Acylation of benzene over clay and mesoporous Si-MCM-41 supported $InCl_3$, $GaCl_3$ and $ZnCl_2$ catalysts

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Liquid phase acylation of benzene by acyl chloride (*e.g.*, benzoyl chloride, butyryl chloride or phenyl acetyl chloride) over $InCl_3$, $GaCl_3$ and $ZnCl_2$ supported on commercial clays (*viz.* montmorillonite-K10, montmorillonite-KSF and kaolin) or high silica mesoporous MCM-41 at 80 °C has been investigated. The Mont.-K10 and Si-MCM-41 supported $InCl_3$ and $GaCl_3$ catalysts showed high activity in the acyation of benzene by benzoyl chloride even in the presence of moisture in the reaction mixture. The redox function of the supported $InCl_3$, $GaCl_3$ or $ZnCl_2$ catalysts seems to play a very important role in the acylation process.

KEY WORDS: acylation of benzene by acyl chloride; $InCl_3$ supported on clay; $InCl_3$ supported on Si-MCM-41; $GaCl_3$ supported on clay; $GaCl_3$ supported on Si-MCM-41; $ZnCl_2$ supported on clay; $ZnCl_2$ supported on Si-MCM-41

1. Introduction

Friedel–Crafts type acylation of aromatic compounds is an important reaction used in the synthesis of aromatic ketones which are fine chemicals and/or intermediates for the preparation of fine chemicals in dyes, pharmaceutical and other chemical industries. The conventional method for the preparation of aromatic ketones is the homogeneous Friedel–Crafts acylation of aromatic hydrocarbons with carboxylic acid derivatives using stoichiometric amount of anhydrous $AlCl_3$ as a catalyst [1]. However, the commonly used homogeneous acid catalyst poses several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, *etc*. Moreover, this catalyst is highly moisture sensitive and hence demands moisture-free solvent and reactants, anhydrous catalysts and also dry atmosphere for their handling. Development of reusable solid acid catalysts having high activity and little or no moisture sensitivity for liquid phase Friedel–Crafts type acylation reactions is, therefore, of great practical importance. Worldwide efforts have been made to achieve this goal, using a number of solid acid catalysts, such as heteropoly acids [2–6], modified ZrO_2 [7,8], H-beta and Ga-, Fe- or In-substituted H-beta [9–11], H-ZSM-5, H-mordenite, HY and H-RE-Y [12–15], supported Ga_2O_3, In_2O_3 or Tl_2O_3 [16,17], montmorillonite-K10 or -KSF clay [18] and EPZG [19] for the acylation of benzene [9,16,17,19] and other aromatic compounds [2–8,10–15,18] by different acyl chlorides. The acylation of aromatic compounds containing an electron-donating group (*e.g.*, alkyl, alkoxy, OH, *etc.*) can be accomplished with ease, but with difficulty in the absence of such an aromatic ring activating group [1]. We report here our preliminary results, showing high activity of Mont.-K10 and Si-MCM-41 supported $InCl_3$ and $GaCl_3$ catalysts in the acylation of benzene by different acyl chlorides, even in the presence of moisture in the reaction mixture. The acylation activity of the $InCl_3$, $GaCl_3$ and $ZnCl_2$ catalysts supported on Si-MCM-41 and different clays was found to be dependent upon the redox potential of the metals present in the catalysts.

2. Experimental

Supported metal chloride catalysts (loading of metal chloride 5–20 wt%) were prepared by impregnating different commercially available clays (*viz.* montmorillonite-K10, montmorillonite-KSF, kaolin; all from 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 their acetonitrile solution by the incipient wetness technique and evaporating the solvent in a vacuum oven at 120 °C for 8 h.

The acylation reaction over the supported metal chloride catalysts was carried out under reflux in a magnetically 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 at the following reaction conditions by the procedure described earlier [16]: reaction mixture $=$ 13 ml of moisture-free benzene $+$ 1.0 ml of acyl chloride, amount of catalyst 0.4 g and temperature 80 °C. Before use, the catalyst was pretreated at 100 °C in a flow of moisture-free nitrogen for 1 h to remove the adsorbed moisture. The reaction was started by injecting acyl chloride in the reaction mixture, containing benzene and the catalyst, under benzene reflux (at 80 °C). The

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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 acyl chloride and acylated product at the end of the experiment by gas chromatography. There was a good agreement between the acyl chloride conversion obtained from the acid–base titration and that from the GC analysis. In all the cases, no product other than acylated aromatics was formed. TON (turnover number) is estimated as moles of acyl chloride converted per mole of metal chloride catalyst per unit time for half the reaction.

In order to study the effect of moisture present in the reaction mixture, the benzene saturated with water at room temperature (concentration of water = 0.37 mol%) was used for the benzene benzoylation reaction.

3. Results and discussion

Results on the $InCl_3$, $GaCl_3$ and $ZnCl_2$ catalysts supported on Si-MCM-41 and different clays on their performance in the acylation of benzene by benzoyl chloride (at 80 °C) are presented in table 1. Kinetic curves (benzoyl chloride conversion *vs.* time plots) for the benzoylation

Table 1
Results on the acylation of benzene by benzoyl chloride (at 80 °C) over the supported $InCl_3$, $GaCl_3$ and $ZnCl_2$ (metal chloride loading 20%) catalysts.

Supported catalyst	Reaction induction period, t_0 (min)	Time required for half the reaction[a], $t_{1/2}$ (h)	TON for half the reaction (h^{-1})
$InCl_3$/Mont.-K10	4.5	1.4	8.5
$InCl_3$/Mont.-KSF	5.4	2.0	6.0
$InCl_3$/kaolin	7.7	7.9	1.5
$InCl_3$/Si-MCM-41	4.9	1.6	7.4
$GaCl_3$/Mont.-K10	5.6	1.7	5.6
$GaCl_3$/Mont.-KSF	6.8	2.6	3.6
$GaCl_3$/kaolin	8.5	10.4	0.9
$GaCl_3$/Si-MCM-41	5.9	1.9	5.0
$ZnCl_2$/Mont.-K10	7.0	7.3	1.0
$ZnCl_2$/Si-MCM-41	7.8	8.4	0.9
Catalyst support[b]	No reaction for 2 h		–

[a] 50% conversion of the acylating agent.
[b] Mont.-K10, Mont.-KSF, kaolin or Si-MCM-41.

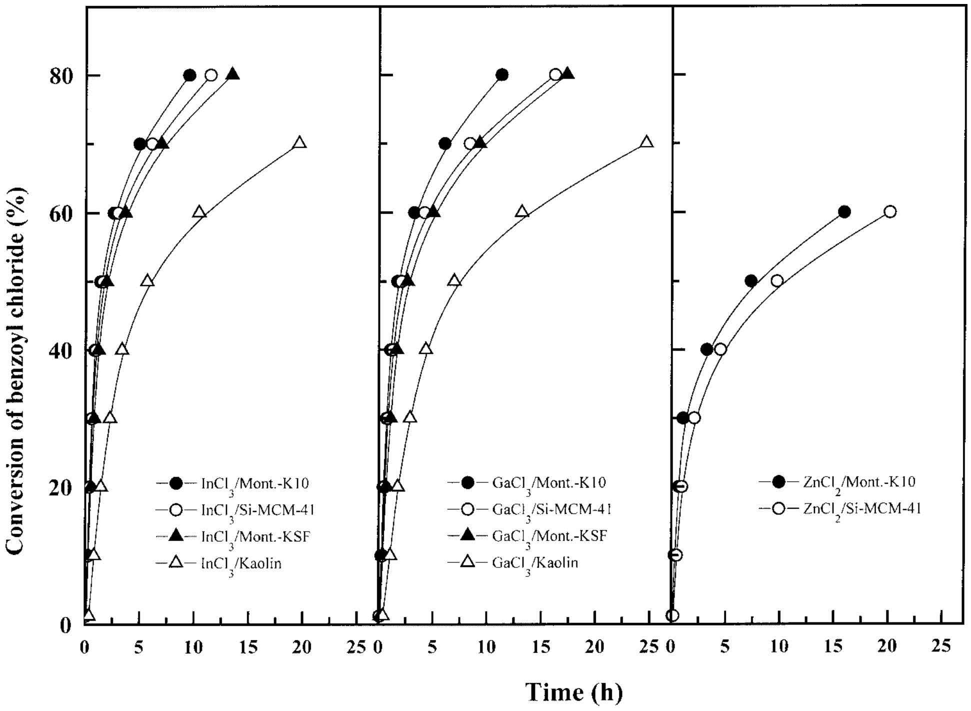

Figure 1. Conversion *vs.* reaction time plots for the acylation of benzene by benzoyl chloride (at 80 °C) over supported $InCl_3$, $GaCl_3$ and $ZnCl_2$ (metal chloride loading 20%) catalysts.

of benzene over the supported metal chloride catalysts (at 80 °C) are presented in figure 1.

From the comparison of results in table 1, the following important observations can be made:

- The catalyst support itself (*viz.* montmorillonite-K10, montmorillonite-KSF, kaolin or mesoporous Si-MCM-41) shows no catalytic activity in the benzoylation of benzene. However, its catalytic activity is increased drastically after its impregnation with $InCl_3$, $GaCl_3$ or $ZnCl_2$.
- Among the metal chloride catalysts deposited on the same support, the supported $InCl_3$ catalyst showed highest activity. The acylation activity of the catalysts is in the following order: supported $InCl_3$ > supported $GaCl_3 \gg$ supported $ZnCl_2$.
- Among the different supports used for the metal chloride catalysts, Mont.-K10 is the best support; the order of the choice for the support is Mont.-K10 > Si-MCM-41 > Mont.-KSF $\gg$ kaolin.

The Mont.-K10 and Si-MCM-41 supported $InCl_3$ and $GaCl_3$ catalysts are compared with the earlier reported solid catalysts [9,16,17] for their benzene benzoylation activity in table 2. Both the supported $InCl_3$ and $GaCl_3$ catalysts show much higher benzene benzoylation activity than that of the earlier reported solid catalysts.

Results showing high activity of the $InCl_3$/Mont.-K10 catalyst in the acylation of benzene also by other acyl chlorides (*viz.* butyryl chloride and phenyl acetyl chloride) at 80 °C are presented in figure 2. The time required for half the acylation reaction for the different acylating agents is in the following order: butyryl chloride (0.85 h) < benzoyl chloride (1.4 h) < phenyl acetyl chloride (1.7 h).

The influence of metal chloride loading on the conversion of benzoyl chloride in the acylation of benzene over the $InCl_3$/Mont.-K10 catalyst is shown in figure 3. The time required for half the acylation reaction ($t_{1/2}$) and the reaction induction period (t_0) are decreased markedly with increasing the metal chloride loading on the Mont.-K10 support (for the loading of 5, 10 and 20%, the observed values for $t_{1/2}$ and t_0 are 4.1, 2.2, 1.4 h and 15.1, 8.4 and 4.5 min, respectively).

Results showing the effect of moisture present in the reaction mixture on the acylation of benzene by benzoyl chloride over the $InCl_3$ (or $GaCl_3$)/Mont.-K10 (or Si-MCM-41) catalyst are presented in figure 4. The acylation activity of the supported $InCl_3$ and $GaCl_3$ catalysts is increased slightly due to the presence of moisture in the reaction mixture. A similar increase was observed earlier for the benzoylation of toluene over In_2O_3/Si-MCM-41 [16]. The observed high acylation activity of the supported $InCl_3$ or $GaCl_3$ catalyst even in the presence of moisture in the reaction mixture, is of great practical importance. These catalysts do not demand stringent moisture-free conditions for them to be highly active in the acylation process.

Table 2

Comparison of the earlier solid catalysts with the present ones for their benzene benzoylation activity (at 80 °C).

Catalyst	Time required for 54% conversion of benzoyl chloride (h)	Ref.
H-beta	18.0	[9]
In_2O_3/Si-MCM-41	5.6	[16]
Tl_2O_3/zirconia (LS)	3.4	[17]
$InCl_3$/Mont.-K10	1.9	Present
$InCl_3$/Si-MCM-41	2.2	Present
$GaCl_3$/Mont.-K10	2.4	Present
$GaCl_3$/Si-MCM-41	2.8	Present

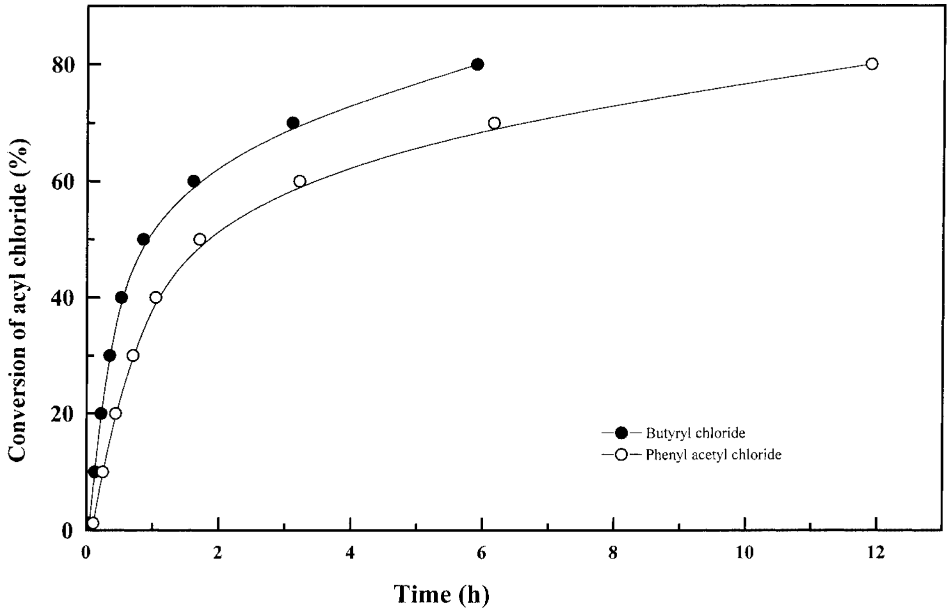

Figure 2. Conversion *vs.* reaction time plots for the acylation of benzene by butyryl chloride and phenyl acetyl chloride (at 80 °C) over $InCl_3$ (20%)/Mont.-K10 catalyst.

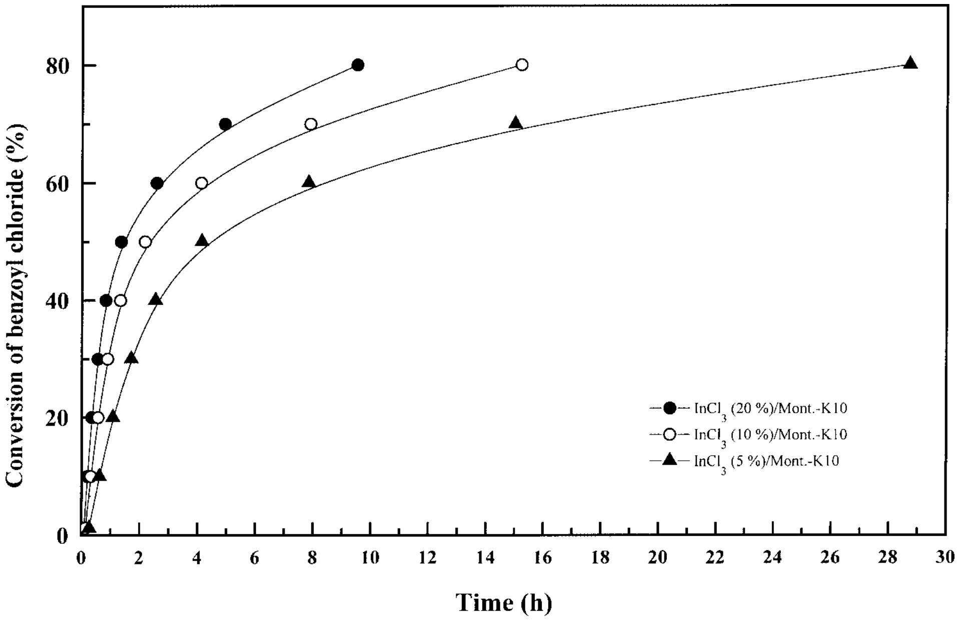

Figure 3. Effect of metal chloride loading in the $InCl_3$/Mont.-K10 catalyst on its activity in the conversion of benzoyl chloride in the acylation of benzene (at 80 °C).

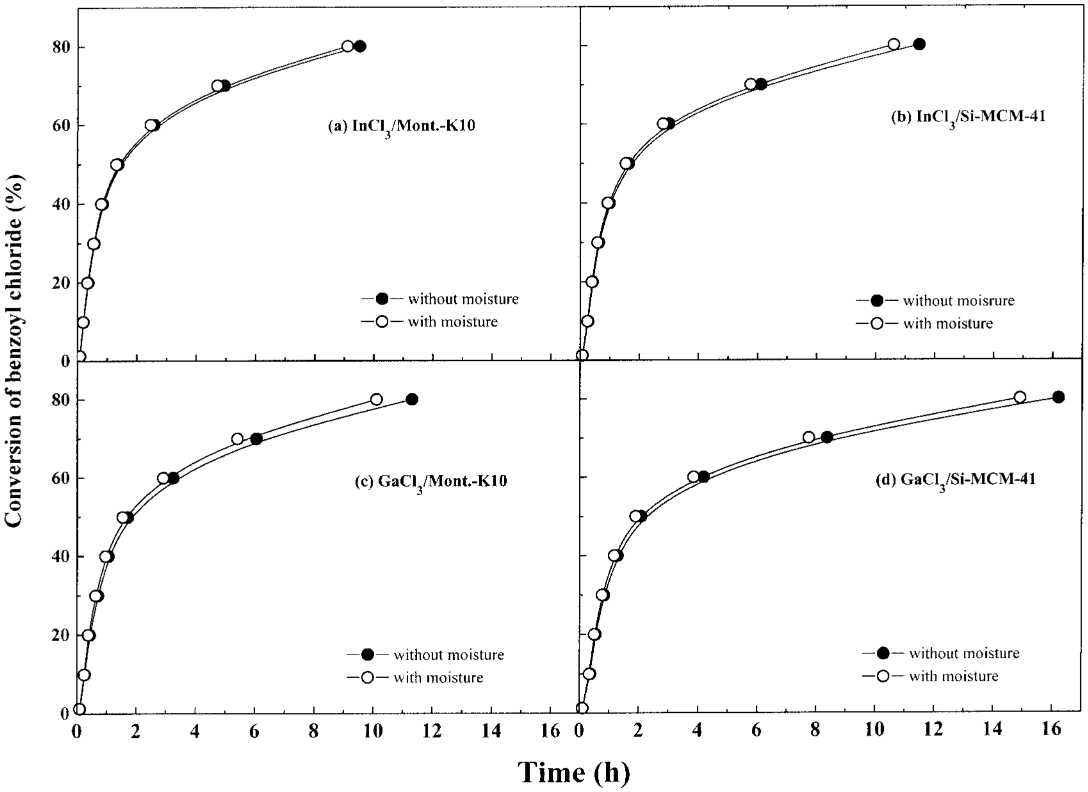

Figure 4. Effect of moisture in the reaction mixture on the conversion of benzoyl chloride in the acylation of benzene over $InCl_3$ or $GaCl_3$ (20%)/Mont.-K10 or Si-MCM-41 catalyst (at 80 °C).

The metal chloride species present in the catalysts have redox properties, which are expected to play an important role in the acylation reaction over the present catalysts. It is interesting to note that the order for the acylation activity of the supported metal chloride catalysts ($InCl_3 > GaCl_3 \gg ZnCl_2$) is quite similar to that for the redox potential of the metal in the catalysts ($E^0_{In^{3+}/In^{+}}$ or $E^0_{Ga^{3+}/Ga^{+}}$ (−0.44 V) > $E^0_{Zn^{2+}/Zn}$ (−0.74 V) and $E^0_{In^{3+}/In}$ (−0.34 V) > $E^0_{Ga^{3+}/Ga}$ (−0.53 V) > $E^0_{Zn^{2+}/Zn}$ (−0.74 V)). This indicates a close relationship between the redox potential and the catalytic activity of the supported metal chlorides. The following probable redox mechanism for the acylation reaction over the catalyst is proposed:

$$m\mathrm{RCOCl} + \mathrm{M}^{n+} \rightarrow m\mathrm{RCOCl}^{+\cdot} + \mathrm{M}^{(n-m)+} \tag{1}$$

where R = C_6H_5, $C_6H_5CH_2$ or C_3H_7, M = In, Ga or Zn, $n = 3$ (for In and Ga) or 2 (for Zn) and $m = 2$ (for In and Ga) and 1 (for Zn).

$$m\mathrm{RCOCl}^{+\cdot} \rightarrow m\mathrm{RCO}^{+} + m\mathrm{Cl}^{\cdot} \tag{2}$$

$$m\mathrm{Cl}^{\cdot} + \mathrm{M}^{(n-m)+} \rightarrow \mathrm{M}^{n+} + m\mathrm{Cl}^{-} \tag{3}$$

$$\mathrm{RCO}^{+} + \mathrm{ArH} \rightarrow \mathrm{RCOAr} + \mathrm{H}^{+} \tag{4}$$

$$\mathrm{H}^{+} + \mathrm{Cl}^{-} \rightarrow \mathrm{HCl} \tag{5}$$

The above mechanism is similar to that proposed earlier for the acylation reactions [17,20].

4. Conclusion

In summary, the Mont.-K10 and Si-MCM-41 supported $InCl_3$ and $GaCl_3$ are highly active catalysts for the acylation of benzene by acyl chlorides and these catalysts do not demand stringent moisture-free conditions for them to be highly active in the acylation process. Among the catalysts, the $InCl_3$/Mont.-K10 shows best performance in the benzene acylation.

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