

Highly active and reusable catalyst from Fe-Mg-hydrotalcite anionic clay for Friedel–Crafts type benzylation reactions

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Abstract. Fe-Mg-hydrotalcite (Mg/Fe = 3) anionic clay with or without calcination (at 200–800°C) has been used for the benzylation of toluene and other aromatic compounds by benzyl chloride. Hydrotalcite before and after its calcination was characterized for surface area, crystalline phases and basicity. Both the hydrotalcite, particularly after its use in the benzylation reaction, and the catalyst derived from it by its calcination at 200–800°C show high catalytic activity for the benzylation of toluene and other aromatic compounds. The catalytically active species present in the catalyst in its most active form are the chlorides and oxides of iron on the catalyst surface.

Keywords. Fe-Mg-hydrotalcite; activation by calcinations; benzylation of toluene; benzylation of aromatic compounds.

1. Introduction

Liquid-phase Friedel–Crafts type benzylation of aromatic compounds, using homogeneous catalysts, are the general Friedel–Crafts type reactions used in organic synthesis.¹ However, the commonly used homogeneous catalysts (viz. AlCl₃, BF₃ and H₂SO₄) 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 require moisture-free solvent and reactants and anhydrous conditions, and also dry atmosphere for their handling. A number of highly acidic solid catalysts, such as heteropolyacids,² sulphated ZrO₂ or Fe₂O₃,³ Nafion-H² and Fe- and Ga-substituted H-ZSM-5⁴ for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene⁵ are reported in the literature. However, the reports on the use of basic catalysts for the benzylation reactions are scarce.⁶

Recently, we have observed high activity of supported basic In₂O₃ in these reactions.⁷ Hydrotalcite anionic clays are known to be highly basic solids.⁸ Very recently, we have found that Ga-Mg-hydrotalcite anionic clay, after its first use in the reaction or HCl

gas pretreatment, shows very high activity in the benzylation of toluene and benzene, even in the presence of moisture in the reaction mixture.^{9,10} In the present paper, we report that Fe-Mg-hydrotalcite shows high activity in the benzylation of toluene and substituted benzene by benzyl chloride (ArH + C₆H₅CH₂Cl → ArCH₂C₆H₅ + HCl). Influence of the calcination (at different temperatures) of the hydrotalcite on its catalytic performance in the benzylation has also been thoroughly investigated.

2. Experimental

Fe-Mg-hydrotalcite (Mg/Fe mole ratio = 3), having a formula: [Fe_{0.25}Mg_{0.75}(OH)₂]^{+0.25}[CO₃²⁻]_{0.125}.nH₂O, was synthesized by the co-precipitation method described earlier.¹¹ The hydrotalcite was dried at 80°C for 12 h and this sample is designated as Fe-Mg-HT-80. Fe-Mg-HT-200, Fe-Mg-HT-500, and Fe-Mg-HT-800 hydrotalcite derived samples were obtained by calcining the Fe-Mg-HT-80 at 200, 500 and 800°C, respectively, for 4 h in a muffle furnace. All these solid samples were characterized for their specific area (using surface area Analyzer, Quantachrome, USA) and also by XRD [using a Philips Diffractometer (1730 series) and CuK α radiation]. The hydrotalcite (Fe-Mg-HT-80) was characterized by its thermal

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analysis – thermal gravimetric (TG), differential thermal gravimetric (DTG) and differential thermal analysis (DTA) in the presence of static air at a linear heating rate of 10°C/min from 25° to 900°C.

The benzylation reactions over the different Fe-Mg-hydrotalcite based catalysts were carried out in a magnetically stirred glass reactor (capacity: 25 cm³) fitted with a reflux condenser, mercury thermometer and arrangement for continuously bubbling moisture-free N₂ (30 ml 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 was started by injecting 1.0 ml of benzyl chloride in the reaction mixture, containing 13 ml of liquid aromatic substrate and catalyst (0.1 g). All the reactions were carried out at 80 or 110°C following the procedures described earlier.^{4,7} In all the cases, the product formed in the benzylation was mainly mono-benzylated one (ArCH₂C₆H₅, Ar = aromatic substrate group) and there was no formation of polycondensation products, such as poly benzyl chloride. The reaction products were identified by GC.

To study the reusability of the catalyst, the catalyst used in the particular reaction was removed from the reaction mixture by filtration and then washed (with the aromatic substrate) before its reuse in the reaction.

3. Results and discussion

3.1 Characterization of Fe-Mg-HT

The hydrotalcite structure of the synthesized Fe-Mg-anionic clay material was confirmed by its X-ray analysis (figure 1a); the XRD spectra of the material correspond to that of hydrotalcite.⁸

The hydrotalcite and its solid products of calcination (in air at 200, 500 and 800°C) have been characterized for their surface area and basicity (in terms of the pH of catalyst–water slurry) and crystalline phases (table 1). However, only qualitative information could be obtained on the concentration of various phases (e.g. MgO, Fe₂O₃, MgFe₂O₄ spinel etc.) in the active catalyst.

The Fe-Mg-hydrotalcite was characterized also by its thermal gravimetric (TG) analysis and differential thermal gravimetric (DTG) and differential thermal analysis (DTA) from 25° to 900°C, as shown in figure 2. The thermal decomposition of the hydrotalcite occurs in three steps: (1) 12.6% wt. loss from 25° to 185°C, (2) 35.1% wt. loss from 185° to 398°C and (3) 41.0% wt. loss from 398° to 814°C. The peak maxi-

imum temperatures for the observed DTG/DTA peaks are 174° and 364°C. The DTA peaks indicate that the decomposition in all the steps is endothermic. The weight loss in the first step is expected owing to the desorption of adsorbed water, whereas that in the second step may be due to the removal of the water of hydration from the hydrotalcite. However, the weight loss in the third step is expected because of the dehydroxylation and decarbonation of the hydrotalcite with the destruction of its structure.

3.2 Benzylation over Fe-Mg-HT-80

Results of the benzylation of toluene and other aromatic compounds over the fresh and used (in the respec-

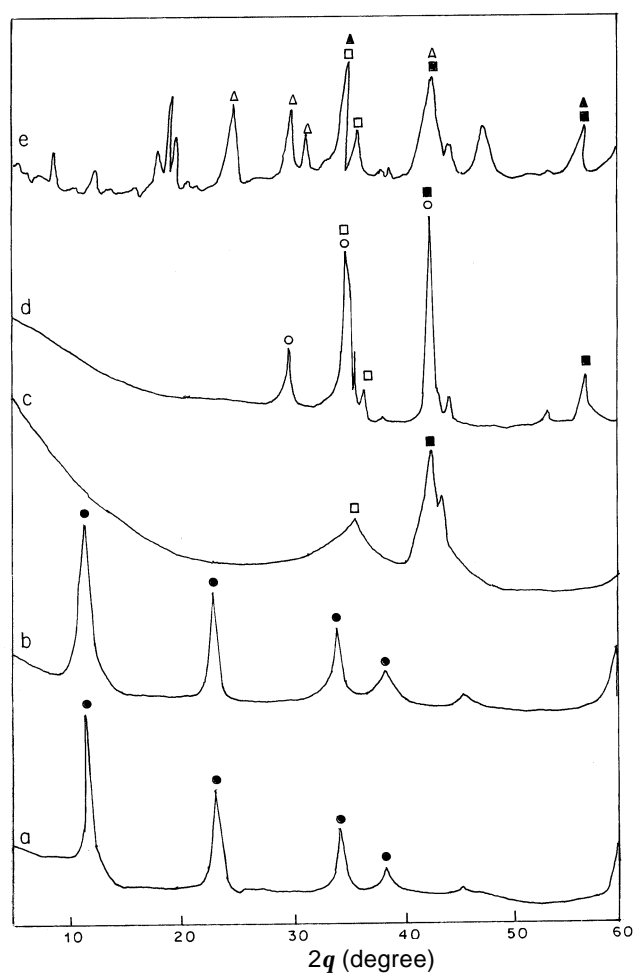
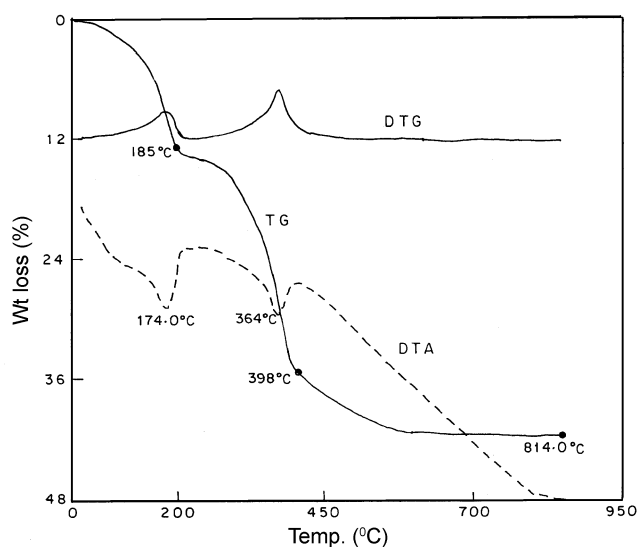
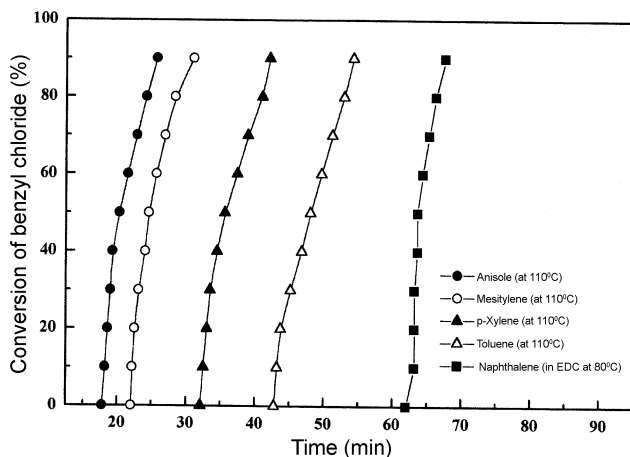


Figure 1. XRD of (a) Fe-Mg-HT-80 (fresh), (b) Fe-Mg-HT-200 (fresh), (c) Fe-Mg-HT-500 (fresh), (d) Fe-Mg-HT-800 (fresh) and (e) used Fe-Mg-HT-80 after use in the benzylation of toluene. [Crystalline phases: Pure HT (●), MgFe₂O₄ spinel (○), MgO (■), Fe₂O₃ (□), MgCl₂ (▲) and FeCl₃ (△).]

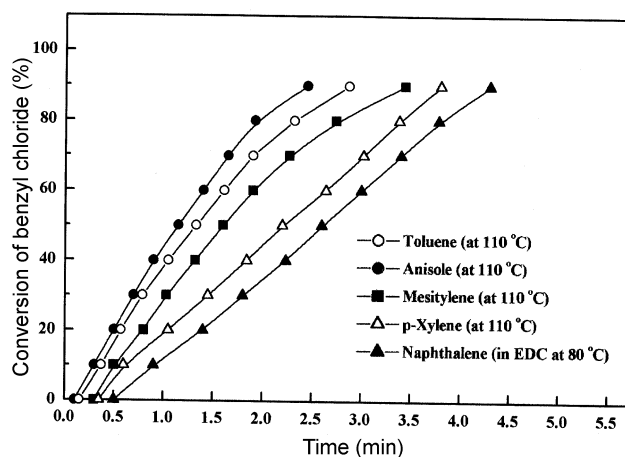
Table 1. Physico-chemical properties of fresh, calcined and used Fe-Mg-HT (Mg/Fe = 3) catalysts.

Catalyst	Colour	Surface area (m ² g ⁻¹)	pH of catalyst ^a	XRD phases
Fresh Fe-Mg-HT-80	Light brown	58	9.6	Pure HT
Fresh Fe-Mg-HT-200	Light brown	70	8.7	Pure HT
Fresh Fe-Mg-HT-500	Pale yellow	78	7.8	MgO and Fe ₂ O ₃
Fresh Fe-Mg-HT-800	Pale yellow	95	7.6	MgO, Fe ₂ O ₃ and MgFe ₂ O ₄
Used Fe-Mg-HT-80	Pale yellow	32.3	7.2	MgCl ₂ , FeCl ₃ , Fe ₂ O ₃ and MgO

^a0.15 g catalyst in 10 ml distilled water

**Figure 2.** TG, DTG and DTA of Fe-Mg-HT-80 (heating rate = 10°C/min).**Figure 3.** Activity of fresh Fe-Mg-HT-80 catalyst in the benzylation of toluene and other aromatic compounds by benzyl chloride.

tive benzylation reactions at 80° or 110°C) Fe-Mg-HT-80 are presented in figure 3 and figure 4, respectively. The results can be summarized as follows:

**Figure 4.** Activity of used Fe-Mg-HT-80 catalyst in the benzylation of toluene and other aromatic compounds by benzyl chloride.

– For the fresh Fe-Mg-HT-80, the reaction induction period is large. However, after the induction period the reaction proceeds at a high rate.

– The reaction induction period is found to depend strongly on the aromatic substrate. The induction period for the benzylation of different aromatic compounds was as follows: anisole (17.5 min) < mesitylene (22.0 min) < *p*-xylene (32.0 min) < toluene (43.0 min) < naphthalene (62.5 min).

– Interestingly, the hydrotalcite after it use in the benzylation reaction showed very high benzylation activity (figure 4); the induction period for the benzylation of all the aromatic substrates is reduced drastically.

– Benzylation activity of the used catalyst for different aromatic substrates (measured in terms of time required for half the reaction, $t_{1/2}$) is found to be in the following order: anisole ($t_{1/2} = 1.1$ min) < toluene (1.3 min) < mesitylene (1.6 min) < *p*-xylene (2.2 min) < naphthalene (2.6 min).

The XRD of the used catalyst (table 1) showed the presence of crystalline phases (viz. Fe₂O₃, MgO,

MgCl₂ and FeCl₃) different from that observed for the fresh Fe-Mg-HT-80. This clearly shows a phase transformation and/or structural breakdown for the hydrotalcite during its use in the reaction, mainly by the HCl produced in the reaction. The basicity of the hydrotalcite also decreases after its use in the reaction (table 1). It would be interesting to know the activity of chloride anion exchanged Fe-Mg-HT. This study will be carried out later.

The observed high benzylation activity of the hydrotalcite after the induction period is therefore attributed to the formation of catalytically active species (viz. Fe₂O₃ and FeCl₃) on the surface of the hydrotalcite during the induction period by the interaction of benzyl chloride and HCl (formed in the initial reaction) with the basic hydrotalcite. The HCl formed in the benzylation reaction is responsible for the structural breakdown of the hydrotalcite.

The induction period for the different aromatic substrates is different (figure 3). This is attributed to a difference in the reactivity of the aromatic substrates with benzyl chloride on the catalyst. It is interesting to note from the results in figure 4 that the rate of benzylation shows no expected (by the classical Friedel–Crafts mechanism) dependence on the presence of different electron donating group(s) in the aromatic substrate; the rate of toluene benzylation is much higher than that of the mesitylene or *p*-xylene benzylation. Thus, the classical Friedel–Crafts mechanism does not simply hold good in the present catalytic system. This is consistent with that observed earlier in case of the benzylation of substituted benzenes over supported In₂O₃, Ga₂O₃, GaCl₃ and InCl₃ catalysts.^{7,12–14}

3.3 Effect of calcination temperature of Fe-Mg-HT

Results showing the influence of calcination temperature of the Fe-Mg-HT catalyst on its performance in the benzylation of toluene at 110°C are presented in figure 5. The results can be summarized as follows:

– Increase in the calcination temperature causes a large decrease in the reaction induction period, depending upon the temperature; higher the calcination temperature, lower the induction period (43.0, 11.5, 4.3 and 1.5 min for the catalyst calcined at 80, 200, 500 and 800°C, respectively).

– Benzylation activity of the catalyst is increased markedly on increasing its calcination temperature;

the time for half the reaction (measured in terms of $t_{1/2}$) is 48.1, 13.0, 6.0 and 2.5 min for the catalyst calcined at 80, 200, 500 and 800°C respectively.

The results clearly show that the activation of the hydrotalcite catalyst for the benzylation reaction depend strongly upon the calcination temperature. Catalyst activation is expected because of the dehydration and/or decomposition of the Fe-Mg-HT-80 followed by the formation of single and/or mixed metal oxide phases, as shown by the XRD spectra of the hydrotalcite calcined at different temperatures (table 1). The surface area of the catalyst also increases with increasing calcination temperature. However, the very large increase in the benzylation activity of the catalyst with the increase in calcination temperature cannot be attributed merely to the observed increase in the catalyst surface area. It is attributed mainly to the dehydration (at 200°C) and/or formation of catalytically active metal oxide species during calcination (at ≥ 500°C).

After the calcination at 200°C, the hydrotalcite structure is retained but the XRD peaks are broadened. However, after calcination at 500°C, the hydrotalcite structure is destroyed with the formation of metal oxide (MgO and Fe₂O₃) phases. In the calcination at 800°C, two distinct phases, MgO and MgFe₂O₄ (spinel), are formed. This is consistent with that observed earlier.¹⁵ The activation of the Fe-Mg-HT-80 by its calcination at 200°C is expected because of the removal of the water of hydration present in the parent hydrotalcite, resulting in an increase in the surface

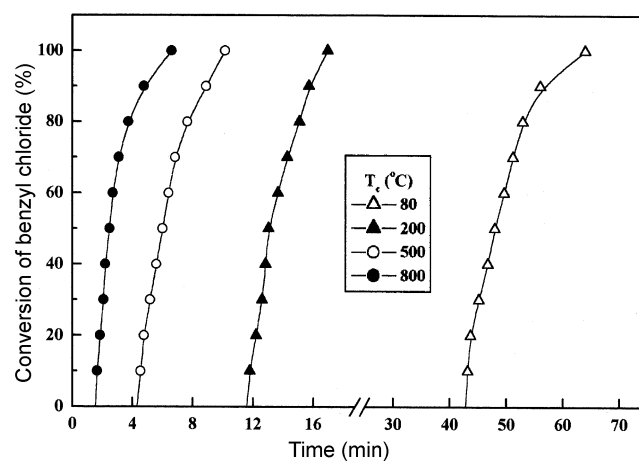


Figure 5. Influence of calcination temperature (T_c) of Fe-Mg-HT on its activity in the benzylation of toluene (at 110°C) by benzyl chloride.

area (from 58 to 70 m² g⁻¹). The activation of the hydrotalcite by its calcination at the higher temperature is attributed to both the removal of the water of hydration from the catalysts and the formation of single and/or mixed metal oxide phases such as finely dispersed Fe₂O₃ on MgO (formed at 500°C) or finely dispersed MgFe₂O₄ on MgO (formed at 800°C), with increase in the surface area.

4. Conclusions

Fe-Mg-hydrotalcite (Mg/Fe = 3) showed high activity in the benzylation of toluene and other aromatic compounds (anisole, mesitylene, *p*-xylene and naphthalene). After its use in the benzylation, the reaction induction period for the benzylation of toluene and other aromatic compounds is drastically reduced. During the reaction the hydrotalcite is structurally collapsed with the formation of metal chlorides and oxides. Upon its calcination at higher temperature (≥ 300°C), the calcined hydrotalcite shows high benzylation activity; its benzylation activity increases with increase in the calcination temperature. Catalyst activation due to the calcination at different temperatures (T_c) is attributed to dehydration (for $T_c = 200^\circ\text{C}$), formation of metal oxides (for $T_c = 500^\circ\text{C}$) or MgO and MgFe₂O₄ (for $T_c = 800^\circ\text{C}$), causing successive increases in surface area. For the catalyst (hydrotalcite or derived from hydrotalcite) in its most active form, the catalytically active species for benzylation are the finely dispersed FeCl₃ and Fe₂O₃ on MgO.

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