Chemoselective Reduction of α,β-Unsaturated Carbonyls over Novel Mesoporous CoHMA Molecular Sieves under Hydrogen Transfer Conditions

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Abstract: Chemoselective reduction of α,β-unsaturated carbonyls to the corresponding alcohols was achieved by a catalytic transfer hydrogenation (CTH) method using cobalt(II)-substituted hexagonal mesoporous aluminophosphate (CoHMA) molecular sieve catalyst. Further, the catalyst was found to be promising as a heterogeneous catalyst as the yield was practically unchanged after up to six cycles.

Keywords: cobalt catalyst; hydrogen transfer; mesoporous aluminophosphate molecular sieves; selective hydrogenation; α,β-unsaturated alcohols; α,β-unsaturated carbonyls

The selective reduction of α,β-unsaturated carbonyls is one of the active research areas of great practical importance as the products, *viz.*, α,β-unsaturated alcohols, are useful for the preparation of several important fine chemicals and as versatile intermediates in organic synthesis.[1] The reduction of α,β-unsaturated carbonyls by molecular hydrogen has been attempted on heterogeneous catalysts for some time with very limited success.[2,3] On the other hand, the reduction of α,β-unsaturated carbonyls by the catalytic transfer hydrogenation (CTH) method is emerging as a highly selective and safe method compared to the conventional reduction employing molecular H_2. Thus, a number of homogeneous and metal oxide catalysts have been used for the production of unsaturated alcohols from unsaturated carbonyls but these catalysts are not selective.[4–7] Recently, we have reported on several transition metal-based mesoporous silicate and aluminophosphate molecular sieves for the regioselective and chemoselective reduction of various organics under transfer hydrogenation conditions.[8–10] In this communication, we present cobalt(II)-substituted hexagonal mesoporous aluminophosphate (CoHMA) molecular sieve as an eco-friendly heterogeneous catalyst for the chemoselective reduction of α,β-unsaturated carbonyls to the corresponding α,*β*-unsaturated alcohols.

The CoHMA catalyst was prepared and characterized as per the procedure described elsewhere.[11] Powder X-ray diffraction (XRD) patterns of both the as-synthesized and calcined CoHMA showed well-resolved reflections typical of the mesoporous MCM-41 structure. The surface area (930 $m^2\,g^{-1}$) was estimated using the Brunauer–Emmett–Teller (BET) method and the average pore size (26 $Å^2$) was calculated by the Horvath–Kawazoe (HK) method. The pore volume (0.44 $cm^3\,g^{-1}$) was determined form the amount of nitrogen adsorbed at $P/P_o = 0.5$. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis showed 3.8 wt % of cobalt content in the sample. The appearance of a peak in the range 773–940 K in ammonia-temperature programmed desorption (NH_3-TPD) measurements indicates the presence of strong Lewis acid sites in CoHMA. The hydrogen transfer reaction was carried out over this mesoporous catalyst as per the procedure described in the experimental section

In Table 1 are summarized the results of CTH of several aromatic and aliphatic α,*β*-unsaturated carbonyls over CoHMA catalyst, wherein the compounds were reduced with good yields. The catalyst selectively reduces the carbonyl functions without affecting the olefinic bonds. As can be seen from Table 1, the catalyst exhibits excellent selectivity towards unsaturated alcohols which is in contrast with certain reported catalysts with which only aldehydes were reduced and which fail with unsaturated carbonyls.[12] At this juncture, it is interesting to note that nearly similar yields were obtained for all the substrates under investigation over cobalt oxide supported on zirconium oxide (CoO/ZrO_2) catalyst with a cobalt content twice (8.7 wt %) as much as that CoHMA catalyst (3.8 wt %). Table 2 presents the results of the reduction of cinnamaldehyde under various reaction conditions. This table also gives the isolated yield of cinnamyl alcohol which is comparable to the GC yield. Furthermore, it can also be seen from Table 2 that the reduction of cinnamaldehyde over CoO and Co-free HMA gives much lower yields. Likewise, the reaction does not proceed if the catalyst is used without the promoter (KOH) or if no catalyst is used. This indicates that the observed

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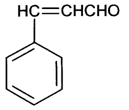
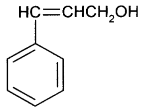
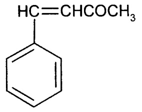
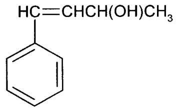
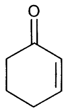
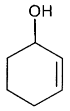
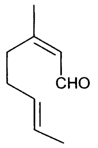
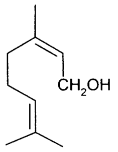
Table 1. Reduction of α,β-unsaturated carbonyls over CoHMA.

Entry	Substrate	Time [h]	Product	Yield [%][a]	
				First run	Third run
1		2.0		75	75
2		3.0		66	65
3		3.5		73	73
4		6.0		62	59
5	$CH_3CH{=}CHCHO$	2.5	$CH_3CH{=}CHCH_2OH$	80	82
6	$CH_3CH_2CH_2CH{=}CHCHO$	2.0	$CH_3CH_2CH_2CH{=}CHCH_2OH$	75	74

[a] GC yields.

Reaction condition: Substrate (20 mmol), KOH pellets (20 mmol), catalyst (100 mg) in 2-propanol (20 mL) refluxed at 356 K.

high activity of CoHMA is mainly due to the presence of the transition metal ion in the structure. It is, however, noteworthy here that the CoO/ZrO_2 catalyst showed nearly the same yield at the expense of excess cobalt as compared to CoHMA.

The reaction mechanism for the reactions under study can be presumed to be similar to the classical Meerwein–Ponndorf–Verley (MPV) reduction of carbonyls reported for aluminium isopropoxide.[13] Accordingly, at the initial stage, 2-propanol adsorbs on the catalyst followed by the formation of an alkoxide, which is also known to be the activated H-donor in MPV reductions.[14] Further, the coordinative interaction of the substrates with the Lewis acid centre allows the formation of a six-membered transition state in which hydride transfer takes place.[15,16] Thus, the role of CoHMA 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.[17] The surface alkoxide species thus formed may transfer the hydride ion that attacks the substrates, which is promoted by the presence of KOH.[13,18]

The catalyst was also tested for its reusability for the reduction of cinnamaldehyde. Interestingly, the yield was practically unaffected up to six cycles (Table 2). The filtrate and quenched solutions of the catalyst did not show any catalytic activity. This confirms that the activity observed is due only to the solid catalyst and not partly due to the leached active species. The XRD pattern of the recycled CoHMA catalyst did not show any significant change 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

Table 2. Reduction of cinnamaldehyde to cinnamyl alcohol under different reaction conditions.

Entry	System	Yield [%]
1	CoHMA with promoter	81[a] 75[b] 73[b, c]
2	CoHMA without promoter	–[d]
3	No catalyst	–[d]
4	Filtrate	–[d]
5	Quenched solution	–[d]
6	Co-free HMA	17[a]
7	CoO	35[a]
8	CoO supported on ZrO_2[e]	80[a, e]
9	ZrO_2	26[a]

Reaction condition: Cinnamaldehyde (20 mmol), KOH pellets (20 mmol), catalyst (100 mg) in 2-propanol (20 mL) refluxed at 356 K for 2 h.

[a] Isolated yield on single experiment.

[b] GC yield.

[c] Yield after sixth run.

[d] No reaction.

[e] The CoO/ZrO_2 catalyst contains 8.7 wt % Co as against 3.8 wt % of Co in CoHMA catalyst.

catalyst generated after recycling. Furthermore, the mesoporous nature of the reused catalyst was also confirmed by nitrogen sorption measurements (BET surface area = 890 $m^2\,g^{-1}$, pore volume = 0.45 $cm^3\,g^{-1}$, and pore size = 26 Å). Thus, the catalyst behaves truly as a heterogeneous solid acid catalyst by keeping its structural integrity.

In conclusion, for the first time, a mesoporous molecular sieve is proposed for the chemoselective reduction of a variety of α,β-unsaturated carbonyls having importance for fine chemicals and drugs. The catalyst, CoHMA, was found to be highly selective for this purpose and yields only unsaturated alcohols with 100% selectivity. The yield and reaction time are highly encouraging. The catalyst was found to be heterogeneous in nature for this reaction.

Experimental Section

CoHMA Catalyst Preparation

Cobalt(II) substituted hexagonal mesoporous aluminophosphate (CoHMA) molecular sieve catalyst was prepared as per the following procedure. Phosphoric acid was first diluted with water and then aluminium isopropoxide was added under vigorous stirring followed by the addition of cobalt acetate solution. The mixture was kept under constant stirring at 343 K for 1 h and then tetramethylammonium hydroxide (TMAOH; 25 wt % in water) was added drop-wise. The slurry was kept under stirring for a few hours. Then cetyltrimethylammonium chloride (CTAC; 25% in water) was added drop-wise and 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 ([Al + P]/Co = 50). It was then transferred into a Teflon-lined autoclave and heated for crystallization at 373 K for 72 h. The resultant solid product was washed repeatedly with distilled water, filtered and dried at 343 K for 12 h. The as-synthesized samples were then calcined at 823 K for 1 h under flowing N_2, followed by 2 h in O_2.

CTH Reaction Procedure

In a typical CTH reaction procedure, the substrate (20 mmol) and KOH pellets (20 mmol) dissolved in 20 mL of 2-propanol (20 mL) were stirred in the presence of 100 mg of the catalyst. The mixture was then refluxed at 356 K for 2–6 h depending upon the substrate. The resulting products were analyzed using a gas chromatograph (Eshika) fitted with an OV-101 column. In order to check the reusability of the catalyst, the filtered catalyst was washed with acetone for several times followed by washing with water to remove alkali, if any present. The filtered residue was then activated at 373 K for 6 h, and the activated catalyst was used for the recycling studies. Furthermore, the reaction was carried out with the filtrate solution so as to check the leachability of the active metal ions from the matrix. In addition, quenching studies were also performed with the filtrate obtained under the reaction (hot) conditions.

Product Isolation

In a typical isolation procedure, after the reaction is completed, the reaction mixture was filtered out and the filtrate was washed several times with distilled water in order to remove the base, which resulted in the formation of an emulsion. The crude product was extracted from this emulsion with CH_2Cl_2, dried over anhydrous Na_2SO_4, and the excess solvent was removed under reduced pressure. This was further subjected to column chromatography to isolate the pure products.

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