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Heterogeneous catalytic transfer hydrogenation of aromatic nitro and carbonyl compounds over cobalt(II) substituted hexagonal mesoporous aluminophosphate molecular sieves

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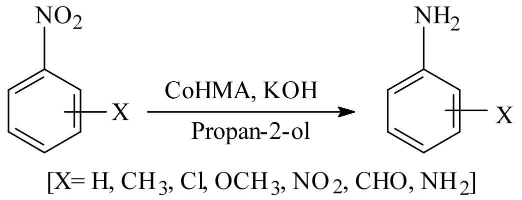
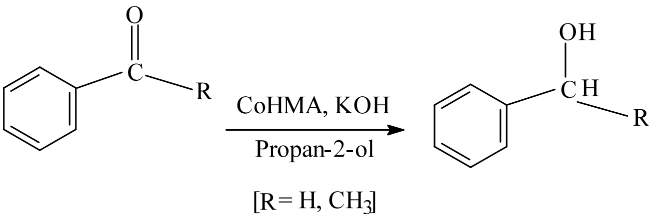
Abstract—Catalytic transfer hydrogenation of aromatic nitro and carbonyl compounds was carried out using novel cobalt(II) substituted hexagonal mesoporous aluminophosphate molecular sieves. The catalyst showed excellent yield with good recycling capability. © 2002 Elsevier Science Ltd. All rights reserved.

The reduction of nitro and carbonyl compounds is very important in organic synthesis both from the academic and industrial view points.[1] Hydrogen transfer reduction is safer, highly selective and eco-friendly compared to the commonly used reduction processes which involve hazardous molecular hydrogen or Fe/HCl.[2] A wide variety of soluble metal complexes have been reported for this purpose.[3] However, it has been observed that controlling the reduction rates is quite difficult with these highly active homogeneous catalysts.[4] On the other hand, the use of heterogeneous catalysts offers several advantages over homogeneous systems with respect to easy recovery and recycling of catalysts as well as minimization of undesired toxic wastes. Hence, several metal oxide supported systems have been employed,[5] however, the activity of most of these catalysts decreases with subsequent recycling. In this letter, we report, for the first time, a very efficient and highly selective method for the catalytic transfer hydrogenation (CTH) of aromatic nitro and carbonyl compounds using a newly developed mesoporous based heterogeneous catalyst, viz., Co(II) substituted hexagonal mesoporous aluminophosphate (CoHMA) molecular sieves,[6] using potassium hydroxide and propan-2-ol (Schemes 1 and 2).

Hexagonal mesoporous aluminophosphate (HMA) materials[7] are novel mesoporous molecular sieves, analogues to mesoporous silica (MCM-41),[8] having high surface area, and large pore size and volume. Various transition metal ion incorporated HMA catalysts have also been reported.[9] They can be used to carry out certain important organic transformations more efficiently than the corresponding microporous analogues or supported metal oxide systems. Since the CTH process requires acidic sites, mesoporous CoHMA, which possesses such characteristics,[10] may be very well suited for this purpose. Hence, in this



Scheme 1.



Scheme 2.

Keywords: catalytic transfer hydrogenation; aromatic nitro and carbonyl compounds; cobalt(II); mesoporous molecular sieves; aluminophosphates.

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Table 1. CTH of aromatic nitro and carbonyl compounds over the mesoporous CoHMA catalyst[a]

Entry	Substrate	Product	Reaction time (h)	Yield (%)[b]	
				1st run	6th run
1	Nitrobenzene	Aniline	2	91	91
2	2-Chloronitrobenzene	2-Chloroaniline	1.5	83	83
3	3-Chloronitrobenzene	3-Chloroaniline	1.5	88	88
4	4-Chloronitrobenzene	4-Chloroaniline	1.5	93	93
5	4-Bromonitrobenzene	4-Bromoaniline	1.5	90	89
6	4-Fluoronitrobenzene	4-Fluoroaniline	1.5	84	84
7	2-Nitrotoluene	2-Toluidine	2	67	66
8	3-Nitrotoluene	3-Toluidine	2	81	81
9	4-Nitrotoluene	4-Toluidine	2	83	80
10	4-Nitroanisole	4-Anisidine	5	88	87
11	2-Nitroaniline	1,2-Diaminobenzene	3	92	90
12	3-Nitroaniline	1,3-Diaminobenzene	3	86	86
13	Benzaldehyde	Benzylalcohol	1.5	96	96
14	Acetophenone	1-Phenylalcohol	3	96	95
15	3-Dinitrobenzene	3-Nitroaniline	3	71	69
		1,3-Diaminobenzene		16	17
16	2,4-Dinitrochlorobenzene	4-Chloro-3-nitroaniline	3	81	80
17	2,4-Dinitrofluorobenzene	4-Fluoro-3-nitroaniline	3	79	80
18	2,4-Dinitrotoluene	4-Methyl-3-nitroaniline	3	78	78
19	2-Nitrobenzaldehyde	2-Aminobenzaldehyde	4	81	80
20	3-Nitrobenzaldehyde	3-Aminobenzaldehyde	4	90	90
21	4-Chloro-3-nitrobenzaldehyde	4-Chloro-3-amino-benzaldehyde	4	88	88
22	4-Nitroacetophenone	4-Aminoacetophenone	4	85	85
23	Benzophenone	Benzhydrol	5	90	90
24	β-Hydroxy-α-napthaldehyde	β-Hydroxy-α-napthyl-alcohol	5	78	78

[a] Reaction conditions: 100 mg catalyst, 20 mmol KOH, 20 ml propan-2-ol, 20 mmol substrate, refluxed at 356 K.

[b] Yield = [conversion×selectivity]/100.

investigation, we have used CoHMA for CTH reactions. The catalyst was hydrothermally synthesized[11] and characterized using several analytical and spectroscopic techniques,[12] and the CTH reactions were carried out as per standard procedures.[13]

Table 1 summarizes the results of CTH of several aromatic nitro and carbonyl functions attached to an aromatic ring over the CoHMA catalyst, wherein the compounds were reduced with excellent yields. However, the activity was significantly influenced by the nature/position of the substituents on the aromatic ring. For example, in the case of nitroarenes, only amines were obtained in the product. The presence of a methyl group, *ortho* to the nitro group, decreased the yield to a larger extent than at the *para*-position due to steric effects. On the other hand, electron withdrawing/donating groups such as chloride, amine, methoxy, do not have a significant influence on the reaction. However, nitro groups attached to aromatic rings can withdraw electrons more strongly from benzene compared with carbonyl groups. Hence, they can easily be adsorbed on the catalyst surface. This may be the reason for the chemoselective reduction of a nitro group ahead of a carbonyl group (entries 19–22). Similarly, the catalyst also shows promise for regioselective reduction of dinitro compounds (entries 15–18). The catalyst was also tested for its reusability.[14] Interestingly, unlike the supported system,[15] the yield was practically unaffected during up to six cycles. This could be attributed to the stabilization of the Co(II) in the mesoporous matrix and hence it behaves truly as a heterogeneous solid acid catalyst. The reduction of nitrobenzene was also performed without a catalyst or in the absence of potassium hydroxide. In both the cases, the reaction failed completely. Hence, the observed high activity could be accounted for by the presence of the Co(II) in the aluminophosphate framework as well as by the acidic characteristics of the catalyst. As a result, the substrates may be adsorbed onto the acidic sites of the CoHMA and propan-2-ol on the basic sites (potassium hydroxide). Subsequently, hydrogen may be transferred from the alcohol to adjacent substrate molecules. Furthermore, this reduction was also successfully carried out on bulkier molecules (entries 23 and 24) with high yields being obtained.

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10. Thermogravimetric analysis of calcined CoHMA shows a 25% weight loss indicating its acidic nature. This is well supported by the temperature programmed desorption of ammonia.
11. Dilute phosphoric acid (85%; Qualigens) and aluminium isopropoxide (97%; Merck) were mixed under vigorous stirring followed by the addition of aq. cobalt acetate (99%; S.D. fine chemicals). The mixture was kept under constant stirring at 343 K for 1 h and then tetramethyl ammonium hydroxide (TMAOH; 25 wt% in water; Aldrich) was added drop-wise and the mixture stirred for a few hours. Cetyltrimethylammonium chloride (CTAC; 25 wt% in water; Aldrich) was then added drop-wise and the slurry was stirred for another 12 h. The pH was maintained at 10 with a final (molar) gel composition of: 0.96 Al_2O_3:P_2O_5:0.08 CoO:0.5 $(CTA)_2O$:1.25 $(TMA)_2O$:70 H_2O. It was then transferred into a Teflon-lined autoclave and heated at 373 K for 3 days for crystallization. The resultant solid product (90% yield) was washed repeatedly with distilled water, filtered and dried at 343 K for 12 h. The sample was then calcined at 823 K for 1 h under flowing N_2, followed by 2 h in O_2.
12. XRD, TEM and ED studies of CoHMA indicate a mesoporous hexagonal MCM-41 structure. Further, N_2 sorption measurements (BET surface area; 931 $m^2\ g^{-1}$, pore volume; 0.44 $cm^3\ g^{-1}$ and pore size; 26 Å.) support the mesoporous nature of the sample. DRUV-VIS (triplet absorption band at 540, 580 and 626 nm) and XANES studies (Co-K pre-edge at 7710 eV) confirm the substitution and stabilization of Co(II) in the tetrahedral framework. ICP-AES analysis shows 3.8 wt% Co in calcined CoHMA.
13. 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 100 mg catalyst. The mixture was then refluxed at 356 K for a few hours depending upon the nature of the substrate. The products were analyzed using a gas chromatograph (Eshika) fitted with OV-101 column.
14. After the first reaction, the catalyst was recovered by simple filtration, washed three times with acetone, activated at 773 K for 6 h and then the reaction was repeated for the subsequent cycles.
15. For a comparison, the reduction of nitrobenzene was also carried out over CoO/ZrO_2 (3.1 wt% Co). The reaction, however, requires more catalyst (150 mg) and a longer reaction time (5 h) to attain the maximum yield (86%) indicating that the rate of hydride transfer is very slow. In addition, the activity is lost significantly during recycling studies (79% yield after the 6th recycle).