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Benzylation of benzene and substituted benzenes by benzyl chloride over $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on clays and Si-MCM-41

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Abstract

Liquid phase benzylation of benzene by benzyl chloride to diphenyl methane over $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on commercial clays (viz. Montmorillonite-K10, Montmorillonite-KSF and Kaolin) or on high silica mesoporous MCM-41 (at 60, 70 and 80 °C) has been investigated. The supported $InCl_3$, $GaCl_3$ and $FeCl_3$ showed high activity for the benzylation of benzene. The redox function created due to the impregnation of the clays or Si-MCM-41 by $InCl_3$, $GaCl_3$, $FeCl_3$ or $ZnCl_2$ seems to play a very important role in the benzylation process. Among the catalysts, the $InCl_3$/Mont.-K10 showed both high activity and high selectivity for the benzylation. The activity of this catalyst for the benzylation of different aromatic compounds is in the following order: benzene $>$ toluene $>$ mesitylene $>$ anisole. The $InCl_3$ (or $GaCl_3$)/Mont.-K10 (or Si-MCM-41) catalyst showed high benzene benzylation activity even in the presence of moisture in the reaction mixture. The catalyst can also be reused in the benzylation for several times. Kinetics of the benzene benzylation (using excess of benzene) over the supported metal chloride catalysts have also been thoroughly investigated. A plausible reaction mechanism for the benzylation over the supported metal chloride catalysts is proposed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzylation of benzene by benzyl chloride; Diphenylmethane; $InCl_3$ supported on clay; $InCl_3$ supported on Si-MCM-41; $GaCl_3$ supported on clay; $GaCl_3$ supported on Si-MCM-41; $FeCl_3$ supported on clay; $FeCl_3$ supported on Si-MCM-41; $ZnCl_2$ supported on clay; $ZnCl_2$ supported on Si-MCM-41

1. Introduction

Liquid phase benzylation of aromatic compounds, using homogeneous acid catalysts (e.g. $AlCl_3$, BF_3 and H_2SO_4, etc.), are commonly practiced 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, etc. Moreover, this catalyst is highly moisture sensitive and hence demands moisture-free solvent and substrates for the reaction and also demands moisture-free atmosphere for their handling. Development of reusable solid catalysts having high activity with little or no moisture sensitivity for the liquid phase Friedel–Crafts type reactions is therefore of great practical importance. Hence, efforts are made to replace the homogeneous acid catalysts by heterogeneous solid acid catalysts, such as heteropoly acid salts [2,3], sulfated ZrO_2 or Fe_2O_3 [4,5], supported Ga_2O_3, In_2O_3 or Tl_2O_3 [6,7], Fe/MCM-41 [8], cation exchanged clays [9,10], $FeCl_3$/Mont.-K10 [11], clayzic [12,13], acid treated clays [14,15], HY,

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H-beta and H-ZSM-5 zeolites [16–18] and Ga- or Fe-substituted H-ZSM-5 [19] for the benzylation of benzene and other aromatic compounds.

In our preliminary studies [20], we have found that $InCl_3$ and $GaCl_3$ supported on Mont.-K10 or Si-MCM-41 show high activity/selectivity in the benzylation of benzene by benzyl chloride. The redox function created by the impregnation of clay or Si-MCM-41 by $InCl_3$ or $GaCl_3$ seems to be important for deciding the benzylation activity of the supported metal chloride catalysts. It is, therefore, interesting to carry out a detailed investigation including kinetics of the benzylation of benzene and other aromatic compounds over different supported metal chloride catalysts having redox function, such as $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on different clays or Si-MCM-41, in the presence or absence of moisture in the reaction mixture. The present investigation was undertaken for this purpose.

2. Experimental

Supported $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ catalysts (loading of metal chloride $= 0.23$–$2.0\,\mathrm{mmol\,g^{-1}}$) were prepared by impregnating different commercially available clays (viz. Montmorillonite-K10, Montmorillonite-KSF, Kaolin; all from Aldrich, USA) and Si-MCM-41 (high silica mesoporous MCM-41 having surface area of $1140\,\mathrm{m^2\,g^{-1}}$) with anhydrous metal chloride (purity 99.99%, Aldrich) from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 120 °C for 8 h.

The liquid phase benzylation reactions over the supported metal chloride catalysts were carried out in a magnetically stirred glass reactor (capacity: $25\,\mathrm{cm^3}$) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N_2 ($30\,\mathrm{cm^3\,min^{-1}}$) through the liquid reaction mixture at the following reaction conditions by the procedure given earlier [6]: reaction mixture $=$ 13 ml of moisture-free aromatic compound (or 1.5 ml of moisture-free aromatic compound mixes with 11.5 ml of moisture-free solvent) $+$ 1.0 ml of benzyl chloride, amount of catalyst $=$ 0.1 g and temperature $=$ 60, 70 or 80 °C. The reaction was started by injecting benzyl chloride in the reaction mixture, containing catalyst and aromatic compound with or without solvent, after attaining the reaction temperature. In all the cases, the major product formed was mainly mono-benzylated aromatic compound, along with polybenzyl chloride as side product, depending upon the catalyst used.

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

In order to study the reusability of the catalyst ($InCl_3$/Mont.-K10) for the benzene benzylation, the catalyst was reused after removing the supernatant liquid reaction mixture, while retaining the catalyst in the reaction and avoiding, as far as possible, the removal of the catalyst fine particles.

3. Results and discussion

3.1. Comparison of the supported metal chloride catalysts for benzene benzylation

The $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported metal chloride catalysts are compared for their performance in the benzene benzylation (at 80 °C) in Table 1. Kinetic curves (benzyl chloride conversion versus time plots) for the benzylation of benzene over the supported metal chloride catalysts at 80 °C are presented in Fig. 1.

From the comparison of results in Table 1, the following important observations can be made.

- The catalyst support itself (Mont.-K10, Mont.-KSF, Kaolin or high silica mesoporous MCM-41) shows very little or no activity in the benzylation of benzene, however, its catalytic activity is increased drastically because of the impregnation of $InCl_3$, $GaCl_3$, $FeCl_3$ or $ZnCl_2$.
- Among the different supported metal chloride catalysts, the supported $FeCl_3$ catalyst (for the chemically similar support) showed higher activity but lower selectivity in the benzene benzylation reaction. The lower selectivity for diphenyl methane is attributed to its higher benzyl chloride polycondensation activity [21].
- The benzylation activity of the supported metal chloride catalysts is in the following order:

Table 1

Comparison of the supported $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ (metal chloride loading = 1.13 mmol g^{-1}) catalysts for their performance in the benzylation of benzene (at 80 °C)

Catalyst	Time (min) required for benzyl chloride conversion		Reaction induction period (min)	Apparent reaction rate constant, k_a ($\times 10^3$ min^{-1})	Selectivity for diphenyl methane at complete conversion of benzyl chloride (%)
	50%	90%			
$InCl_3$/Mont.-K10	1.3	4.7	0.0	523.0	>98
$InCl_3$/Mont.-KSF	1.8	5.8	0.1	418.7	>98
$InCl_3$/Kaolin	4.8	14.1	0.8	180.0	96
$InCl_3$/Si-MCM-41	1.6	5.4	0.1	460.6	>98
$GaCl_3$/Mont.-K10	2.2	7.6	0.0	320.0	>98
$GaCl_3$/Mont.-KSF	4.9	13.4	1.2	198.5	>98
$GaCl_3$/Kaolin	8.0	19.7	2.7	143.9	97
$GaCl_3$/Si-MCM-41	4.8	12.9	1.4	215.3	>98
$FeCl_3$/Mont.-K10	1.2	4.5	0.0	548.0	91
$FeCl_3$/Si-MCM-41	1.5	5.2	0.1	470.0	92
$ZnCl_2$/Mont.-K10	4.5	23.1	0.1	126.0	82
$ZnCl_2$/Si-MCM-41	10.4	38.0	1.6	72.0	83
Mont.-K10	5% conversion upto 1 h			–	–
Mont.-KSF	5% conversion upto 1 h			–	–
Kaolin	1.5% conversion upto 1 h			–	–
Si-MCM-41	No reaction upto 1 h			–	–

supported $FeCl_3$ > supported $InCl_3$ > supported $GaCl_3$ > supported $ZnCl_2$. It is interesting to note that this order for the benzylation activity is quite similar to that of the redox potential of the metal in the supported metal chloride catalysts [$E^0_{Fe^{3+}/Fe^{2+}}(+0.77\,V) > E^0_{In^{3+}/In^{+}}$ or $E^0_{Ga^{3+}/Ga^{+}}$ $(-0.44\,V) > E^0_{Zn^{2+}/Zn}(-0.76\,V)$]. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal chlorides.

- Among the different supports used for the supported metal chloride catalysts, the Mont.-K10 is the best support and the order of the choice for the support is Mont.-K10 > Si-MCM-41 > Mont.-KSF > Kaolin.
- Among the supported metal chloride catalysts, the $InCl_3$/Mont.-K10 showed both high activity and high selectivity in the benzylation (Table 1). This catalyst can also be reused for the benzylation several times (Fig. 2).

When the $ZnCl_2$/Mont.-K10 catalyst was thermally activated at 280 °C and cooled in air, the resulting catalyst showed only a small improvement in the benzene benzylation activity ($k_a = 0.153\,min^{-1}$). The benzene benzylation activity of the Mont.-K10 and Si-MCM-41 supported $InCl_3$, $GaCl_3$ and $FeCl_3$ catalysts (Table 1) is much higher than that of the $ZnCl_2$/Mont.-K10 even after its thermal activation. Earlier studies [12,13] showed that a clayzic catalyst (which is a thermally activated $ZnCl_2$/Mont.-K10 at 280 °C) shows high benzene benzylation activity. However, the clayzic catalyst is less selective (≈80% selectivity for diphenylmethane) [12] and moreover it is highly hygroscopic in nature, it rapidly loses its activity when exposed to air [13]. The above results of the $ZnCl_2$/Mont.-K10 are consistent with this. The high hygroscopic nature of clayzic catalyst puts a severe restriction on it's use strictly under moisture-free conditions.

The kinetic data (time dependent benzyl chloride conversion data) for the benzene benzylation reaction (with the excess of benzene) over all the supported metal chloride catalysts could be fitted well to a pseudo-first-order rate law:

$$\log\left[\frac{1}{1-x}\right] = \left(\frac{k_a}{2.303}\right)(t - t_0) \quad (1)$$

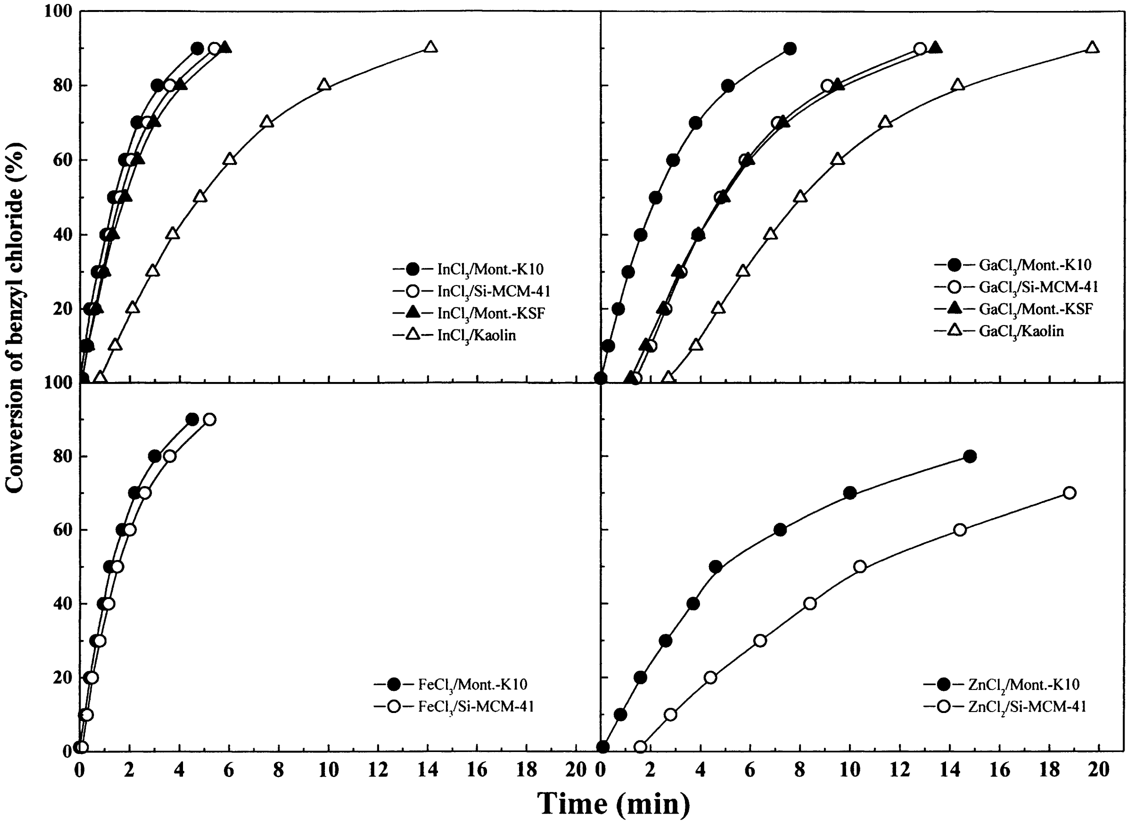


Fig. 1. Conversion vs. reaction time plots for the benzylation of benzene (at 80 °C) over supported $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ catalysts.

Table 2
Kinetic parameters for the benzylation of benzene over different supported metal chloride catalysts

Catalyst	Apparent rate constant, k_a ($\times 10^3$ min^{-1})			Activation energy, E (kcal mol^{-1})	Frequency factor, A (min^{-1})
	80 °C	70 °C	60 °C		
$InCl_3$/Mont.-K10	523.0	274.0	152.0	14.52	4.16×10^{11}
$InCl_3$/Mont.-KSF	418.7	224.9	115.0	15.1	7.7×10^{11}
$InCl_3$/Kaoline	180.0	85.0	45.2	16.2	1.58×10^{12}
$InCl_3$/Si-MCM-41	460.6	225.0	123.8	15.4	1.32×10^{12}
$GaCl_3$/Mont.-K10	320.0	171.0	89.0	15.05	5.62×10^{11}
$GaCl_3$/Si-MCM-41	215.3	111.0	54.7	16.1	1.7×10^{12}
$FeCl_3$/Mont.-K10	548.0	289.2	203.8	11.62	7.2×10^{9}
$FeCl_3$/Si-MCM-41	470.0	287.1	139.5	14.28	2.89×10^{11}
$ZnCl_2$/Mont.-K10	126.0	59.2	30.1	16.8	2.6×10^{12}
$ZnCl_2$/Si-MCM-41	72.0	31.8	14.7	18.7	2.05×10^{13}

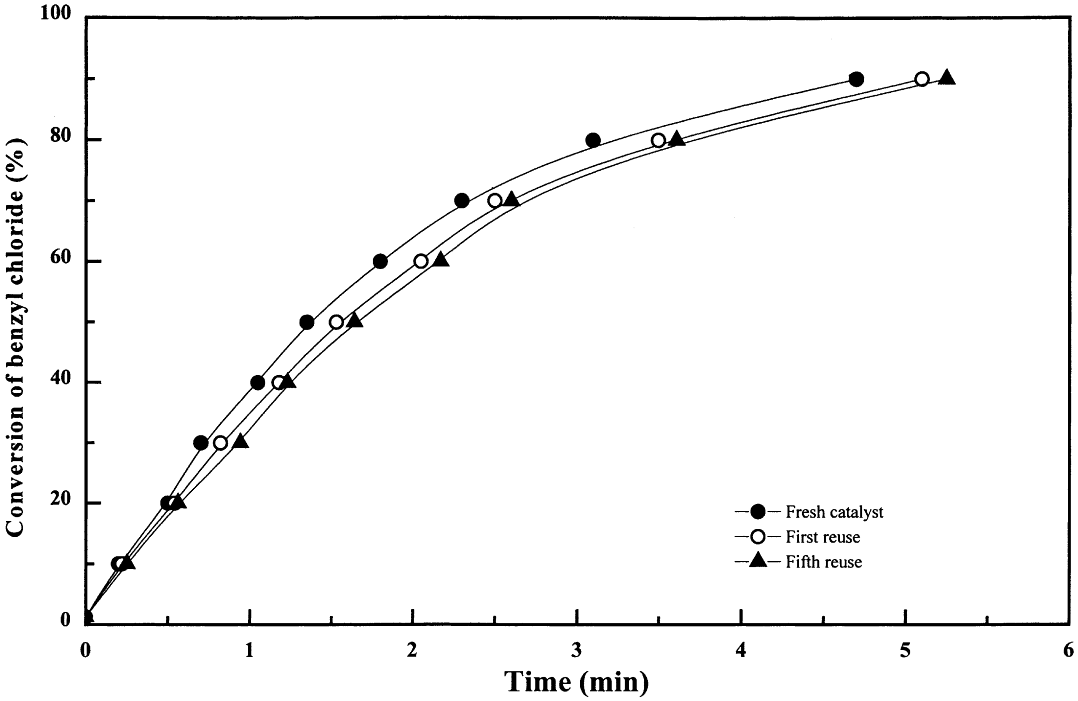


Fig. 2. Reusability of $InCl_3$/Mont.-K10 catalyst in the benzylation of benzene (at 80 °C).

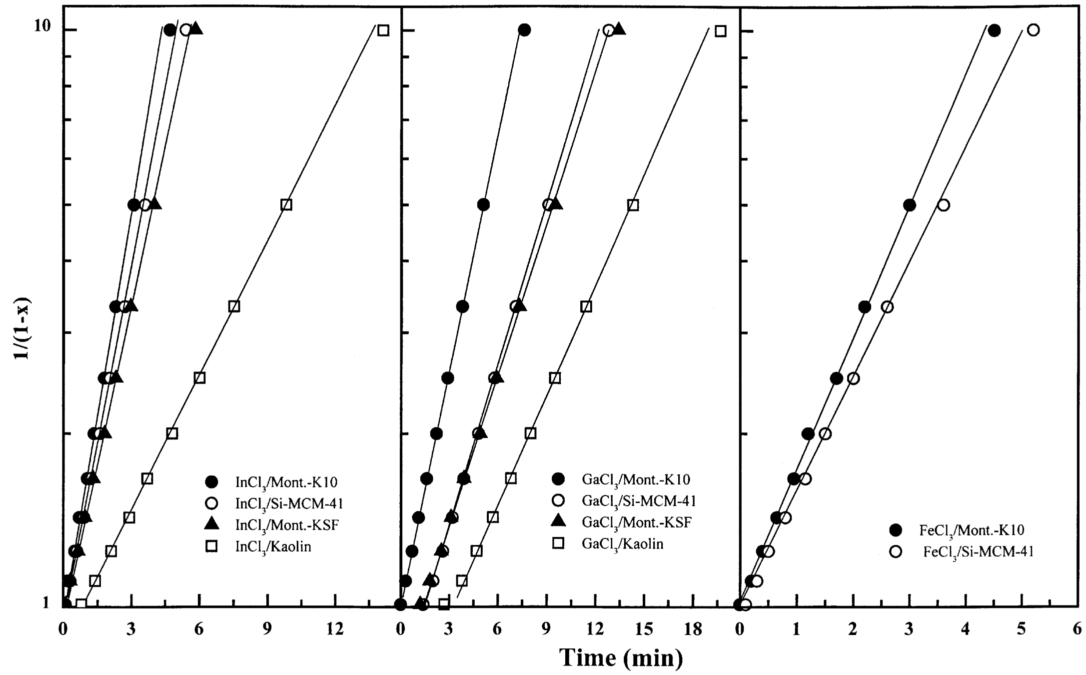


Fig. 3. Representative pseudo-first-order plots for the benzylation of benzene over the different supported metal chloride catalysts.

where x is the fractional conversion of benzyl chloride, k_a the apparent first-order rate constant, t the reaction time and t_0 the reaction induction period. Representative linear $\log[1/(1-x)]$ against $(t-t_0)$ plots, according to the above rate law, are given in Fig. 3. The best fit of the rate data to the first-order rate law could however, be obtained over the benzyl chloride conversion range from 10 to 90%. The values of the apparent rate constants for the reaction over the different catalysts have been included in Tables 1 and 2.

The values of the activation energy and frequency factor for the different catalysts were obtained from the Arrhenius expression. These values are included in Table 2. Among the supported metal chloride catalysts, the $FeCl_3$/Mont.-K10 has the lowest activation energy but also the lowest frequency factor. Whereas, the $ZnCl_2$/Si-MCM-41 has the highest activation energy but also the highest frequency factor.

3.2. Effect of metal chloride loading

Fig. 4 shows the influence of metal chloride loading on the reaction rate constant and induction period in the benzylation of benzene over the $InCl_3$/Mont.-K10 catalyst. The induction period is decreased and the rate constant is increased with increasing the metal chloride loading on Mont.-K10 support. At the lower metal chloride loading ($<1.1\,\mathrm{mmol\,g^{-1}}$), its effect on the two is very appreciable but at the higher metal chloride loading, both the reaction rate and induction period are leveled-off. Thus the metal chloride loading of $1.1\,\mathrm{mmol\,g^{-1}}$ seems to be the optimum one.

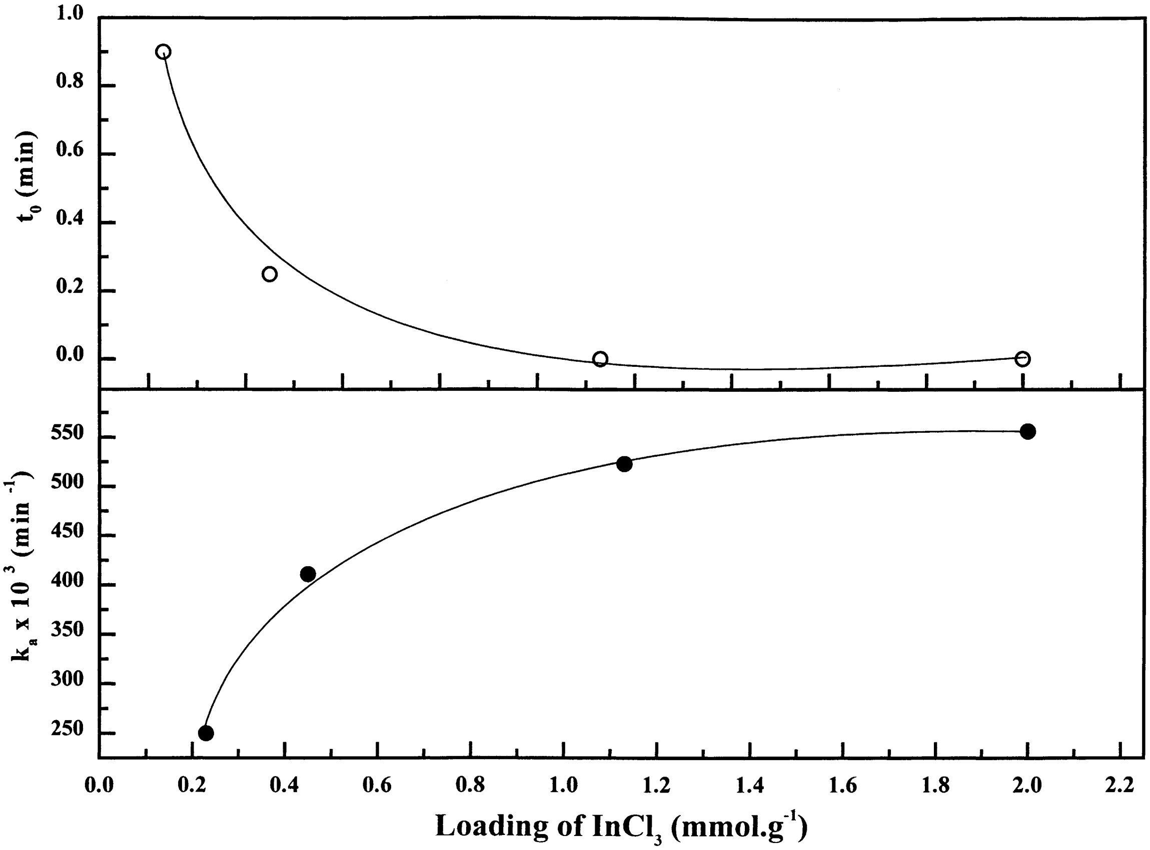


Fig. 4. Effect of $InCl_3$ loading in the $InCl_3$/Mont.-K10 catalyst on the conversion of benzyl chloride (at 80 °C) in the benzylation of benzene.

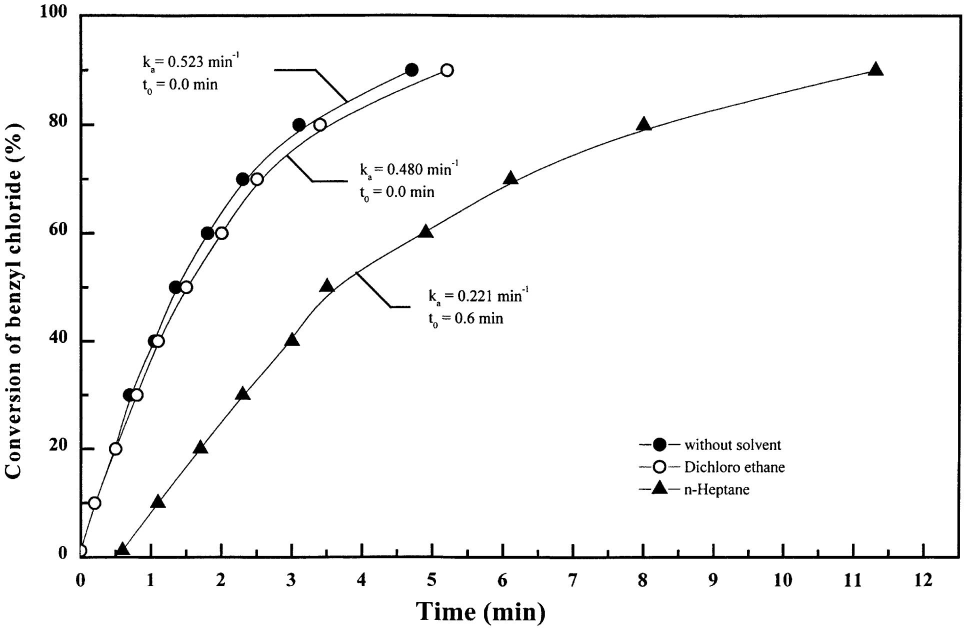


Fig. 5. Effect of solvent on the conversion of benzyl chloride (at 80 °C) in the benzylation of benzene over $InCl_3$/Mont.-K10.

3.3. Effect of solvent

Results showing the effect of solvent on the rate of benzylation of benzene over $InCl_3$/Mont.-K10 are presented in Fig. 5. The reaction rate is highest in the absence of any solvent. It is decreased when the solvent (viz. dichloroethane and *n*-heptane) is used, the decrease is quite large when *n*-heptane is used as a solvent but it is small for dichloroethane as a solvent. The reaction induction period is increased when *n*-heptane was used as a solvent. The observed solvent effect on the reaction rate is expected because of the competitive adsorption of both the reactants and the solvent on the catalyst. The results show that among the two solvents, dichloroethane is a better solvent for the benzylation reaction.

3.4. Effect of moisture

In order to study the effect of moisture present in the reaction mixture, benzene saturated with water at RT was used for the benzylation of benzene. Results showing the effect of moisture present in the reaction mixture on the benzene benzylation over the $InCl_3$ (or $GaCl_3$)/Mont.-K10 (or Si-MCM-41) are presented in Fig. 6.

Because of the presence of moisture in the reaction mixture, the reaction induction period is increased slightly without affecting significantly the reaction rate once the reaction started after the induction period. Apart from their very high activity in the benzylation process, the low moisture sensitivity of these catalysts, is of great practical importance. Thus, unlike clayzic catalyst [13], the $InCl_3$ (or $GaCl_3$)/Mont.-K10 (or Si-MCM-41) catalysts do not demand stringent moisture-free conditions for them to be highly active/selective in the benzylation process. The results obtained with these catalysts are quite reproducible.

3.5. Effect of electron donating substituent group(s)/reaction mechanism

Results showing the influence of different substituent groups attached to aromatic benzene nucleus on the conversion of benzyl chloride in the benzylation of corresponding substituted benzenes (at 80 °C) over the $InCl_3$/Mont.-K10 catalyst are presented in Fig. 7. The first-order rate constants (k_a) and induction period

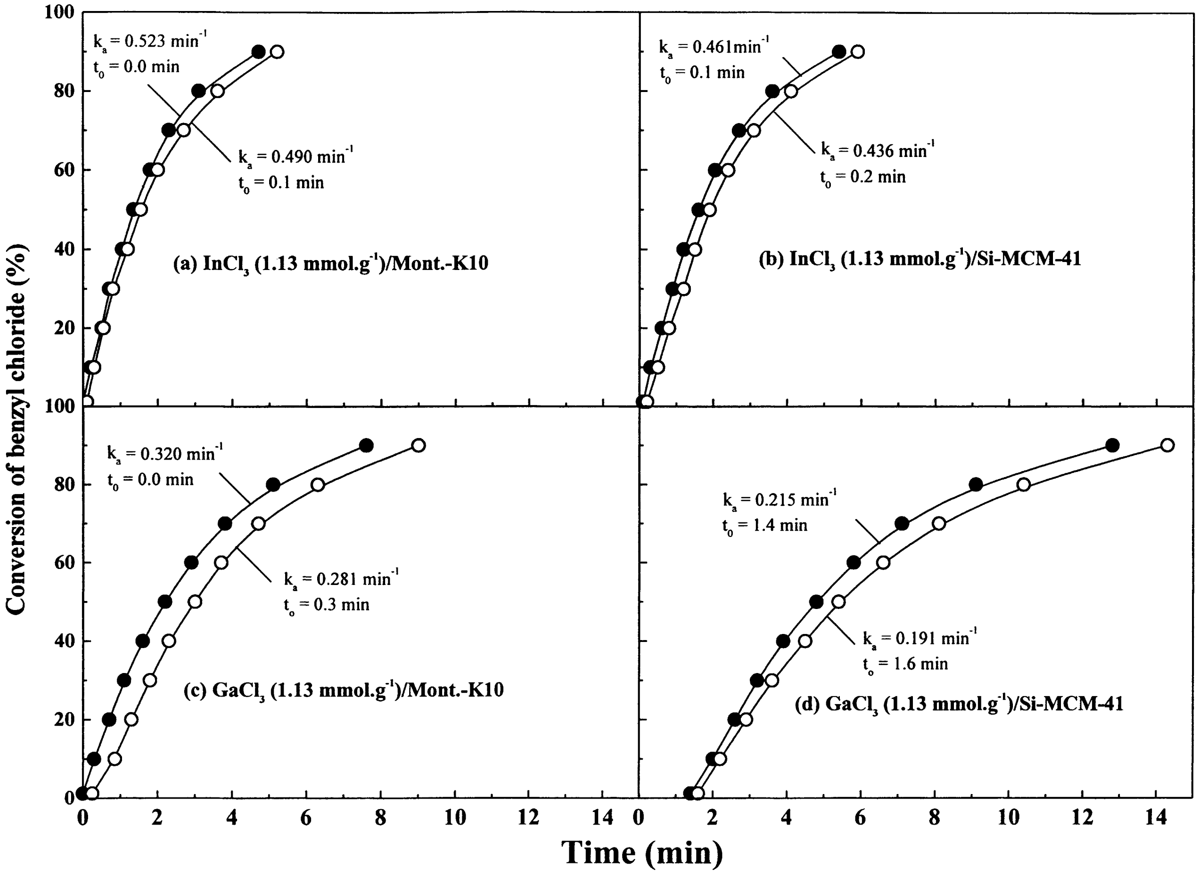


Fig. 6. Effect of moisture in the reaction mixture on the conversion of benzyl chloride (at 80 °C) in the benzylation of benzene over $InCl_3$ (or $GaCl_3$)/Mont.-K10 (or Si-MCM-41) catalyst.

for the benzylation reactions are as follows:

Substrate	Benzene	Toluene	Mesitylene	Anisole
k_a (min^{-1})	0.52	0.42	0.37	0.24
Induction period (min)	0.0	0.2	0.25	1.7

According to the classical mechanism of the Friedel–Crafts type acid catalyzed benzylation reaction, the benzylation of an aromatic compound is easier if one or more electron donating groups are present in the aromatic ring [1]. Hence, the order for the rate of benzylation for the aromatic compound is expected as follows: anisole > mesitylene > toluene ≫ benzene. But, what is observed in the present case is totally opposite to that expected according to the classical mechanism. The first-order rate constant for the benzylation of benzene and substituted benzenes is in the following order: benzene > methyl benzene > tri-methyl benzene > methoxy benzene. This indicates that, for this catalyst, the reaction mechanism is different from that for the classical acid catalyzed benzylation reactions.

The metal chloride species present in the catalysts have redox properties, which are expected to play important role in the benzylation reaction over the present catalysts. The following probable redox mechanism

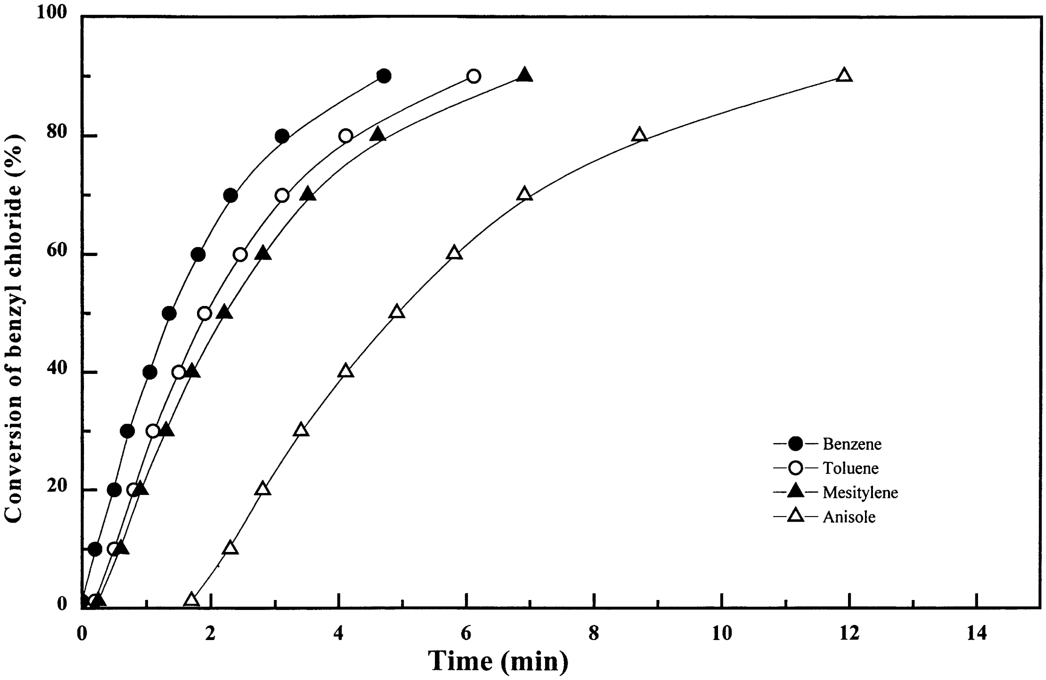


Fig. 7. Effect of substituents present in the benzene ring on the conversion of benzyl chloride (at 80 °C) in the benzylation over $\mathrm{InCl_3}$/Mont.-K10.

for the activation of both benzyl chloride and aromatic compound by the metal chloride species leading to the benzylation reaction, is proposed.

3.5.1. Activation of benzyl chloride

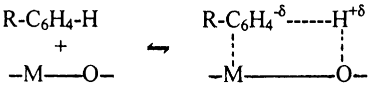
$$m\mathrm{C_6H_5CH_2Cl} + \mathrm{M}^{n+} \leftrightarrows m\mathrm{C_6H_5CH_2Cl}^{\bullet+} + \mathrm{M}^{(n-m)+} \qquad (2)$$

where M = In, Ga, Fe or Zn, $n = 3$ (for In, Ga and Fe) or 2 (for Zn) and $m = 2$ (for In and Ga) and 1 (for Fe and Zn)

$$m\mathrm{C_6H_5CH_2Cl}^{\bullet+} \leftrightarrows m\mathrm{C_6H_5CH_2^+} + m\mathrm{Cl}^{\bullet} \qquad (3)$$

$$\mathrm{M}^{(n-m)+} + m\mathrm{Cl}^{\bullet} \leftrightarrows \mathrm{M}^{n+} + m\mathrm{Cl}^{-} \qquad (4)$$

3.5.2. Activation of aromatic compound



$$\begin{array}{c} \mathrm{R\text{-}C_6H_4\text{-}H} \\ + \\ -\mathrm{M}\text{——}\mathrm{O}- \end{array} \leftrightarrows \begin{array}{c} \mathrm{R\text{-}C_6H_4}^{-\delta}\text{------}\mathrm{H}^{+\delta} \\ \vdots \qquad\qquad \vdots \\ -\mathrm{M}\text{————}\mathrm{O}- \end{array} \qquad (5)$$

3.5.3. Reaction between benzyl carbocation and activated aromatic compound

$$\mathrm{R{-}C_6H_4}^{\delta-}\cdots\mathrm{H}^{\delta+} + \mathrm{C_6H_5CH_2}^{+} \leftrightarrows \mathrm{R{-}C_6H_4CH_2C_6H_5} + \mathrm{H}^{+} \qquad (6)$$

$$\mathrm{H}^{+} + \mathrm{Cl}^{-} \leftrightarrows \mathrm{HCl} \qquad (7)$$

The above redox mechanism is similar to that proposed earlier for the alkylation or acylation reactions [7,9,22]. This mechanism is quite consistent with the observations, the order for the benzene benzylation activity of the supported $\mathrm{InCl_3}$, $\mathrm{GaCl_3}$, $\mathrm{FeCl_3}$ and $\mathrm{ZnCl_2}$ catalysts is almost same as that for the redox potential of the metal present in the supported metal chloride catalysts (Section 3.1).

4. Conclusions

Following important conclusions have been drawn from this investigation.

1. All the supported metal chloride catalysts show high activity for the benzene benzylation. The benzylation activity of the supported metal chloride catalysts is in the following order: supported $FeCl_3$ > supported $InCl_3$ > supported $GaCl_3$ > supported $ZnCl_2$. But the catalyst order for the diphenyl methane selectivity is supported $InCl_3$ or $GaCl_3$ > supported $FeCl_3$ > supported $ZnCl_2$.
2. Among the different supports employed, Mont.-K10 is found to be the best support for all the supported metal chloride catalysts. The $InCl_3$/Mont.-K10 catalyst showed both high activity and high selectivity for the benzylation.
3. The benzene benzylation is influenced by the solvent used in the process. Among dichloroethane and *n*-heptane, the former is a better solvent for the reaction.
4. The presence of moisture in the reaction mixture has little or no effect when supported $InCl_3$ or $GaCl_3$ catalysts are used for the benzene benzylation reaction.
5. The benzene benzylation reaction (with the excess of benzene) over all the supported metal chloride catalysts follows first-order kinetics. The data for the benzyl chloride conversion in the range of 10–90% could be fitted very well to the first-order rate law.
6. $InCl_3$/Mont.-K10 catalyst shows a following trend for its activity in the benzylation of benzene and substituted benzenes: benzene > methyl benzene > tri-methyl benzene > methoxy benzene, which is totally opposite to that observed for the classical acid catalyzed Friedel–Crafts type benzylation reaction. The order for the benzene benzylation activity of the supported $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ catalysts is found to be same as that for the redox potential of the metal present in the supported metal chloride catalysts, indicating a possibility of redox mechanism in the benzylation process.

Acknowledgements

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