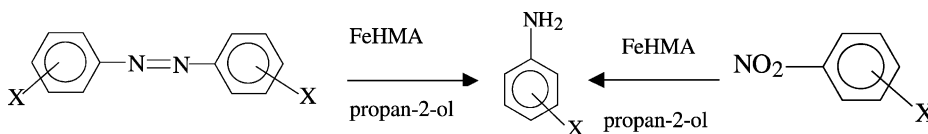
functions can be done by the reductive cleavage into aromatic amines, which are much less toxic and easily biodegradable. On the other hand, selective reduction of organic nitro compounds is widely used at the industrial scale [13] and the resulting aromatic amines are extensively used as intermediates for dyes, photographic, pharmaceutical and agricultural chemicals as well as antioxidants. However, when the substrate contains several reactive groups, the selective reduction becomes particularly difficult. Intermediates such as hydroxylamines are often formed in the process, which are unstable, toxic, and yield by-products [14,15].

Synthetic organic transformations performed under non-traditional conditions are becoming popular primarily to circumvent the growing environmental and ecological concerns. In recent years, emphasis is being paid towards viable alternatives for the reductive processes via environmental catalysis. In comparison

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Scheme 1.

to the commonly used reduction processes, which involve hazardous molecular hydrogen or Fe/HCl or Sn/HCl [16], catalytic transfer hydrogenation (CTH) employing hydrogen donors, e.g. propan-2-ol, is easy, safer, highly selective and eco-friendly [17,18]. The application of CTH for reductive cleavage and reduction of organic compounds, in general, are centered on the use of expensive catalysts such as Pd/C, Pt/C, Ru/C or Raney-Ni as well as systems like Raney-Ni/hydrazine, Pd-C/triethyl ammonium formate or formic acid [19–25]. However, in the case of reductive cleavage of azo compounds, much longer reactions time, typically 22–48 h are often employed [19,24]. Moreover, poor yields are reported owing to the formation of hydazo intermediates. It is also noteworthy here that the Raney-Ni catalyst is flammable and presents considerable hazards during handling. On the other hand, a useful alternative to the well established reduction with hydrogen donors and metal-catalysts, complex hydrides or metal ion in solution is metal oxides-based heterogeneous catalysts [26–31]. However, in the case of iron oxide hydroxide/hydrazine hydrate system hydroxylamine is also formed with selectivity of the product reaching 40% when electron-attractive substituent is present on the aromatic ring [28]. Furthermore, increase of particles size of the active catalysts as well as the formation of  $\alpha$ -iron oxide lead to a significant decrease in activity [29]. On the other hand, nickel-based metal oxide catalysts [27,31] contain much higher metal content and that the heterogeneous nature of the catalysts has not been demonstrated. In addition, they also have several drawbacks such as longer reaction times, nucleophilic attack, by-products, low yield and poor recyclability. Thus, the development of highly efficient processes/catalysts that generates low amounts of residues/byproducts with good activity is one of the main challenges to the scientific community.

Recently, we have reported several transition metal-based mesoporous silicate and aluminophos-

phate molecular sieves, which show promise for a variety of industrially relevant organic reactions and may represent a possible alternative to traditional synthesis of a wide variety of significant precursors and intermediates [32–41]. Further, the catalysts transform some of these reactions, e.g. reduction of aromatic nitro and carbonyl functions, oxidation of alkyl aromatics, phenols, cyclohexane and cyclohexene as well as alkylation of phenols, more efficiently than the corresponding microporous analogues or supported metal oxide systems. However, in the present investigation, trivalent iron substituted hexagonal mesoporous aluminophosphate (FeHMA [36]; analogues to FeMCM-41 [33]) is considered for a wide variety of functional groups containing azo and nitro compounds are described and the methodology is exemplified by concise reductive cleavage of azo functions as well as reduction of nitroarenes (Scheme 1). The choice of FeHMA as catalyst for the chosen reaction is based on the following additional considerations. It is a unique material and that it possesses high surface area, large pore size and pore volume as well as the required acidic sites for CTH reactions. More importantly, unlike most of the iron containing molecular sieves, dislodgement of tetrahedral Fe(III) was not observed upon various process treatments like calcinations, recycling, etc. indicating high thermal stability of FeHMA [36,37]. In addition, the catalyst can also be regenerated without any loss of structure, surface area and active species by simple reactivation at 373 K.

## 2. Experimental

### 2.1. Synthesis

The synthesis of FeHMA was carried out hydrothermally as per the procedure described elsewhere [36]. Accordingly, aluminium isopropoxide was added to dilute phosphoric acid under constant

stirring followed by the addition of ferric nitrate solution at room temperature. The mixture was stirred at 343 K for 1 h and then tetramethyl ammonium hydroxide (TMAOH; 25 wt.% in water) was added drop-wise. After few hours of stirring, cetyltrimethylammonium chloride (CTAC; 25 wt.% in water) was added slowly drop-by-drop and the stirring was continued for another 12 h. The final gel having a molar composition of:  $0.96\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:0.04\text{Fe}_2\text{O}_3:\text{CTAC}:2.8\text{TMAOH}:70\text{H}_2\text{O}$  ( $(\text{Al} + \text{P})/\text{Fe} = 49$ ) with a pH of 10 was kept in a Teflon-lined autoclave and heated in an air oven at 373 K for 6 d for crystallization. The resultant solid product was washed repeatedly with distilled water, filtered and dried overnight at 343 K. The surfactant template was removed from the mesoporous matrix by calcination in a tubular furnace at 823 K for 1 h in a flow of  $\text{N}_2$ , followed by 2 h in air.

## 2.2. Characterization

All the samples were systematically characterized by various physico-chemical techniques, viz. powder X-ray diffraction (XRD), transmission electron microscopy (TEM) image, electron diffraction (ED), diffuse reflectance ultraviolet-visible (DRUV-Vis) spectroscopy, electron spin resonance (ESR) spectroscopy, Mössbauer spectroscopy, inductively coupled plasma-atomic emission (ICP-AES) spectroscopy and Brunauer–Emmett–Teller (BET) surface area analysis. The pore size was calculated by the Horvath–Kawazoe (H–K) method. More information about the experimental details can be seen elsewhere [36].

## 2.3. Reaction procedure

The CTH reaction was carried out as per standard procedures. In a typical CTH reaction, KOH pellets (20 mmol) were dissolved in propan-2-ol (20 ml) to which substrate (20 mmol) was added along with 100 mg catalyst. The mixture was then refluxed at 356 K for few hours depending upon nature of the substrate. After the first reaction, the catalyst was recovered by simple filtration, washed several times with acetone followed by distilled water, activated at 373 K for 6 h and then the reaction was repeated for the subsequent cycles. The products were analyzed using a gas chromatograph (Eshika) fitted with OV-101 column.

## 3. Results and discussion

Fig. 1 depicts the XRD patterns of as-synthesized and calcined FeHMA. For a comparison, the iron-free hexagonal mesoporous aluminophosphate (henceforth referred as HMA) material [42] is also included, which is a novel molecular sieve, analogous to hexagonal mesoporous MCM-41 silicate [43,44], having one-dimensional pores with high surface area, and large pore size and volume. It is clear from this figure that the as-synthesized samples show well-resolved reflections corresponding to mesoporous MCM-41 type structure [42–44]. On the other hand, the diffraction patterns of the corresponding calcined samples shows a single broad reflection typical of disordered mesoporous structure [38,40,42,44]. The disorder arrangement was further confirmed by TEM and ED studies [36]. The BET surface area ( $923\text{ m}^2\text{ g}^{-1}$ ), pore volume ( $0.48\text{ cm}^3\text{ g}^{-1}$ ) and average pore size ( $28\text{ \AA}$ ) of the calcined FeHMA are typically in the mesopore range. ICP-AES analysis of calcined FeHMA contained 2.3 wt.% of iron. Further, DRUV-Vis, ESR and Mössbauer studies suggest the presence of trivalent iron in distorted tetrahedral framework sites [36]. The  $\text{NH}_3$ -TPD measurements of the calcined FeHMA give a desorption peak in the temperature range 873–893 K, which is indicative of the presence of strong

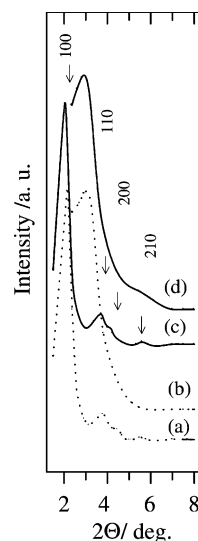
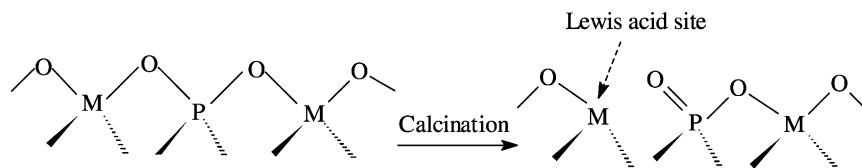


Fig. 1. XRD patterns of: (a) as-synthesized HMA; (b) calcined HMA; (c) as-synthesized FeHMA; and (d) calcined FeHMA.



Scheme 2.

Lewis acid sites. The occurrence of such strong Lewis acid sites could be attributed to the structural breakage after calcinations to yield tri-coordinated metal (trivalent aluminium or iron) ion as shown in Scheme 2[45].

Table 1 presents the results of a smooth and rapid ( $\leq 4$  h) reductive cleavage of azo ( $-N=N-$ ) functions into the corresponding amines over FeHMA. All the compounds reduced were obtained in very good

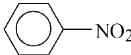
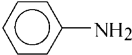
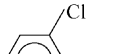
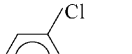


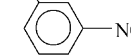
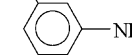
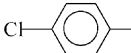
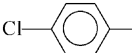
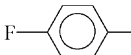
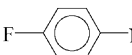
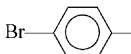
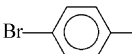
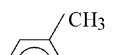
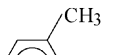
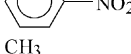
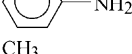
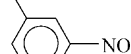
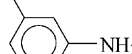
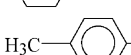
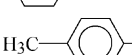
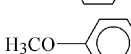
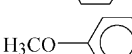
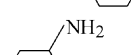
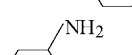
Table 1  
Reductive cleavage of azo compounds over FeHMA<sup>a</sup>

Entry	Substrate	Time (h)	Product	Yield <sup>b</sup> (%)	
				First run	Sixth run
1		2.0		87	89
2		2.0		85	85
3		3.0		81	81
4		2.0		86	85
5		2.5		88	90
6		3.5		87	86
7		4.0		51	48
8		2.0		38	36
				49	48
				36	34

<sup>a</sup> Reaction conditions: 100 mg catalyst, 20 mmol substrate, 20 mmol KOH, 20 ml propan-2-ol, 356 K.

<sup>b</sup> Yield = (conversion  $\times$  selectivity)/100.

Table 2  
Transfer hydrogenation of nitroarenes over FeHMA<sup>a</sup>

Entry	Substrate	Time (h)	Product	Yield <sup>b</sup> (%)	
				First run	Sixth run
1		3.0		92	92
2		3.0		79	80
3		3.0		84	84
4		3.0		89	88
5		3.0		82	81
6		3.5		85	85
7		3.0		70	70
8		3.0		85	84
9		3.0		90	89
10		2.5		88	87
11		3.5		73	75
12		3.5		80	80
13		3.5		86	84

<sup>a</sup> Reaction conditions: 100 mg catalyst, 20 mmol substrate, 20 mmol KOH, 20 ml propan-2-ol, 356 K.

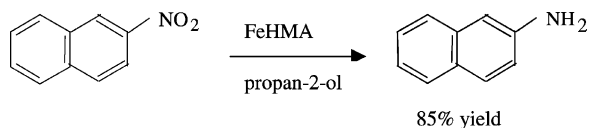
<sup>b</sup> Yield = (conversion × selectivity)/100.

yields. Many functional groups such as –Cl, –Br, –CH<sub>3</sub>, –OCH<sub>3</sub> and –NH<sub>2</sub> are tolerated. Furthermore, the catalyst is more effective than several other catalytic systems, which require longer reaction times typically 22–48 h under refluxing conditions [19,24]. Table 2 summarizes the results of CTH of several

aromatic nitro compounds over FeHMA. Almost a complete reduction was achieved easily to the corresponding amines in excellent yields. The electron withdrawing/donating groups such as –F, –Cl, –Br, –CH<sub>3</sub>, –OCH<sub>3</sub> and –NH<sub>2</sub> do not have any significant influence. Since the nitro group attached to ring can

pull electrons more strongly from the benzene ring compared to other functional groups, it can easily be adsorbed on the catalyst surface leading to chemoselective products. Furthermore, amines were found to be the only product of the reactions. The reduction of nitrobenzene was also performed without a catalyst or in the absence of potassium hydroxide. In both the cases, the reaction was failed completely. Furthermore, the use of iron-free HMA as a catalyst for the nitrobenzene reduction (3–4 h) showed about 35–45% yield. Thus, the observed high activity (Table 2; entry 1) could be accounted for by the presence of the Fe(III) in the aluminophosphate framework of the catalyst. It is also noteworthy here that the presence of a methyl/halide/amine group, *ortho* to the nitro group (Table 2 entries 2–4, 7–9 and 11–13), decreased the yield to a larger extent than at the *meta*- or *para*-position due to steric effects.

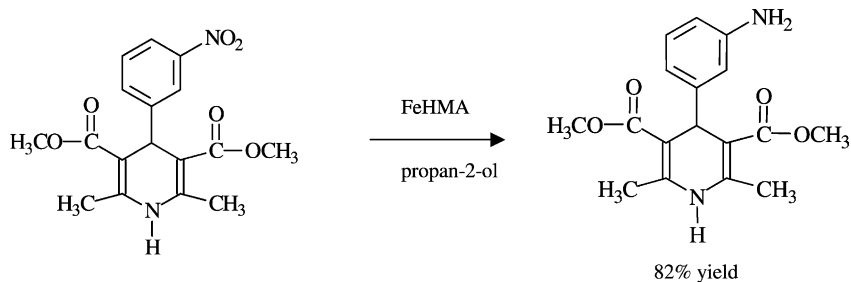
The FeHMA catalyst was also tested for its reusability. Interestingly, unlike the supported system, the yield was practically unaffected during up to six cycles. This could be attributed to the stabilization of the Fe(III) in the mesoporous matrix. The XRD pattern of the recycled FeHMA catalyst (after sixth run) did not show any significant change (not reproduced here) compared to the fresh catalyst, however a slight broadening of the reflection was observed, which may possibly be due to the finer particle size of the catalyst generated after recycling. The unit cell parameter ( $a_0 = 37.0 \text{ \AA}$ ) of the catalyst is nearly the same even after the sixth run. Furthermore, the mesoporous nature of this catalyst is also confirmed by  $\text{N}_2$  sorption measurements (BET surface area =  $885 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $0.45 \text{ cm}^3 \text{ g}^{-1}$ , and pore size =  $28 \text{ \AA}$ ). The reduction was also successfully extended for bulkier molecules (Schemes 3 and 4) with



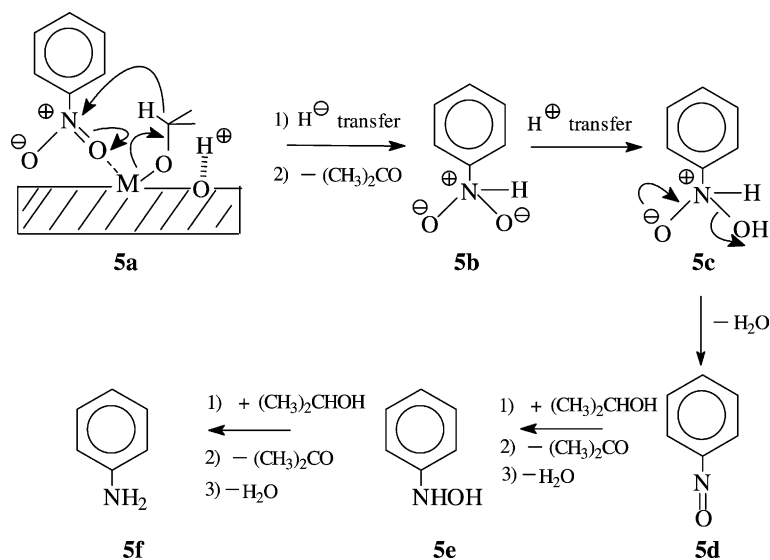
Scheme 3.

high yields being obtained. It is, however, important to mention here that, unlike many other oxide based systems, the FeHMA catalyst with a very low iron content (2.3 wt.%), the reaction proceeds smoothly in much shorter time (4 h). For example, under identical reaction conditions, for the nitrobenzene reduction,  $\text{Fe}_2\text{O}_3/\text{ZrO}_2$  (3.3 wt.% Fe) gave low yields with loss in activity upon cycling (first run, 80%; sixth run 68%). Likewise,  $\text{NiO}/\text{ZrO}_2$  and  $\text{CoO}/\text{ZrO}_2$  systems also show a continuous decrease in activity upon cycling. It is, however, noteworthy here that under the same reaction conditions, the FeMCM-41 (Si/Fe = 50; 2.1 wt.% Fe) catalyst took longer reaction time for the maximum conversion (nitrobenzene: 5 h, 81% yield; 2-nitronaphthalene: 5.5 h, 73% yield) than the FeHMA catalyst.

The reaction mechanism for the reactions under study can be derived in similar way to the classical Meerwin–Ponderof–Verley (MPV) reduction of ketones that reported for the aluminium isopropoxide [46]. Scheme 5 depicts the possible pathway for the reduction of nitrobenzene over FeHMA. Accordingly, at the initial stage, propan-2-ol adsorbs on the on the catalyst followed by the formation of an alkoxide, which is also known to be the activated H-donor in MPV reduction [47]. Further, the coordinative interaction of the substrates (nitrobenzene) with the Lewis acid center allows the formation of a six membered transition state in which hydride transfer takes place



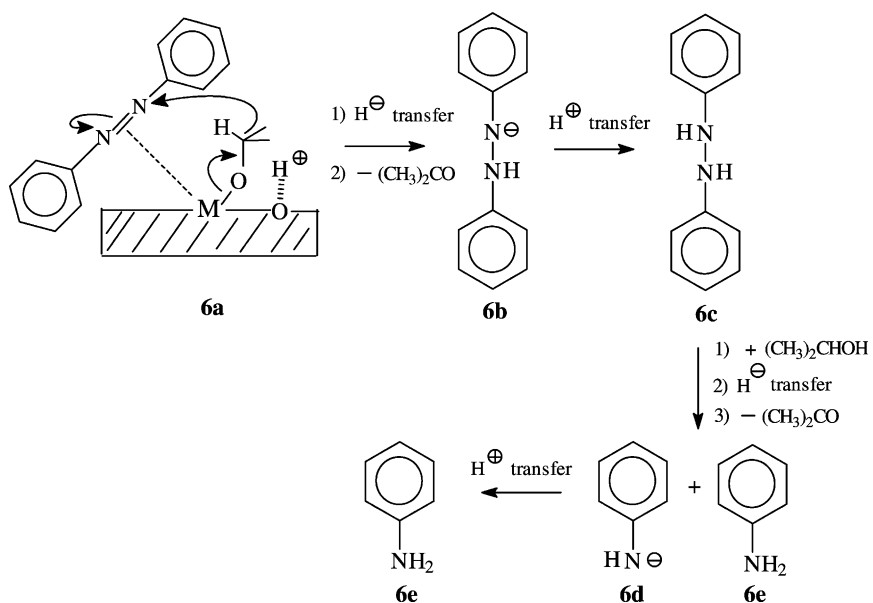
Scheme 4.



Scheme 5.

[19,48–50]. Thus the role of FeHMA is to hold both the H-donor and the H-acceptor through the Lewis acid sites in close proximity so that direct hydrogen transfer can take place smoothly [50]. The surface alkoxide species thus formed may lead to transfer the hydride ion that attacks the substrates, which is pro-

motivated by the presence of KOH [46,51,52]. Thus, the formation of aniline from nitrobenzene goes through three steps via the formation of nitrosobenzene (**5d**) and *N*-phenylhydroxylamine (**5e**) as the intermediates [53]. In a similar way, the reductive cleavage of azobenzene (Scheme 6) can also proceed by the



Scheme 6.

hydride transfer from H-donor to the  $-N=N-$  of the adsorbed azobenzene on the Lewis acid site, followed by a proton transfer, which in turn goes through the intermediate hydrazobenzene (**6c**) to form aniline.

#### 4. Conclusion

In summary, the present investigation clearly demonstrate that the mesoporous-based FeHMA catalyst as a versatile heterogeneous catalyst for the reductive cleavage of azo functions as well as reduction of nitroarenes. The salient eco-friendly features of these processes namely the selectivity, experimental ease of manipulation, and the enhanced reaction is also described. This strategy is also adaptable for bulkier molecules. Furthermore, the CTH reactions proceed in an elegant and rapid manner in much shorter time. In addition, the transformation was also achieved with excellent with the active catalyst containing as low as 2.3 wt.% Fe, and that amines were found to be the only products of the reactions.

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