

Catalytic Transfer Hydrogenation of Nitro and Carbonyl Compounds over Novel Fe(III) Substituted Hexagonal Mesoporous Aluminophosphates

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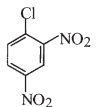
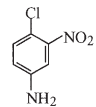
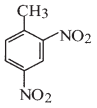
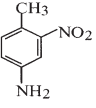
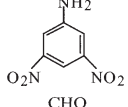
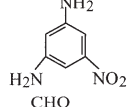
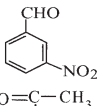
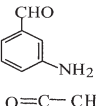
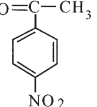
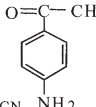
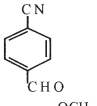
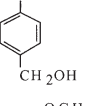
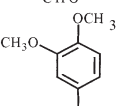
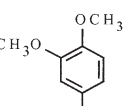
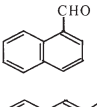
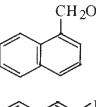
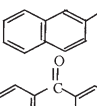
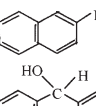
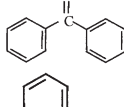
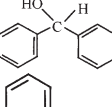
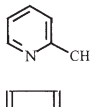
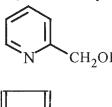
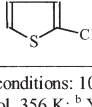
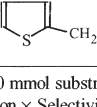
Catalytic transfer hydrogenation (CTH) of aromatic nitro and carbonyl compounds over novel Fe(III) substituted hexagonal mesoporous aluminophosphate (FeHMA) molecular sieve catalyst showed excellent regioselectivity/chemoselectivity as well as superior recycling capability. Furthermore, the reduction occurs without affecting other functional groups such as $-\text{CN}$, $-\text{CHO}$, $-\text{Cl}$, $-\text{CH}_3$, $-\text{OCH}_3$ and $-\text{NH}_2$.

Reduction of nitro and carbonyl compounds is an important step in the synthesis of dyes, biologically active compounds, pharmaceuticals, rubber chemicals, photographic and agricultural chemicals.¹ Although a wide variety of homogeneous catalysts has been reported for such reductions,² the control of the reaction rates is highly difficult.³ On the other hand, catalytic transfer hydrogenation (CTH)^{4,5} employing hydrogen donors and heterogeneous catalysts is easy, safer, highly selective, and eco-friendly compared to commonly practiced reduction processes.⁶ In general, CTH of organic compounds is centered on the expensive Pd/C, Pt/C, Ru/C, Raney-Ni catalysts as well as systems like Raney-Ni/hydrazine, Pd-C/triethyl ammonium formate or formic acid.^{4,5,7,8} However, these systems require much longer reaction times. Moreover, nucleophilic attack (hydrazine) and low yields associated with the formation of by-products make these processes unattractive. Hence, attempts have been made to develop suitable heterogeneous catalysts for CTH reactions.^{9,10} In the case of iron oxide hydroxide/hydrazine hydrate system,⁹ hydroxylamine is also formed with selectivity of the product reaching 40% when electron-attractive substituent is present on the aromatic ring. In addition, a significant decrease in activity was noticed as a consequence of the formation of $\alpha\text{-Fe}_2\text{O}_3$ as well as the increase of particles size of the active catalysts. On the other hand, the heterogeneous nature of the catalysts has not been demonstrated for the nickel based oxides.¹⁰ Furthermore, our own studies on the metal oxide supported systems showed a continuous decrease in activity upon recycling.¹¹

In this letter, we present a very efficient and highly selective heterogeneous catalyst, viz., trivalent iron substituted hexagonal mesoporous aluminophosphate (FeHMA), for CTH of nitro and carbonyl compounds using propan-2-ol as hydrogen donor. The synthesis and characterization of FeHMA ([Al+P]/Fe = 50) was carried out as per the methods described elsewhere.¹² The CTH reactions were performed as per the following standard procedure. In a typical reaction, KOH pellets (20 mmol) were dissolved in propan-2-ol (20 ml) to which substrate (20 mmol) was added along with the catalyst (100 mg), and refluxed at 356 K for few hours depending upon nature of the substrate. The products were analyzed using a gas chromatograph (Eshika) fitted with OV-101

column. For recycling purpose, the catalyst was recovered by simple filtration, after the first reaction, and washed several times

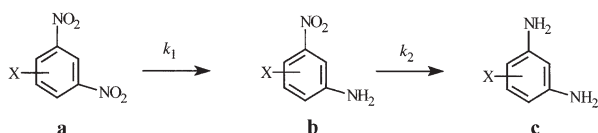
Table 1. CTH of nitro and carbonyl compounds over FeHMA^a

| Entry | Substrate | Time / h | Product | Yield / wt % ^b | |
|-------|--|----------|---|---------------------------|---------|
| | | | | 1st run | 6th run |
| 1 |  | 2.5 |  | 82 | 81 |
| 2 |  | 3.5 |  | 74 | 74 |
| 3 |  | 5.0 |  | 83 | 83 |
| 4 |  | 3.5 |  | 83 | 83 |
| 5 |  | 3.0 |  | 80 | 80 |
| 6 |  | 5.0 |  | 77 | 76 |
| 7 |  | 6.0 |  | 62 | 60 |
| 8 |  | 5.0 |  | 81 | 80 |
| 9 |  | 4.5 |  | 85 | 83 |
| 10 |  | 3.0 |  | 80 | 78 |
| 11 |  | 6.0 |  | 63 | 63 |
| 12 |  | 5.5 |  | 68 | 67 |

^a Reaction conditions: 100 mg catalyst, 20 mmol substrate, 20 mmol KOH, 20 ml propan-2-ol, 356 K; ^b Yield = [Conversion × Selectivity] / 100.

with acetone followed by a thorough washing with water to remove any alkali, if any present, and dried at 373 K. This catalyst was reused for the subsequent runs.

Table 1 summarizes the results of regioselective (entries 1–3) and chemoselective (entries 4–7) reduction of several aromatic nitro and carbonyl compounds over FeHMA. The reduction of nitro and carbonyl groups produces the corresponding amines and alcohols, respectively as the only products. Since the nitro group attached to ring can pull electrons more strongly from the benzene ring compared to the carbonyl or nitrile group, the former can easily be adsorbed on the catalyst surface leading to chemoselective products. In this context, it is also interesting to note that the reduction of substituted dinitrobenzenes, **a** is a time dependent process (entries 1–3). That is, up to a maximum reaction time of 2.5–5.0 h, only substituted nitro anilines, **b** were formed with high yields along with negligible amounts (<2%) of substituted diaminobenzenes, **c**. However, with a further increase of the reaction time, the yields of substituted **c** increases at the expense of **b**. It is possible that the successive reduction of the nitro groups occurs in consecutive reaction steps as given in Scheme 1, where $k_1 \gg k_2$. Accordingly, the reaction has a long induction period for the accumulation of **b**, as it is also known that the time required to reach at maximum concentration is higher since k_1 is much larger. If the reaction is stopped well within this period then we obtain **b** as the major product.



Scheme 1. CTH of substituted dinitrobenzenes ($x = \text{Cl}, \text{CH}_3$ or NH_2).

It can also be seen from Table 1 that the reduction process is also successful for bulkier molecules (entries 8–10). It is, however, worth mentioning here that the microporous iron substituted aluminophosphate (FeAPO-5) catalyst showed much lower yields¹³ than FeHMA. The lower activity of the former may be attributed to the small pore opening of the former (7.3 Å) than the latter (26 Å), which in principle restricts the diffusion of the larger substrates. Furthermore, it is also important to note that the activity is significantly influenced by the nature/position of the substituents on the aromatic ring. On the other hand, electron withdrawing/donating groups such as $-\text{CN}$, $-\text{CHO}$, $-\text{Cl}$, $-\text{CH}_3$, $-\text{OCH}_3$, and $-\text{NH}_2$ do not have a significant influence on the reaction. The catalyst was also used for the reduction of heterocyclic compounds with high yields (entries 11 and 12). Finally, the catalyst was tested for its reusability. Interestingly, unlike the supported systems,¹¹ the performance of FeHMA was

practically unaffected for up to six cycles (Table 1).

In conclusion, the present study clearly demonstrates that the mesoporous-based FeHMA is an efficient, ecofriendly heterogeneous catalyst for the chemoselective/regioselective hydrogen transfer reduction of nitroarenes and carbonyl compounds including bulkier molecules.

References and Notes

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- The reduction of nitrobenzene was carried out over NiO/ZrO₂ (7.85% Ni) under identical reaction condition, which gives >95% yield in the 1st run, and 83% yield for 6th run. Likewise, Fe₂O₃/ZrO₂ and CoO/ZrO₂ systems also show a continuous decrease in activity upon cycling.
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- The observed yields were 13, 25 and 21% respectively for entries 8–10.