Highly active, reusable and moisture insensitive catalyst obtained from basic Ga–Mg-hydrotalcite anionic clay for Friedel–Crafts type benzylation and acylation reactions

Vasant R. Choudhary *, Suman K. Jana and A.B. Mandale

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India
E-mail: vrc@ems.ncl.res.in

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Liquid phase benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of benzene and toluene over a Ga–Mg hydrotalcite (which is a basic anionic clay) with or without HCl gas pretreatment and also over the hydrotalcite used earlier in the toluene benzylation (at 110 °C) have been investigated. The fresh, used and HCl-gas-pretreated hydrotalcite catalysts were characterized for their surface area, basicity, crystalline structure and phases and also for their surface composition. The fresh hydrotalcite showed no catalytic activity for both the benzylation and benzoylation reactions for a long period. However, after a long induction period (2.7 h), the catalyst showed a very high activity in the toluene benzylation (at 110 °C). Whereas, the catalyst after its use in the toluene benzylation or after its HCl gas pretreatment showed very high activity for both the reactions with a much shorter induction period. The hydrotalcite-derived catalyst consists essentially highly dispersed gallium and magnesium chlorides on MgO. The presence of moisture in the reaction mixture has beneficial effects on the acylation reactions over the used catalyst.

KEY WORDS: benzylation of benzene; benzylation of toluene; benzoylation of benzene; benzoylation of toluene; Ga–Mg hydrotalcite

1. Introduction

Liquid phase benzylation and acylation of aromatic compounds, using homogeneous acid catalysts, are commonly practiced Friedel–Crafts type reactions in organic synthesis [1]. However, the commonly used homogeneous acid catalysts (*viz.* $AlCl_3$, BF_3 and H_2SO_4) pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, *etc.* Moreover, these catalysts are highly moisture sensitive and hence demand moisture-free solvent and reactants and anhydrous catalyst, and also dry atmosphere for their handling. In order to develop reusable solid acid catalysts for these reactions, world-wide efforts have been made using a number of highly acidic solid catalysts, such as heteropolyacids [2], sulfated ZrO_2 or Fe_2O_3 [3], Nafion-H [2] and Fe- or Ga-substituted H-ZSM-5 [4] for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene [5], and heteropolyacids [2], H-beta [6], H-ZSM-5 [7] and sulfated ZrO_2 [8] for benzoylation of aromatic compounds. However, reports on the use of basic catalysts for the benzylation and acylation reactions are scarce [9]. Very recently, we [10] have observed high activity of supported basic In_2O_3 in these reactions. Hydrotalcite anionic clays are known to be highly basic solids [11]. The use of these anionic clays after their thermal decomposition to mixed metal oxides has been reported for a number of catalytic reactions [11]. However, their direct use as catalyst is scarce [12,13]. No information is available on the use of hydrotalcites or also the basic catalysts derived from them for the benzylation and acylation reactions. In this communication, we show that Ga–Mg hydrotalcite anionic clay, after its first use in the reaction or HCl gas pretreatment, shows very high activity both in the benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of toluene and even of benzene, which is otherwise very difficult by the known acidic catalysts. It is also shown that the active catalyst, obtained from the hydrotalcite after its first use or HCl gas pretreatment, has little or no moisture sensitivity and also has excellent reusability, which is of great practical importance.

2. Experimental

Ga–Mg hydrotalcite (Mg/Ga mole ratio = 3.0), having the formula $[Ga_{0.25}Mg_{0.75}(OH)_2]^{0.25+}[CO_3^{2-}]_{0.125}\cdot nH_2O$, was synthesized by the co-precipitation method described earlier [14]. Ga–Mg-HT-80 and Ga–Mg-HT-200 hydrotalcite samples were obtained by calcining the as-synthesized hydrotalcite at 80 °C (for 12 h) and 200 °C (for 4 h), respectively. Their structure was confirmed by XRD and FTIR.

The benzylation and acylation reactions over the Ga–Mg-hydrotalcite catalyst or the catalyst derived from the hydrotalcite were carried out in a magnetically stirred glass reactor (capacity 25 cm^3) fitted with a reflux condenser, mercury thermometer and arrangement for continuously bubbling moisture-free N_2 (30 $cm^3\ min^{-1}$) through the liquid reaction mixture. Before the reaction, the catalyst was refluxed with an aromatic substrate for a period of 0.25 h. The reaction

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[*] To whom correspondence should be addressed.

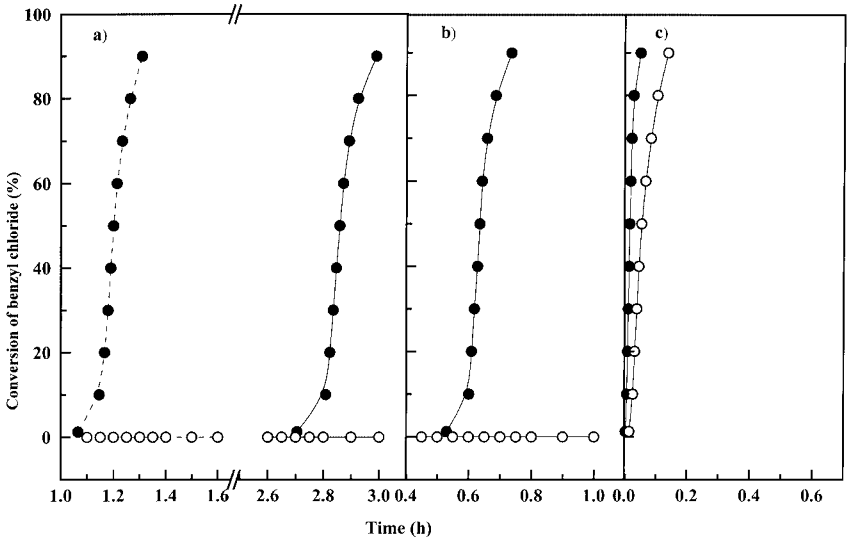

Figure 1. Benzylation of benzene at 80 °C (○) and toluene at 110 °C (●) with benzyl chloride over (a) Ga–Mg-HT-80, (b) Ga–Mg-HT-200 and (c) Ga–Mg-HT-80 (or 200) used before in the toluene benzylation (the catalyst refluxed in pure aromatic substrate for a period of (—) 0.25 and (- - -) 7.0 h, respectively, before the reaction).

was started by injecting 1.0 ml of benzyl chloride or benzoyl chloride in the refluxing reaction mixture, containing 13 ml of benzene or toluene as the substrate and catalyst (0.1 g for benzylation and 0.4 g for benzoylation). All the reactions were carried out under reflux conditions (at 110 °C for toluene as the substrate and at 80 °C for benzene as the substrate) following the procedures described earlier [4,10]. In all the cases, the product formed was mainly mono benzylated or benzoylated and there was no formation of polybenzyl or polybenzoyl chloride. To study the effect of moisture, a known amount of water was injected in the reaction mixture before starting the reaction. To study the reusability of the catalyst, the catalyst used in a particular reaction was removed from the reaction mixture by filtration and then washed (with the aromatic substrate) before its reuse in the reaction. HCl gas treatment to the catalyst, Ga–Mg-HT-200, was given by bubbling HCl gas (25 ml min^{-1}) through a catalyst (0.1 or 0.4 g)–toluene (13 ml) mixture in the glass reactor at room temperature (26 °C) for a period of 0.5 h. The HCl-treated catalyst was filtered, washed with an aromatic substrate (benzene or toluene) then used for the benzylation or acylation reaction.

The fresh, HCl-pretreated and used (in the toluene benzylation) Ga–Mg-HT catalysts were dried under vacuum at 60 °C for 6 h before their characterization. These catalysts have been characterized by XRD (using a Phillips diffractometer (1730 series) and Cu Kα radiation), FTIR (in Nujol medium) (using Perkin–Elmer FTIR (1600 series)) and XPS (using VG-Scientific ESCA-3 MK II electron spectrometer) for their bulk and surface properties.

3. Results and discussion

Results of the benzylation of toluene in figure 1 (a) and (b) show a very strong influence of the calcination temperature and pre-reflux period of the Ga–Mg-hydrotalcite catalyst on the reaction induction period. The induction period is decreased very markedly with increasing the calcination temperature (from 80 to 200 °C) or the pre-reflux period (from 0.25 to 7.0 h), mostly due to removal of water molecules occluded between the interlamellar layers of the hydrotalcite [14]. However, the Ga–Mg-HT-80 (or 200) does not show any benzene benzylation activity for the reaction period of 3 h. Interestingly, the hydrotalcite after its use in the toluene benzylation shows very high activity with almost zero induction period not only for the toluene benzylation but also for the benzene benzylation, which is relatively more difficult to accomplish [1] because of the absence of any electron-donating group (figure 1(c)). Moreover, the used catalyst also shows high activity for the acylation (by benzoyl chloride) of both toluene and benzene (figure 2 (b) and (c)). The used Ga–Mg-HT catalyst shows much higher activity in the benzylation or acylation reaction than the highly acidic catalysts, such as H-ZSM-5, HY, H-beta, sulfated ZrO_2 (or ZrO_2–Fe_2O_3), heteropolyacids, H–Ga(or Fe)MFI and H–GaAlMFI, reported earlier [2–8]. This catalyst also shows higher benzene or toluene benzylation activity when compared to the $GaCl_3$/Mont. K-10 [15] and Ga_2O_3/Si-MCM-41 [10] catalysts. Moreover, the hydrotalcite-based catalyst showed excellent reusability in both the benzylation and acylation reactions. After its fifth reuse, the half reaction time for the toluene benzylation and toluene benzoylation was 1.1 and 77 min, respectively.

Apart from its high activity and excellent reusability, the used hydrotalcite catalyst shows a very small effect of the presence of moisture in the reaction mixture on its performance in both the benzylation and acylation reactions (figure 2). Thus, unlike the commonly used acidic catalysts, the used hydrotalcite catalyst shows almost no moisture sensitivity. In the benzylation reaction, the presence of moisture causes a small increase in the induction period depend-

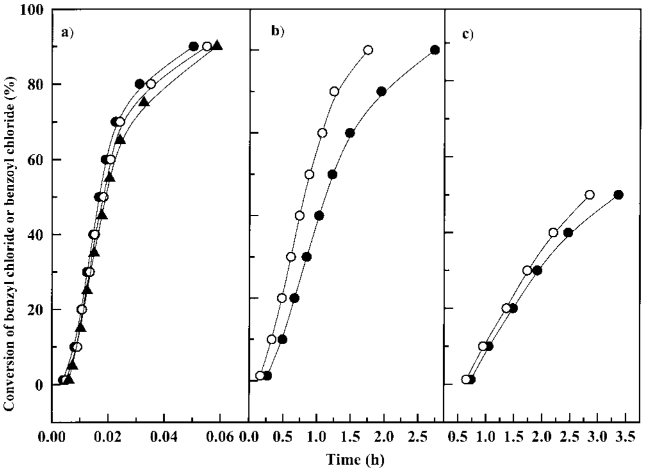

Figure 2. Influence of moisture in the reaction mixture on (a) benzylation of toluene, (b) acylation of toluene and (c) acylation of benzene over the Ga–Mg-HT-200 used before in the toluene benzylation (reaction mixture: without moisture (●), with (○) 1.5 or (▲) 2.5 g l^{-1} water).

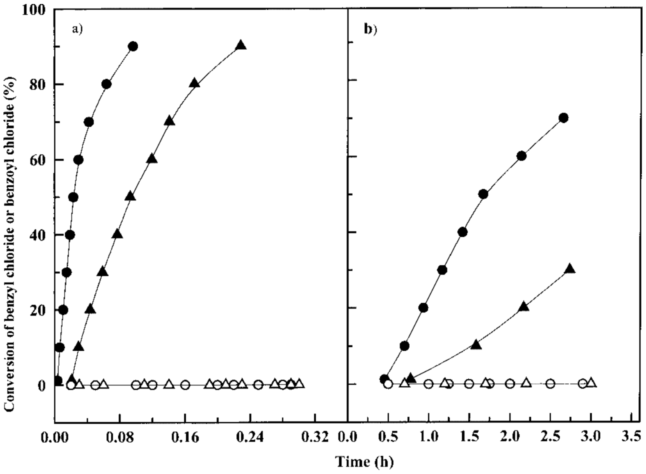

Figure 3. Influence of HCl treatment to Ga–Mg-HT-200 on its activity in (a) benzylation and (b) acylation reactions (benzylation or acylation of toluene (●) and benzene (▲) over the HCl-treated catalyst, benzylation or acylation of toluene (○) and benzene (△) over the untreated catalyst).

Table 1
Physico-chemical properties of the fresh, HCl-treated and used Ga–Mg-HT catalysts.

Catalyst	Color	Surface area (m^2 g^{-1})	pH of catalyst (0.1 g)–water (20 ml) mixture	XRD phases
Fresh Ga–Mg-HT-80	White	–	–	Pure HT
Fresh Ga–Mg-HT-200	White	9.7	9.4	Pure HT
HCl-treated Ga–Mg-HT-200	Off-white	6.1	7.8	HT (major), $MgCl_2$ (minor) and $GaCl_3$ (minor)
Used Ga–Mg-HT-200	Yellowish	2.3	7.3	$GaCl_3$, $MgCl_2$ and MgO, $MgCO_3$ (trace)

Table 2
XPS data for the fresh, HCl-treated and used Ga–Mg-HT catalysts.

Catalyst	Binding energy (eV)					Relative surface composition (mol ratio)		
	C_{1s}	O_{1s}	Mg_{2p}	Ga_{2p}	Cl_{2p}	Ga/Mg	Cl/(Ga + Mg)	CO_3^{2-}/(Ga + Mg)
Fresh Ga–Mg-HT-200	285.0 288.3	531.8	50.1	1119.1	–	0.014	0.0	0.18
HCl-treated Ga–Mg-HT-200	285.0 288.2	532.0	50.2	1118.8	198.8	0.014	0.21	0.16
Used Ga–Mg-HT-200	285.0 288.4	532.4	51.6	1119.0	195.5	0.021	0.98	0.03

ing upon the concentration of water in the reaction mixture. However, after the induction period, the benzylation reaction proceeds with almost the same rate (figure 2(a)). In contrast, in the case of the acylation, the presence of moisture causes a small decrease in the induction period and an appreciable increase in the reaction rate, thus showing a beneficial effect (figure 2 (b) and (c)).

It is interesting to note that the induction period for the fresh hydrotalcite catalyst is quite large but after its use, it is drastically reduced (figure 1). Also, after the induction period the toluene benzylation proceeds rapidly almost at the same rate in all these cases. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and this process of the catalyst activation is enhanced after the removal of strongly held water molecules between the interlamellar space. For confirming this hypothesis, the fresh hydrotalcite catalyst was first treated with HCl vapors and then used for the reactions; the results on both the fresh and HCl-treated hydrotalcite catalysts are compared in figure 3. The results are consistent with the hypothesis. After the HCl treatment, the benzylation and acylation activity of the catalyst is increased drastically. The HCl-treated catalyst shows performance in both the reactions comparable to that showed by the used catalyst (figures 1(c), 2 (b) and (c) and 3).

Results of the characterization of the fresh, HCl-treated and used (in the toluene benzylation) Ga–Mg-HT catalysts are presented in tables 1–3. After the HCl treatment and/or use in the reaction of the hydrotalcite catalysts,

Table 3
IR data for the fresh, HCl-treated and used Ga–Mg-HT catalysts.

Catalyst	IR frequency in different regions (cm^{-1})			
	$>$3000 cm^{-1}	1600–1700 cm^{-1}	1300–1400 cm^{-1}	500–600 cm^{-1}
Fresh Ga–Mg-HT-200	3525	1643	1377.1	577
HCl-treated Ga–Mg-HT-200	3400	1639	1377.1	575
Used Ga–Mg-HT-200	3360	1614	1377.1	540

- its color and crystalline phases are changed (table 1);
- its surface area and basicity are reduced (table 1);
- its surface composition is changed drastically, the surface Cl/(Ga + Mg) ratio is increased markedly, while the surface CO_3^{2-}/(Ga + Mg) ratio is decreased (table 2), and
- its IR frequency in the different regions (except 1377.1 cm^{-1}) are shifted towards lower side (table 3).

All the above reveal that the catalyst undergoes an appreciable change in its surface properties by the HCl treatment and a structural collapse after its use in the reaction. The catalyst in its most active form seems to consist of chlorides of Ga and Mg dispersed on MgO.

Further studies are needed for understanding the reaction mechanism and beneficial moisture effect for the acylation reactions over the used and/or HCl-gas-pretreated Ga–Mg-HT catalysts.

4. Conclusions

Ga–Mg hydrotalcite, a basic anionic clay, shows a very large induction period in the benzylation of toluene. But after its use in the reaction or HCl pretreatment, the hydrotalcite-derived catalyst shows very high activity in the benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of toluene and also high activity in the benzene benzylation or acylation reaction, with a drastic reduction in the induction period, even in the presence of appreciable moisture in the reaction mixture. The structure and basic nature of the hydrotalcite are changed, but not very significantly, by the HCl pretreatment. However, after the use in the reaction, there is a structural collapse of the hydrotalcite, forming different crystalline phases, *viz.* $GaCl_3$, $MgCl_2$ and MgO as major phases and also the surface composition (Ga/Mg, Cl/(Ga + Mg) and CO_3^{2-}/(Ga + Mg) mole ratios) is changed markedly. The hydrotalcite-derived catalyst in its most active form consists of highly dispersed gallium and magnesium chlorides on MgO. The presence of moisture has beneficial effects on the acylation reactions; because of the moisture the induction period is decreased and the reaction rate is enhanced.

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