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Highly active and moisture-insensitive solid catalysts – $GaCl_3$ and $InCl_3$ supported on montmorillonite-K10 and Si-MCM-41 for benzylation of benzene

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$InCl_3$ and $GaCl_3$ supported on montmorillonite-K10 or on high silica mesoporous MCM-41 show very high activity in the benzylation of benzene by benzyl chloride (at 80 °C) with little or no effect in the presence of moisture in the catalyst or in the reaction mixture on their benzylation activity; the supported $InCl_3$ catalyst shows superior performance in the benzylation reaction in regard to both the activity and moisture insensitivity.

Keywords: benzylation of benzene by benzyl chloride, diphenylmethane, $InCl_3$/montmorillonite-K10, $GaCl_3$/montmorillonite-K10, $InCl_3$/Si-MCM-41, $GaCl_3$/Si-MCM-41

1. Introduction

Friedel–Crafts type reactions (e.g., alkylation of aromatic compounds) using homogeneous acid catalysts (e.g., $AlCl_3$, BF_3 and H_2SO_4, etc.) are practiced very commonly in organic synthesis [1]. The most commonly used acid catalyst for these reactions is anhydrous $AlCl_3$. This catalyst, however, poses several problems, such as difficulty in its separation and recovery, disposal of spent catalyst, corrosion, high toxicity, and, moreover, it demands moisture-free solvent and substrates for the reaction because of its very high moisture sensitivity. Its handling also demands moisture-free atmosphere. It is, therefore, of great practical importance to replace $AlCl_3$ and other similar homogeneous catalysts by reusable and easily separable catalysts (e.g., heterogeneous solid catalysts) having high activity for Friedel–Crafts type reactions, even in the presence of moisture. Earlier studies indicated that highly acidic solid catalysts, such as HY [2], H-ZSM-5 [2,3] and sulfated ZrO_2 [4] show poor activity in the benzylation of benzene and other aromatic compounds. Clark et al. [5] and Barlow et al. [6] reported high activity of a thermally activated clayzic catalyst ($ZnCl_2$ supported on montmorillonite-K10) for the benzylation of aromatic compounds. However, this clayzic catalyst showed low selectivity (~80%) for the monoalkylated product [5], and, moreover, it is very hygroscopic and, hence, highly moisture sensitive [6]. Recently, the $FeCl_3$/Mont.-K10 [7], sulfated Fe_2O_3–ZrO_2 [4] and H-FeMFI zeolite [3] catalysts are reported to have high activity in the benzylation of benzene. However, we have observed that these catalysts and other Fe-containing catalysts are highly active but less selective in the benzylation because of their very high activity also for the self-condensation of benzyl chloride [8]. We report here our preliminary results, showing very high activity/selectivity of $InCl_3$ and $GaCl_3$ supported on montmorillonite-K10 and high silica mesoporous MCM-41 in the benzylation by benzyl chloride of benzene (which is difficult to benzylate as compared to other aromatic compounds containing electron-donating groups, such as alkyl, alkoxy, OH, etc.), even in the presence of moisture in the catalyst or in the reaction mixture. The performance shown by the supported $InCl_3$ catalysts is far superior to that of supported $AlCl_3$, $ZnCl_2$ and $GaCl_3$.

2. Experimental

Supported metal chloride catalysts (loading of metal chloride = 10 wt%) were prepared by impregnating Mont.-K10 (montmorillonite-K10, Aldrich) and Si-MCM-41 (high silica mesoporous MCM-41 having surface area of 1140 $m^2\,g^{-1}$) with anhydrous metal chloride (purity 99.99%, Aldrich) from its acetonitrile solution by the incipient wetness technique and evaporating the solvent in vacuum oven at 120 °C for 8 h. The Lewis acid sites of the catalysts were studied by the IR spectroscopic studies of the pyridine adsorbed on the catalysts. The pyridine adsorption on the powdered catalyst was done by exposing the catalyst to pyridine vapors at room temperature and then evacuating at 150 °C for 4 h. Before use for the benzylation reaction or the IR studies, the catalysts were pretreated in a flow of moisture-free helium (20 $cm^3\,min^{-1}$) at 120 °C for 2 h to remove the adsorbed moisture from them. The benzylation reaction over the supported and unsupported metal chloride catalysts was carried out in a magnetically

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stirred glass reactor (capacity 25 cm^3) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N_2 (30 $cm^3\,min^{-1}$) through the liquid reaction mixture. The reaction was started by injecting benzyl chloride in the reaction mixture, containing benzene and the catalyst, under benzene reflux (at 80 °C). 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 N_2 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 that from the GC analysis. The conversion data were corrected for a small time lag (1.1 min) between the evolution of HCl in the reaction and the analysis of the evolved HCl by the titration. In all the cases except for clayzic catalysts, the product formed was mainly diphenylmethane; the formation of di- and higher alkylated benzenes was only 3–5 wt% of the products and there was no formation of polybenzyl chloride. TON (turnover number) is estimated as moles of benzyl chloride converted per mole of metal chloride per unit time for half the reaction. In order to study the effect of moisture present in the catalyst and in the reaction mixture, the catalyst stored over water at room temperature for 14 h and benzene saturated with water at room temperature (0.37 mol% water in benzene), respectively, were used for the reaction.

3. Results and discussion

Results on the $GaCl_3$ and $InCl_3$ catalysts, with or without support, for the benzylation of benzene under moisture-free conditions (table 1) reveal the following:

- On supporting, the benzylation activity of $GaCl_3$ (except for Si-MCM-41) and $InCl_3$ is increased; the increase is very large in case of $InCl_3$.
- Both the supported $GaCl_3$ and $InCl_3$ catalysts show very high benzylation activity; the supported $InCl_3$, however, shows higher activity. The supported $AlCl_3$, however, shows poor activity.
- Among the two supports, Mont.-K10 is a better support for both the supported $GaCl_3$ and $InCl_3$ catalysts. Si-MCM-41 shows no activity and Mont.-K10 shows very low activity for the benzylation.

The supported $GaCl_3$ and $InCl_3$ catalysts also show very high activity in the benzylation of other aromatic compounds containing electron-donating groups [9].

Earlier studies [10] showed that benzylation reactions catalyzed by clayzic ($ZnCl_2$ impregnated on montmorillonite-K10) are much faster than with $AlCl_3$ as the catalyst. The thermally activated (at 280 °C) clayzic catalyst showed high benzylation activity [5]. In order to compare the present catalysts with the clayzic catalysts, performance of the clayzic catalysts, prepared by the methods reported earlier [5,6], for the benzylation reaction under the same conditions was measured and the results are presented in table 2. A comparison of the results in tables 1 and 2 clearly shows that the performance of the $GaCl_3$/Mont.-K10, $InCl_3$/Mont.-K10 and $InCl_3$/Si-MCM-41catalysts is much superior to that of the clayzic catalysts. The supported $GaCl_3$ and $InCl_3$ catalysts (table 1) are also much more active in the benzylation reaction than the ion-exchanged clays [11], sulfated ZrO_2 [4], HY zeolite [2] and H-ZSM-5 with its Al partially or completely substituted by Fe or Ga [3] catalysts reported earlier.

Results showing the effect of moisture present in the catalyst or reaction mixture on the catalytic activity of the supported $GaCl_3$ and $InCl_3$ catalysts are given in table 3. A comparison of the results in table 3 with those in table 1 clearly shows that the activity of the $InCl_3$/Mont.-K10 catalyst is almost not influenced by the presence of moisture in the catalyst or in the reaction mixture. Thus, the supported $InCl_3$ catalyst shows superior performance in the benzylation of benzene.

Table 1
Result of benzylation of benzene over different supported and unsupported metal chloride catalysts.[a]

Catalyst	Time (min) required for benzyl chloride conversion: 50%	Time (min) required for benzyl chloride conversion: 90%	Reaction induction period (min)	TON (min^{-1}) for half the reaction
$GaCl_3$ (0.01 g, without support)	8.6	26.0	0.6	8.90
$InCl_3$ (0.01 g, without support)	8.1	23.0	1.1	11.87
$GaCl_3$/Mont.-K10	4.7	14.9	0.1	16.3
$InCl_3$/Mont.-K10	2.0	6.2	0.1	48.1
$AlCl_3$/Mont.-K10	10% conversion for 1 h		12.0	–
Mont.-K10	5% conversion for 1 h		–	–
$GaCl_3$/Si-MCM-41	12.0	26.8	4.4	6.4
$InCl_3$/Si-MCM-41	2.9	8.9	0.2	33.2
$AlCl_3$/Si-MCM-41	No reaction for 2 h		–	–
Si-MCM-41	No reaction for 2 h		–	–

[a] Reaction conditions: reaction mixture = 13 cm^3 dry benzene and 1.0 cm^3 benzyl chloride, amount of catalyst = 0.1 g (dried before use), temperature = 80 °C.

Table 2
Result of benzylation of benzene over clayzic catalysts prepared by different methods.[a]

Catalyst	Time (min) required for benzyl chloride conversion[b]		Reaction induction period (min)	TON (min^{-1}) for half the reaction
	50%	90%		
$ZnCl_2$(13.6 wt%)/Mont.-K10[c]	4.6	31.4	0.1	9.4
$ZnCl_2$(13.6 wt%)/Mont.-K10[d]	3.9	26.0	0.3	11.1
$ZnCl_2$(10 wt%)/Mont.-K10[e]	6.0	38.0	0.3	9.8

[a] Reaction conditions: reaction mixture = 13 cm^3 dry benzene and 1.0 cm^3 benzyl chloride, amount of catalyst = 0.1 g supported metal chloride, temperature = 80 °C.

[b] Selectivity for monoalkylation (i.e., diphenylmethane formation) was found to be 75 ± 3%; the other product was mainly dibenzyl benzene.

[c] Prepared by impregnating $ZnCl_2$ from its methanol solution and calcining at 120 °C (as per [2]).

[d] Prepared by impregnating $ZnCl_2$ from its methanol solution and calcining at 280 °C (as per [2]).

[e] Prepared by impregnating $ZnCl_2$ from its acetonitrile solution and calcining at 120 °C (as per [3]).

Table 3
Results on the montmorillonite-K10-supported $AlCl_3$, $GaCl_3$ and $InCl_3$ catalysts for their moisture sensitivity in the benzylation of benzene.[a]

Catalyst	Catalyst pretreatment	Quality of benzene used	Time (min) required for benzyl chloride conversion		Reaction induction period (min)	TON (min^{-1}) for half the reaction
			50%	90%		
$AlCl_3$/Mont.-K10	Pretreated with water vapours	Dry	No reaction for 2 h			–
$GaCl_3$/Mont.-K10	Pretreated with water vapours	Dry	9.0	25.6	1.3	8.5
$InCl_3$/Mont.-K10	Pretreated with water vapours	Dry	2.2	7.7	0.1	43.7
$AlCl_3$/Mont.-K10	Dried	Saturated with water[b]	No reaction for 2 h			–
$GaCl_3$/Mont.-K10	Dried	Saturated with water[b]	5.2	16.7	0.5	14.7
$InCl_3$/Mont.-K10	Dried	Saturated with water[b]	2.1	7.0	0.2	45.8

[a] Reaction conditions: reaction mixture = 13 cm^3 benzene and 1.0 cm^3 benzyl chloride, amount of catalyst = 0.1 g, temperature = 80 °C.

[b] Concentration of water in benzene saturated with water (at 30 °C) = 0.37 mol% (0.085 wt%).

Table 4
IR spectroscopic data for the pyridine adsorbed on montmorillonite-K10- and Si-MCM-41-supported $AlCl_3$, $GaCl_3$ and $InCl_3$ catalysts (metal chloride loading = 10 wt%).

Catalyst	IR peaks[a] (cm^{-1})	
	1st	2nd
$AlCl_3$/Mont.-K10	1462	1631
$GaCl_3$/Mont.-K10	1464	1632
$InCl_3$/Mont.-K10	1462	1611
$AlCl_3$/Si-MCM-41	1460	1634
$GaCl_3$/Si-MCM-41	1461	1637
$InCl_3$/Si-MCM-41	1460	1623

[a] Pyridine co-ordinated with Lewis acid sites.

The observed moisture insensitivity of the supported $InCl_3$ and low moisture sensitivity of the supported $GaCl_3$, apart from their very high activity in the benzylation, is of great practical importance. These catalysts can also be separated easily, simply by filtration, and reused in the process.

IR spectroscopic data for the adsorbed pyridine on the supported $AlCl_3$, $GaCl_3$ and $InCl_3$ catalysts are presented in table 4. The observed IR peaks and the shift in their frequencies indicate that the Lewis acidic character of the catalysts is in the following order [12]: supported $InCl_3 \leqslant$ supported $AlCl_3 <$ supported $GaCl_3$. The observed higher Lewis acid character of the supported $GaCl_3$ is consistent with the higher electronegativity of gallium [13]. It is interesting to note that the observed higher moisture sensitivity of the $GaCl_3$/Mont.-K10 (table 3) is attributed to its higher Lewis acid character. The supported $InCl_3$ is almost moisture insensitive for the benzylation reaction because of its low Lewis acid character, resulting in only weak or ineffective interactions of water molecules with the catalyst. The $InCl_3$/Mont.-K10 catalyst showed high activity in the benzylation reaction even in the presence of pyridine (a strong Lewis base) in the reaction mixture; when 2.5 μl pyridine was added to the reaction mixture, the time required for 50 and 90% benzyl chloride conversion was 6.2 and 11.5 min, respectively. All these results suggest that the benzylation activity of the supported $InCl_3$ catalyst does not depend on its acid character. The redox properties rather than the acid properties of this catalyst seem to play an important role in the benzylation reaction. It is interesting to note that the trend for the standard state reduction potential ($E^0_{\mathrm{M}^{n+}/\mathrm{M}}$), which is in the order $E^0_{\mathrm{Al}^{3+}/\mathrm{Al}}$ (−1.66 V) $<$ $E^0_{\mathrm{Zn}^{2+}/\mathrm{Zn}}$ (−0.76 V) $<$ $E^0_{\mathrm{Ga}^{3+}/\mathrm{Ga}}$ (−0.53 V) $<$ $E^0_{\mathrm{In}^{3+}/\mathrm{In}}$ (−0.34 V) [13], is same as that for the benzylation activity of the supported metal chloride catalysts. Thus, there is a correlation between the redox properties of the supported metal chloride catalysts and their benzylation activity. Anhydrous $AlCl_3$ is known to be a highly active catalyst for the homogeneous Friedel–Crafts reactions. However, the supported $AlCl_3$ catalysts showed very poor activity in the benzylation of benzene (table 1). This is expected mostly because of the decrease in the Lewis acidity of $AlCl_3$ due to the presence of Na (for Mont.-K10, which is basic in nature), traces of moisture and/or surface hydroxyls in the supports. Unlike the $GaCl_3$ and $InCl_3$ catalysts, the catalytic activity of the $AlCl_3$ catalyst is attributed to its Lewis acidity and not to its redox property. Further studies are, however, required for understanding the mechanism of benzylation over the supported $InCl_3$ and $GaCl_3$ catalysts.

In summary, the Mont.-K10- and Si-MCM-41-supported $GaCl_3$ and $InCl_3$ are highly active catalysts for the benzylation of benzene and these catalysts do not demand stringent moisture-free conditions for them to be highly active/selective in the alkylation process. Among the catalysts, the $InCl_3$/Mont.-K10 shows best performance in regard to both the catalytic activity and the moisture insensitivity in the benzylation reaction.

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