

In-Mg-hydrotalcite anionic clay as catalyst or catalyst precursor for Friedel–Crafts type benzylation reactions

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Abstract

In-Mg-hydrotalcite (Mg/In=3) anionic clay with or without calcination (at 200–800 °C) or HCl pretreatment at different temperatures (26 and 80 °C) and periods (0.1 or 1.0 h) has been used for the benzylation of benzene and/or substituted benzenes by benzyl chloride. The hydrotalcite before and after its calcination or HCl pretreatment was characterized for its surface area, crystalline phases and basicity. The hydrotalcite particularly after its use in the benzylation reaction, and the catalyst derived from it by its calcination at 800 °C followed by HCl pretreatment (at 80 °C for 1.0 h), shows high catalytic activity even for the benzylation of benzene. The catalytically active species present in the catalyst in its most active form are the chlorides and oxides of indium on the catalyst surface.

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1. Introduction

Liquid phase Friedel–Crafts type benzylation of aromatic compounds, using homogeneous catalysts, are commonly practiced Friedel–Crafts type reactions 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 demand moisture-free solvent and reactants and anhydrous catalyst, and also dry atmosphere for their handling. A number of highly acidic solid catalysts, such as heteropolyacids [2], sulphated ZrO₂ or Fe₂O₃ [3], Nafion-H [2] and Fe- and Ga-substituted H-ZSM-5 [4] for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene [5], 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 In-Mg-hydrotalcite, even without HCl pretreatment, shows high activity in the benzylation of benzene and substituted benzene by benzyl chloride (ArH + C₆H₅CH₂Cl → ArCH₂C₆H₅ + HCl). Influence of the HCl pretreatment and calcination (at different temperatures) of the hydrotalcite on its catalytic performance in the benzylation has also been thoroughly investigated.

2. Experimental

In-Mg-hydrotalcite (Mg/In mole ratio=3), having a formula: [In_{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

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sample is designated as In-Mg-HT-80. In-Mg-HT-200, In-Mg-HT-300, In-Mg-HT-500 and In-Mg-HT-800 hydrotalcite derived samples were obtained by calcining the In-Mg-HT-80 at 200, 300, 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 Cu K α radiation]. The hydrotalcite (In-Mg-HT-80) was characterized by its thermal 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 1000 °C.

The benzylation reactions over the different In-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]. The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N₂ in a 0.1 M NaOH solution containing phenolphthalein indicator) as a function of time and also by analyzing the reaction mixture for unconverted benzyl chloride and benzylation products at the end of the experiment by gas chromatography. There was a good agreement between the benzyl chloride conversion obtained from the acid–base titration and the GC analysis. 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 polybenzyl chloride. 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.

HCl gas treatment to the catalyst, In-Mg-HT-800, was given by bubbling a HCl gas–N₂ mixture (20 mol% HCl) at a rate of 25 ml min⁻¹ through a mixture containing 13 ml liquid aromatic substrate (to be used in the reaction) and 0.1 g catalyst in the glass reactor at room temperature (at 26 °C for 1.0 h) or at 80 °C for different periods (0.1 and

1.0 h). The HCl treated mixture was then flushed with pure N₂ (30 cm³ min⁻¹) at 80 °C for a sufficient period to remove the physically adsorbed or absorbed HCl from the reaction mixture and then the reaction was started by injecting 1.0 ml of the benzylation agent.

3. Results and discussion

3.1. Characterization of In-Mg-hydrotalcite

The hydrotalcite structure of the synthesized In-Mg-anionic clay material was confirmed by its X-ray analysis (Fig. 1a); the XRD spectra of the material correspond to those of hydrotalcite [8].

The In-Mg-hydrotalcite was characterized also by its thermal gravimetric analysis and differential thermal gravimetric and differential thermal analysis from 25 to 1000 °C, as shown in Fig. 2. The thermal decomposition of the hydrotalcite occurs in four steps: (1) 9.7 wt.% loss from 25 to 192 °C, (2) 3.2 wt.% loss from 192 to 282 °C, (3) 12.5 wt.% loss from 282 to 405 °C and (4) 3.6 wt.% loss from 405 to 1000 °C. The peak maximum temperatures for the observed DTG/DTA peaks are 178, 271 and 370 °C. The DTA peaks indicate that the decomposition in all the steps is endothermic. The weight loss in the first step is expected due 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. In the fourth step, a small weight loss is expected to result from the decomposition of metal carbonate, particularly MgCO₃ formed during the third step of the decomposition.

The hydrotalcite and its solid products of calcination (in air at 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).

3.2. Benzylation over In-Mg-HT-80

Results of the benzylation of benzene and substituted benzenes over the fresh and used (at 80 or 110 °C) In-Mg-HT-80 catalysts are presented in Figs. 3 and 4.

In case of the benzylation reaction over the fresh catalysts, the reaction induction period is found to depend

Table 1
Physico-chemical properties of the fresh, calcined, HCl pretreated and used In-Mg-hydrotalcite (Mg/In = 3) catalysts

Catalyst	Color	Surface area (m ² g ⁻¹)	pH of catalyst ^a	XRD phases
Fresh In-Mg-HT-80	White	106	9.45	Pure HT
Fresh In-Mg-HT-800	Yellowish	71	10.2	In ₂ O ₃ , MgIn ₂ O ₄ and MgO
In-Mg-HT-800 pretreated by HCl at 80 °C for 0.1 h	Off-white	17.6	8.75	MgCl ₂ , InCl ₃ , In ₂ O ₃ , MgO and MgIn ₂ O ₄
In-Mg-HT-800 pretreated by HCl at 80 °C for 1.0 h	Off-white	1.8	7.8	MgCl ₂ , InCl ₃ , In ₂ O ₃ , MgO and MgIn ₂ O ₄
Used In-Mg-HT-80	Off-white	35.6	7.68	MgCl ₂ , InCl ₃ , In ₂ O ₃ and MgO

^a 0.15 g catalyst in 10 ml distilled water.

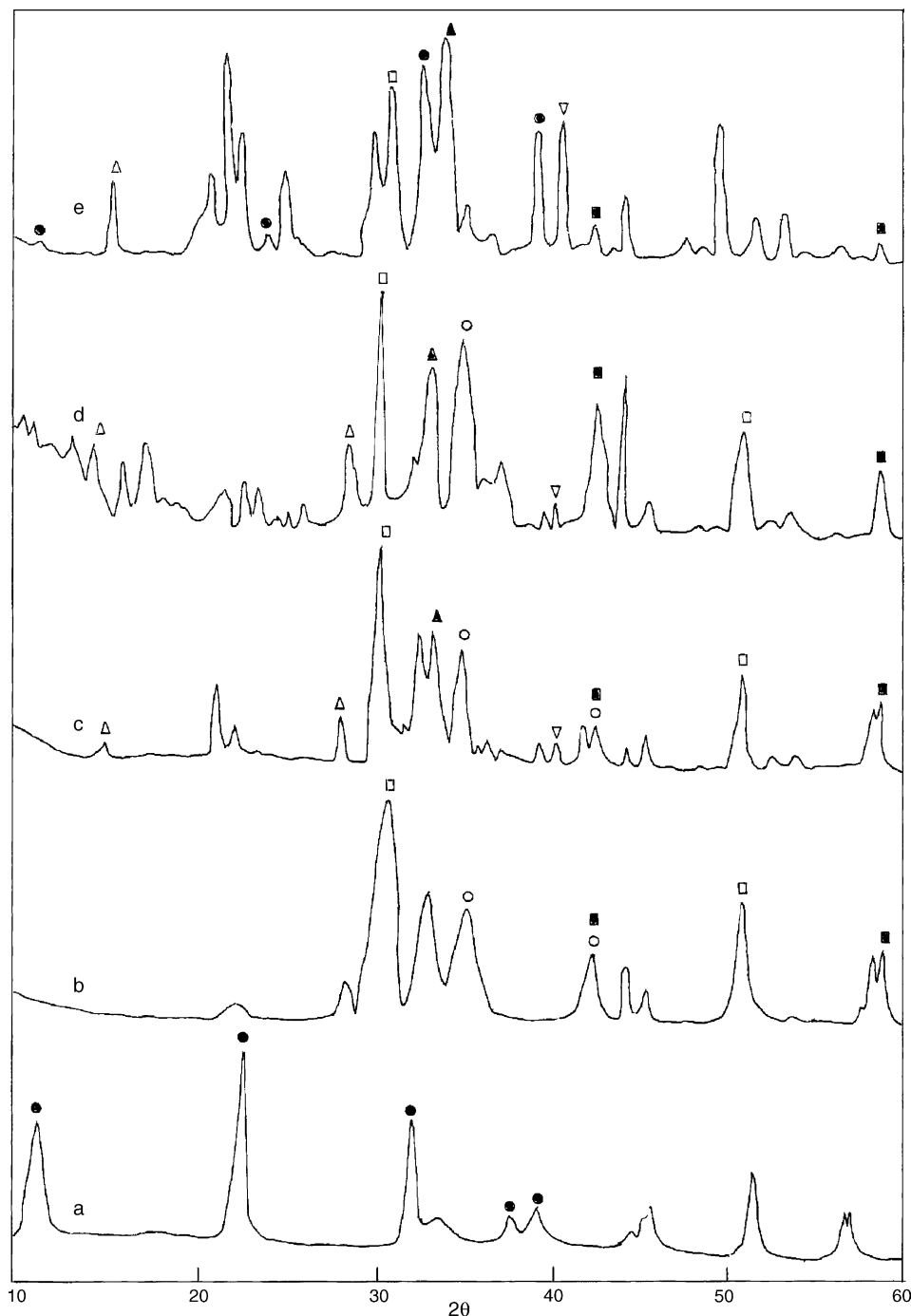


Fig. 1. XRD of: (a) In-Mg-HT-80 (fresh), (b) In-Mg-HT-800 (fresh), (c) In-Mg-HT-800 pretreated by HCl at 80°C for 0.1 h, (d) In-Mg-HT-800 pretreated by HCl at 80°C for 1.0 h and (e) In-Mg-HT-80 after its use in the benzylation of benzene [crystalline phases: pure HT (●), MgIn₂O₄ spinel (○), MgO (■), In₂O₃ (□), MgCl₂ (▲) and InCl₃ (Δ)].

strongly on the aromatic substrate. The induction period for the benzylation of different aromatic compound was as follows: mesitylene (9.1 min) < toluene (9.4 min) < *p*-xylene (46.0 min) < anisole (48.53 min) < naphthalene (52.15 min) < benzene (67.0 min).

Interestingly, the hydrotalcite after its use in the benzylation reaction showed very high activity (i.e. Fig. 4); the induction period for the benzylation of all the aromatic

substrate is reduced drastically. The benzylation activity of the used catalyst for the different aromatic substrates (measured in terms of time required for half the reaction, $t_{1/2}$) is found to be in the following order: toluene ($t_{1/2}$ = 1.2 min) < *p*-xylene (8.5 min) < anisole (9.5 min) < naphthalene (12.3 min) < benzene (32.4 min).

The XRD of the used catalyst (Fig. 1e) showed the presence of crystalline phases (viz. MgCl₂, InCl₃, In₂O₃ and

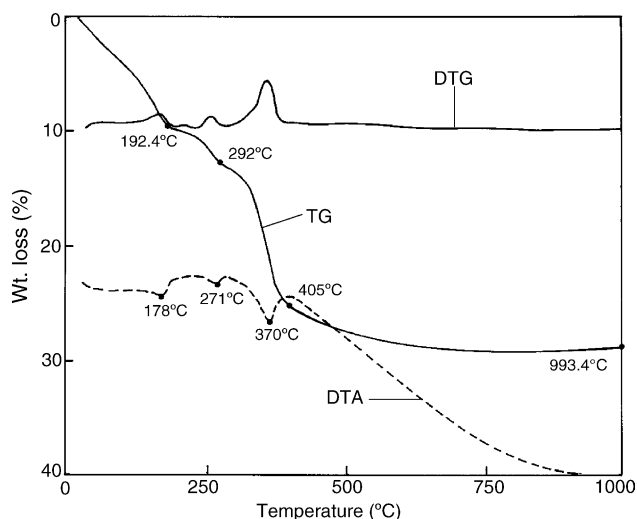


Fig. 2. TG, DTG and DTA of In-Mg-HT-80 (heating rate = 10 °C/min).

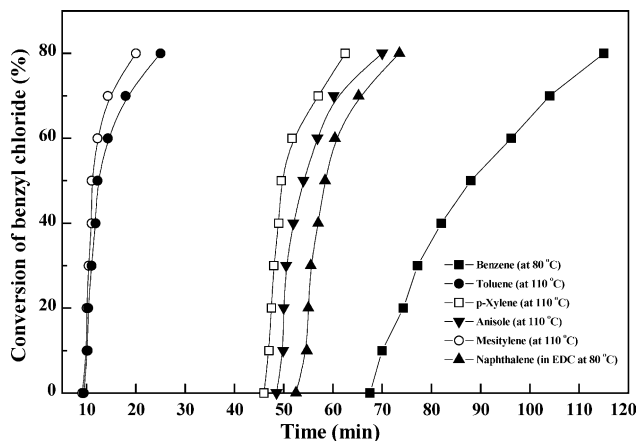


Fig. 3. Activity of fresh In-Mg-HT-80 catalyst in the benzylation of benzene and substituted benzenes.

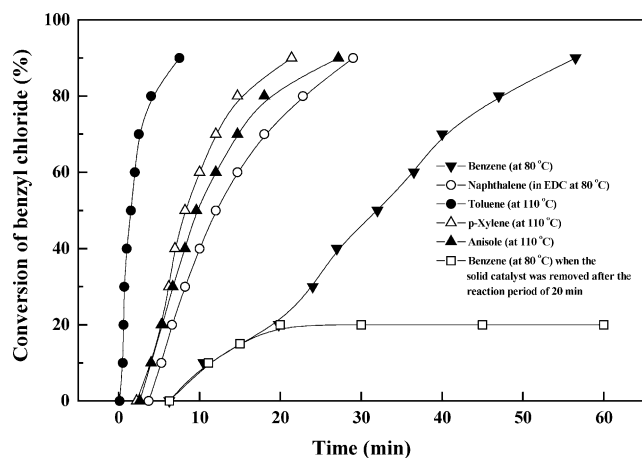


Fig. 4. Activity of used In-Mg-HT-80 catalyst in the benzylation of benzene and substituted benzenes.

MgO) different from that observed for the fresh In-Mg-HT-80. This clearly shows a phase transformation/structural breakdown of the hydrotalcite during its use in the reaction, mainly by the HCl produced in the reaction. The basicity of the hydrotalcite is also decreased after its use in the reaction (Table 1).

From the results in Fig. 4, it is also interesting to note that, when the catalyst was removed after carrying out the benzene benzylation reaction for 20 min by filtration, there was almost no conversion of benzyl chloride. This indicates that the benzylation reaction is mainly catalyzed by the solid catalyst; the leached out metal chloride species, if any, from the catalyst play only a little or no role in the catalytic reaction.

The observed high benzylation activity of the hydrotalcite after the induction period is therefore attributed to the formation of catalytically active species (viz. InCl_3 and In_2O_3 as shown in the XRD), which are strongly adsorbed on the catalyst, during the induction period by the interactions 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.

It may be noted that the induction period of the benzylation for the different aromatic substrates is different (Fig. 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 Fig. 4 that the rate of benzylation showed no 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 anisole 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 In_2O_3 , Ga_2O_3 , GaCl_3 and InCl_3 catalysts [7,12–14].

3.3. Effect of calcination temperature of the hydrotalcite

Results showing the influence of calcination temperature of the In-Mg-HT-80 catalyst on its performance in the benzylation of benzene at 80 °C are presented in Fig. 5. The results can be summarized as follows.

The increase in the calcination temperature from 80 to 200 °C causes a large decrease in the induction period, mostly because of the desorption of adsorbed water from the hydrotalcite [7]. However, a further increase in the calcination temperature up to 300 °C or above (up to 800 °C) results in a drastic increase in the reaction induction period; the calcined hydrotalcite showed no benzene benzylation activity for the reaction period of 2 h. This is expected because of the dehydration and/or structural breakdown of the hydrotalcite at ≥ 300 °C. After its calcination at 800 °C, the hydrotalcite is transformed into a mixture of MgO and MgIn_2O_4 spinel with smaller amounts of In_2O_3 (Fig. 1b and Table 1).

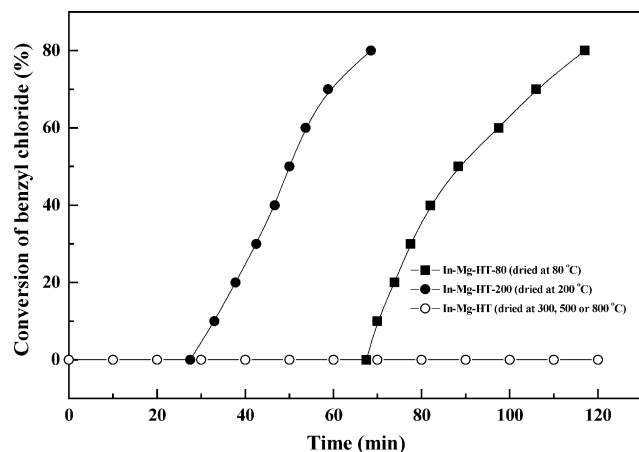


Fig. 5. Influence of calcinations temperature (T_c) of In-Mg-HT on its activity in the benzylation of benzene (at 80 °C).

3.4. Effect of HCl pretreatment to In-Mg-HT-800

Results showing the influence of HCl pretreatment to the In-Mg-HT-800 (at different temperatures and periods) on the benzylation of benzene at 80 °C are presented in Fig. 6. From the results, following important observations can be made:

- The fresh In-Mg-HT-800 catalyst showed no benzylation activity for the reaction period of 3 h. However, after the HCl gas pretreatment, the reaction proceeds at a high rate.
- The HCl pretreatment caused a change in the reaction induction period, depending upon the pretreatment temperature and period. The In-Mg-HT-800 pretreated with HCl at 80 °C for 1.0 h showed the best performance for the benzene benzylation. The reaction induction period for the In-Mg-HT-800 pretreated by HCl at 80 °C for 0.1 h, 26 °C for 1.0 h and 80 °C for 1.0 h is 4.5, 2.5 and 1.4 min, respectively.
- The XRD of the HCl pretreated In-Mg-HT-800 catalyst clearly indicated the chloridation of the catalyst, caus-

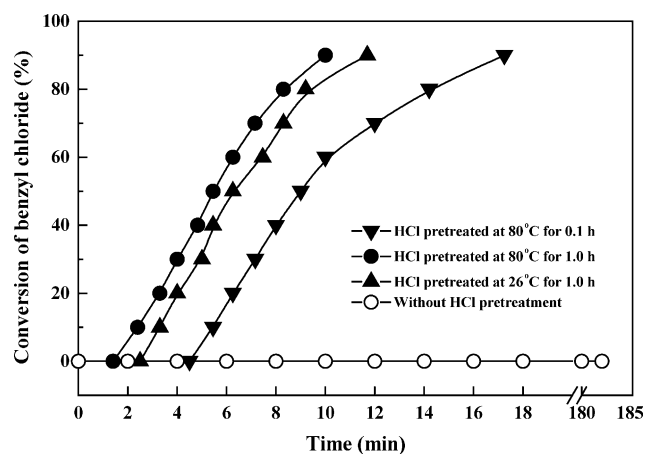


Fig. 6. Influence of HCl pretreatment (at different temperatures and periods) to In-Mg-HT-800 catalyst on its benzyl chloride conversion activity and induction period in the benzylation of benzene (at 80 °C).

ing the destruction of its spinel structure (Fig. 1b–d and Table 1). After the HCl pretreatment, the basicity and surface area of the catalyst are decreased markedly, depending upon the severity of the HCl treatment (Table 1).

All the above results indicate that the active catalytic species involved in the benzylation reactions over the activated (by HCl treatment before the reaction or during the reaction) catalyst are mainly the InCl_3 and In_2O_3 species on the catalyst surface. Unlike the classical Friedel–Crafts Lewis acid catalysts (e.g. AlCl_3), these catalytically active species show little or no sensitivity to the small amount moisture present in the reaction mixture [7,12–14]. The redox properties of the activated catalyst (InCl_3 and In_2O_3) seem to play important role in deciding the catalytic activity in the present case, involving a redox mechanism similar to that suggested earlier for the benzylation reactions over cation exchanged clays [15], supported thallium oxide [16] and oxides and chlorides of gallium and indium [12–17].

4. Conclusions

In-Mg-hydrotalcite ($\text{Mg}/\text{In}=3$) showed high activity in the benzylation of benzene and substituted benzene (toluene, anisole, *p*-xylene, mesitylene and naphthalene). After its use in the benzylation, the reaction induction time for the benzylation of benzene and substituted benzene 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 no benzylation activity for a long period (3 h). However, the calcined (structurally broken) hydrotalcite, containing MgO , In_2O_3 and/or MgIn_2O_4 , can be highly activated by its HCl pretreatment; the HCl pretreated catalyst shows very high activity even for the benzylation of benzene. For the catalyst in its most active form, the catalytically active species for the benzylation are InCl_3 and In_2O_3 on the catalyst surface.

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