

**SYNTHESIS OF FINE CHEMICALS USING  
HETEROGENEOUS CATALYSTS**

**SUMAN KUMAR JANA**

**AUGUST, 2001**

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HETEROGENEOUS CATALYSTS**

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BY

**SUMAN KUMAR JANA, M. Sc.**

**CHEMICAL ENGINEERING DIVISION  
NATIONAL CHEMICAL LABORATORY  
PUNE-411 008  
INDIA**

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# **DEDICATED TO MY PARENTS**

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(Suman Kumar Jana)

PUNE

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## **CERTIFICATE AS PER FORM 'A'**

Certified that the work incorporated in the thesis **“Synthesis of Fine Chemicals using Heterogeneous Catalysts”** submitted by **Mr. Suman Kumar Jana** was carried out by the candidate under my guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. Vasant R. Choudhary)

Research Guide

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# ***SUMMARY AND CONCLUSIONS***

## **SUMMARY AND CONCLUSIONS**

Synthesis of fine chemicals using homogeneous catalysts poses several problems, such as difficulty in its separation and recovery, disposal of spent catalyst, formation of undesirable and/or toxic wastes, etc. Worldwide efforts have been made for replacing homogeneous catalysts by reusable, easily separable heterogeneous solid catalysts for the synthesis of fine chemicals.

Liquid phase benzylation or acylation of aromatic compounds, using homogeneous Lewis acid catalysts, is commonly practiced Friedel-Crafts type reaction in organic synthesis. However, the commonly used homogeneous acid catalyst,  $\text{AlCl}_3$  poses several problems, such as requirement of more than stoichiometric amount, difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Moreover, it is highly moisture sensitive and hence demands moisture-free solvent and reactants and anhydrous catalyst, and also dry atmosphere for catalyst handling. Development of reusable solid acid catalysts having high activity and little or no moisture sensitivity for the liquid phase Friedel-Crafts reactions is, therefore, of great practical importance. The benzylation or acylation of aromatic compound containing electron-donating group (e.g. alkyl, alkoxy, OH, etc) can be accomplished with ease but it is difficult in the absence of such aromatic ring-activating group (e.g. benzene). Hence, worldwide efforts have been made for the benzylation or acylation of benzene and other aromatic compounds, using a number of solid acid catalysts, such as heteropolyacids, sulfated  $\text{ZrO}_2$  or  $\text{Fe}_2\text{O}_3$ , Nafion-H, Fe-containing MCM-41, ion-exchanged clays and clayzic for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene, and heteropolyacids, H-beta, H-ZSM-5 and sulfated  $\text{ZrO}_2$  for benzylation of aromatic compounds. However, these catalysts show low to moderate activity and/or poor selectivity in these reactions.

Benzyl chloride is a commonly used benzylicating agent for the benzylation of aromatic compounds. However, in the presence of many Lewis acid catalysts, benzyl chloride undergoes a self-condensation reaction to form polybenzyl, which can be an undesirable side reaction in the benzylation of aromatic compounds. It is, therefore, interesting to study the polycondensation of benzyl chloride over the solid catalysts to be used in the benzylation reactions. Earlier studies reported on the polycondensation of benzyl chloride are heterogeneous ferrous sulfate and iron oxide catalysts.

Synthesis of tert-butyl ester from tert-butanol using acid catalyst poses a very serious problem of the dehydration of tert-butanol to isobutylene and also the hydrolysis of tert-butyl ester leading to carboxylic acid and isobutylene. Hence, development of a reusable non-acidic or mildly acidic solid catalyst(s) having both high activity and high selectivity for the esterification of tert-butanol is of great practical importance. A few studies have been reported for the esterification of tert-butanol by different acyl chlorides over basic alumina and silica gel. However, these catalysts

show very poor activity and also there is a problem of HCl evolved (which is undesirable) in the reaction.

The present work for the Ph. D. thesis was undertaken as a part of the comprehensive R & D programme in our laboratory for replacing homogeneous catalysts by novel, reusable and highly active/selective heterogeneous solid catalysts for the synthesis of fine chemicals.

The thesis has been divided into nine chapters.

## **CHAPTER-1 INTRODUCTION-OBJECTIVES AND SCOPE**

In this chapter, a brief literature survey on the following reactions:

- benzylation of benzene and other aromatic compounds,
- acylation of benzene and other aromatic compounds,
- polycondensation of benzyl chloride, and
- esterification of tert-butanol

has been presented along with the objectives and scope of the present work.

## **CHAPTER-2 EXPERIMENTAL**

In this chapter, preparation of the following catalysts:

- Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts,
- GaCl<sub>3</sub>, InCl<sub>3</sub> and other metal chlorides supported on commercial clays and Si-MCM-41,
- Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and TiO<sub>x</sub> supported on micro-, meso- and macro-porous catalyst carriers, and
- Ga-Mg-hydrotalcite anionic clay,

characterization of the catalysts for their

- crystalline phases (by XRD),
- surface area (using a Surface Area Analyzer),
- crystal size and morphology (by SEM),
- surface hydroxyls (by FTIR),
- surface composition (by XPS),
- strong acid sites, measured in terms of the pyridine chemisorbed at 400<sup>o</sup>C,

and procedures for carrying out the reactions:

- benzylation of benzene and other aromatic compounds,
- acylation of benzene and other aromatic compounds,
- polycondensation of benzyl chloride, and



- esterification of tert-butanol by acetic anhydride have been described.

### **CHAPTER-3 BENZYLATION OF BENZENE BY BENZYL CHLORIDE OVER Fe-, Zn-, Ga- AND In-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS.**

Liquid phase benzylation of benzene by benzyl chloride to diphenylmethane over H-ZSM-5, H-gallosilicate (MFI), H-galloaluminosilicate (MFI), H-ferrosilicate (MFI), H-ferroaluminosilicate (MFI), Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5, ZnO/H-ZSM-5, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 zeolites (at 60<sup>0</sup>C and 80<sup>0</sup>C) has been investigated. A complete or partial substitution of Al in H-ZSM-5 zeolite by Fe or Ga or an impregnation of the zeolite by Fe<sub>2</sub>O<sub>3</sub>, ZnO, Ga<sub>2</sub>O<sub>3</sub> or In<sub>2</sub>O<sub>3</sub> makes the zeolite highly active in the benzylation process. The redox function created due to the modification of the HZSM-5 zeolite by Fe, Zn, Ga or In seems to play very important role in the benzylation process. However, all these catalysts show a significant induction period for the reaction. The Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5 catalyst showed high benzene benzylation activity even in the presence of moisture in the catalyst and/or in the substrate. However, the reaction induction period is increased markedly with increasing the moisture and it is reduced by removing the moisture from the catalyst by refluxing with moisture-free benzene. It is also reduced by the HCl gas pretreatment to the catalyst before the benzylation reaction. The Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 catalysts showed excellent reusability in the benzene benzylation. Kinetics of the benzene benzylation (using an excess of benzene) over the H-GaMFI, H-GaAlMFI, H-FeMFI, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 catalysts has also been thoroughly investigated. A plausible reaction mechanism for the reaction over the modified ZSM-5 zeolite catalysts is proposed

### **CHAPTER-4 BENZYLATION AND ACYLATION OF BENZENE OR OTHER AROMATIC COMPOUNDS OVER GaCl<sub>3</sub> AND InCl<sub>3</sub> SUPPORTED ON COMMERCIAL CLAYS AND SI-MCM-41.**

Liquid phase benzylation of benzene by benzyl chloride to diphenyl methane over InCl<sub>3</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub> and ZnCl<sub>2</sub> supported on commercial clays (viz. Montmorillonite-K10, Montmorillonite-KSF and Kaolin) or on high silica mesoporous MCM-41 (at 60<sup>0</sup>, 70<sup>0</sup> and 80<sup>0</sup>C) has been investigated. The supported InCl<sub>3</sub>, GaCl<sub>3</sub> and FeCl<sub>3</sub> 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<sub>3</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub> or ZnCl<sub>2</sub> seems to play a very important role in the benzylation process. Among the catalysts, the

InCl<sub>3</sub>/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<sub>3</sub> (or GaCl<sub>3</sub>)/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 has also been thoroughly investigated. A plausible reaction mechanism for the benzylation over the supported metal chloride catalysts is proposed.

Liquid phase acylation of benzene by acyl chloride (e.g. benzoyl chloride, butyryl chloride or phenyl acetyl chloride) over InCl<sub>3</sub>, GaCl<sub>3</sub> and ZnCl<sub>2</sub> supported on commercial clays (viz. Montmorillonite-K10, Montmorillonite-KSF and Kaolin) or high silica mesoporous MCM-41 at 80<sup>0</sup>C has been investigated. The Mont.-K10 and Si-MCM-41 supported InCl<sub>3</sub> and GaCl<sub>3</sub> catalysts showed high activity in the acylation of benzene by benzoyl chloride even in the presence of moisture in the reaction mixture. The redox function of the supported InCl<sub>3</sub>, GaCl<sub>3</sub> or ZnCl<sub>2</sub> catalysts seems to play a very important role in the acylation process.

#### **CHAPTER-5 BENZYLATION AND BENZOYLATION OF BENZENE AND OTHER AROMATIC COMPOUNDS OVER SUPPORTED Ga<sub>2</sub>O<sub>3</sub> AND In<sub>2</sub>O<sub>3</sub> CATALYSTS IN THE PRESENCE OR ABSENCE OF MOISTURE.**

Benylation of benzene by benzyl chloride over In<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> supported on micro-, meso- and macro-porous catalyst carriers at 80<sup>0</sup>C has been investigated. The supported In<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> showed high activity for the benzylation of benzene. The redox function and activation of aromatic substrate by the supported In<sub>2</sub>O<sub>3</sub> or Ga<sub>2</sub>O<sub>3</sub> seem to play a very important role in the benzylation process. Among the catalysts, the In<sub>2</sub>O<sub>3</sub>/Si-MCM-41 showed the highest activity for the benzylation of benzene and also for the benzylation of other aromatic compounds. The supported In<sub>2</sub>O<sub>3</sub> or Ga<sub>2</sub>O<sub>3</sub> catalyst showed high benzene benzylation activity even in the presence of moisture in the reaction mixture. A plausible redox mechanism for the benzylation over the supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts is proposed.

Liquid phase benzylation of benzene by benzoyl chloride over In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and ZnO supported on high silica mesoporous MCM-41 at 80<sup>0</sup>C has been investigated. The supported In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and ZnO catalysts showed high activity for the benzylation of benzene. The redox function and activation of aromatic substrate by

the supported  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  or  $\text{ZnO}$  seem to play a very important role in the benzylation process. Among the catalysts, the  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  showed the highest activity for the benzylation of benzene. The activity of this catalyst for the benzylation of benzene and substituted benzenes is in the following order: anisole > mesitylene > p-xylene > toluene > benzene. The  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 showed high benzene benzylation activity even in the presence of moisture in the reaction mixture. A plausible redox mechanism for the benzylation over the supported metal oxide catalysts is proposed.

#### **CHAPTER-6 HIGHLY ACTIVE AND LOW MOISTURE SENSITIVE SUPPORTED THALLIUM OXIDE CATALYSTS FOR FRIEDEL-CRAFTS TYPE BENZYLIATION AND ACYLATION REACTIONS: STRONG THALLIUM OXIDE-SUPPORT INTERACTIONS.**

Liquid phase benzylation of benzene by benzyl chloride (at  $80^\circ\text{C}$ ) over basic  $\text{TlO}_x$  (without support) and supported  $\text{TlO}_x$  prepared using different low and high surface area commonly used catalyst carriers has been investigated. The catalysts have been characterized for their surface area and also by XRD, FTIR and XPS. Strong  $\text{TlO}_x$  - support interactions (which are chemical in nature) have been observed for the catalysts prepared using high surface area supports, such as Si-MCM-41, silica gel (HS), silica-alumina (HS), alumina (HS) and zirconia (HS), which have surface hydroxyl groups. These catalysts are found to be inactive for the benzene benzylation or benzylation reaction. However, the  $\text{TlO}_x$  supported on sintered low surface area macroporous catalyst carriers [viz. zirconia (LS), silica (LS) and silica-alumina (LS)], which have no surface hydroxyl groups, showed high benzene benzylation activity. The  $\text{TlO}_x$  / zirconia (LS) is a highly promising catalyst for both the benzylation and acylation of benzene and other aromatic compounds and it shows high activity even in the presence of moisture. The activity of this catalyst for the benzylation of benzene and substituted benzenes is in the following order: benzene > toluene > p-xylene > anisole. The induction period for the benzylation and acylation reactions over the catalyst, however, depends strongly on the moisture present in the catalyst and/or in the reaction mixture. The induction period is drastically reduced by the HCl gas pretreatment to the catalyst before the benzylation or acylation reaction. Only the catalyst, which contains  $\text{Tl}_2\text{O}_3$ , shows activity for the benzylation and acylation reactions. A redox mechanism for these reactions over the supported  $\text{TlO}_x$  catalysts has been proposed.

## **CHAPTER-7 HIGHLY ACTIVE, REUSABLE AND MOISTURE INSENSITIVE CATALYST OBTAINED FROM BASIC Ga-Mg-HYDROTALCITE ANIONIC CLAY FOR FRIEDEL-CRAFTS TYPE BENZYLATION AND ACYLATION REACTIONS.**

Liquid phase benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of benzene and toluene over a Ga-Mg hydrotalcite (which is a basic anionic clay) with or without HCl gas pretreatment and also over the hydrotalcite used earlier in the toluene benzylation (at 110<sup>0</sup>C) have been investigated. The fresh, used and HCl gas pretreated hydrotalcite catalysts were characterized for their surface area, basicity, crystalline structure and phases and also for their surface composition. The fresh hydrotalcite showed no catalytic activity for both the benzylation and benzylation reactions for a long period. However, after a long induction period (2.7 h), the catalyst showed a very high activity in the toluene benzylation (at 110<sup>0</sup>C). Whereas, the catalyst after its use in the toluene benzylation or after its HCl gas pretreatment showed very high activity for both the reactions with a much shorter induction period. The hydrotalcite-derived catalyst consists essentially highly dispersed gallium and magnesium chlorides on MgO. The presence of moisture in the reaction mixture has beneficial effects on the acylation reactions over the used catalyst.

## **CHAPTER-8 POLYCONDENSATION OF BENZYL CHLORIDE OVER Fe-, Ga- AND In-CONTAINING SOLID CATALYSTS.**

A number of Fe-containing solid catalysts, such as FeCl<sub>3</sub> deposited on Montmorillonite K10 clay and mesoporous MCM-41 zeolite, Fe<sub>2</sub>O<sub>3</sub> supported on macroporous commercial silica-alumina catalyst carrier or mesoporous MCM-41, and Fe-modified ZSM-5 type zeolites (viz. Fe/H-ZSM-5, H-FeMFI, H-FeAlMFI and Fe/H-GaAl MFI), have been compared for their performance in the polycondensation of benzyl chloride. Influence of solvent (viz. dichloroethane, n-hexane, n-octane and ethanol) and temperature on the rate of polycondensation of benzyl chloride over a selected catalyst has also been studied. All these Fe-containing catalysts show high activity in the polycondensation reaction at the reaction temperature normally employed in the benzylation of aromatic compounds by benzyl chloride. However, the polycondensation is strongly influenced by solvent used as the reaction medium.

Performance of In- and Ga-modified ZSM-5 type zeolites (viz. In<sub>2</sub>O<sub>3</sub>/H-ZSM-5, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5, H-GaMFI and H-GaAlMFI) and InCl<sub>3</sub> or GaCl<sub>3</sub> supported on high silica mesoporous MCM-41 or on Mont.-K10 in the liquid phase polycondensation of benzyl chloride to polybenzyl has been investigated. Influence of solvent (viz. dichloroethane, n-heptane and ethanol) and temperature on the rate of polycondensation

of benzyl chloride over the catalyst (InCl<sub>3</sub>/Si-MCM-41) showing highest polycondensation activity has also been studied. The In- and Ga-containing solid catalysts show moderate activity in the polycondensation reaction at the reaction conditions normally employed in the benzylation of aromatic compounds by benzyl chloride. However, the polycondensation is strongly influenced by the solubility of the polybenzyl polymer in the reaction medium and consequently by the solvent used as the reaction medium.

#### **CHAPTER-9 SELECTIVE ESTERIFICATION OF TERT-BUTANOL BY ACETIC ACID ANHYDRIDE OVER CLAY SUPPORTED InCl<sub>3</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub> AND ZnCl<sub>2</sub> CATALYSTS.**

Esterification of tert-butanol by acetic anhydride over clay (Kaolin, Mont.-K10 and Mont.-KSF) supported InCl<sub>3</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub> and ZnCl<sub>2</sub> catalysts (metal chloride loading = 1.1 mmol.g<sup>-1</sup>) have been investigated. All these catalysts showed high selectivity (≥ 98%) at high conversion in the esterification of tert-butanol by acetic anhydride to tert-butyl acetate and very low activity for the dehydration of tert-butanol at ≤ 50°C. For all the catalysts, Mont.-K10 is the best support and the order of their esterification activity (at 26°C) is: InCl<sub>3</sub>/Mont.-K10 (TOF = 0.025 s<sup>-1</sup>) > GaCl<sub>3</sub>/Mont.-K10 (0.023 s<sup>-1</sup>) > FeCl<sub>3</sub>/Mont.-K10 (0.02 s<sup>-1</sup>) ≥ ZnCl<sub>2</sub>/Mont.-K10 (0.019 s<sup>-1</sup>). InCl<sub>3</sub>/Mont.-K10 is found to be a highly active, selective and reusable catalyst for the esterification.

***CHAPTER-1***  
***INTRODUCTION-OBJECTIVES AND***  
***SCOPE***

## Chapter-1

### **INTRODUCTION-OBJECTIVES AND SCOPE**

#### **1.1 WHAT ARE FINE CHEMICALS?**

There are no universally accepted definitions of bulk, fine and specialty chemicals; there are no classifications based on any intrinsic properties. A substance that is currently viewed as a bulk chemical might well have been classified as a fine chemical at an earlier stage in its development. A useful working definition of a fine chemical is one with a price of more than 10 US dollars.kg<sup>-1</sup> and a volume of less than 10,000 tons per annum on a worldwide basis. There is almost no difference between fine chemicals that are often intermediates and specialty chemicals such as pharmaceuticals, pesticides, flavors and fragrances.

From a chemical point of view, 'Fine chemicals' are generally complex, multifunctional molecules with low volatility and limited thermal stability. This often necessitates carrying out reactions in the liquid phase at moderate temperatures. Fine chemicals manufacture often involves multi-step syntheses and is generally performed in a multipurpose equipment. This contrasts with the manufacture of bulk chemicals, which usually involves continuous processing in dedicated plants. Hence, the emphasis in fine chemicals manufacture is on the development of processes that have broad scope and can be implemented in standard multipurpose equipment.

#### **1.2 ENVIRONMENTAL FACTOR**

It is now widely accepted that there is an urgent need for more environmentally acceptable processes in the chemical industry [1]. This trends towards what has become known as 'Green Chemistry' [2,3] or sustainable technology necessitates a shift from traditional concepts of process efficiency, that focus exclusively on chemical yield, to one that assigns economic value to eliminating waste and avoiding the use of toxic and/or hazardous substances.

The sheer magnitude of the waste problem in the manufacture of chemicals is readily apparent from a consideration of the amount of waste produced per kg of product, the so-called 'E factor' [4,5], in different segments of the chemical industry (Table 1.1).

**Table 1.1** E factors in the chemical industry.

Industry segment	Product tonnage <sup>a</sup>	E factor (kg waste/kg product)
Bulk Chemicals	$< 10^4 - 10^6$	$< 1 \rightarrow 5$
Fine Chemicals	$10^2 - 10^4$	$5 \rightarrow > 50$
Pharmaceuticals	$10 - 10^3$	$25 \rightarrow > 100$

<sup>a</sup> Depending on the product this could be the capacity of a single plant or the world-wide production.

These large quantities of waste consist primarily of inorganic salts, formed in the reaction or in subsequent neutralization steps. The E factor increases dramatically on going downstream from bulk to fine chemicals and pharmaceuticals, partly because of the use of stoichiometric (inorganic) reagents rather than catalytic methodologies. Therefore, the need for greener, low-salt technologies is clearly more urgent in fine chemicals manufacture.

### 1.3 DEVELOPMENT OF ORGANIC SYNTHESIS AND CATALYSIS

The primary cause of waste production in the fine chemicals industry is the widespread use of stoichiometric reagents. Classical 'stoichiometric' technologies that generate copious quantities of inorganic salts are rampant in fine chemicals manufacture, primarily the domain of the synthetic organic chemist. An example, which is widely applied in fine chemicals manufacture, is Friedel-Crafts type alkylation and acylation reactions with more than one equivalent of  $AlCl_3$ .

Because of the requirement of fine chemicals in smaller quantities, the need for a reduction in waste in fine chemicals production was not fully appreciated in the past. But times are changing. Under the mounting pressure of environmental legislation the fine chemicals industry is forced to focus more attention on waste minimization and also avoiding the use of hazardous and/or toxic reagents. Hence, the time is ripe for the widespread application of catalytic methodologies.

### 1.4 WHY HETEROGENEOUS CATALYSIS?

In the drive towards cleaner methodologies the entire arsenal of catalytic methodologies – homogeneous and heterogeneous catalysis will be brought to bear on



organic synthesis. Both the approaches have their advantages and limitations. The major limitations in the homogeneously catalyzed reactions are no possible reuse, troublesome work-up, disposal of spent catalyst, corrosion, high toxicity and also low product selectivity.

Heterogeneous solid catalysts have the advantages of ease of recovery and recycling, separation of the catalyst from the reactants and products involve simple filtration or centrifugation and are environmentally friendly.

The use of microporous and mesoporous solid catalysts has shape selective properties, an additional benefits in fine chemicals synthesis. Furthermore, the modification of the solid catalysts by metals having redox functions along with their acidic or basic properties extends their catalytic scope to redox reactions. Hence, the development of reusable solid catalysts having redox function along with their acidity or basicity for the liquid phase Friedel-Crafts alkylation and acylation reactions and also for the esterification reactions, useful for the preparation of fine chemicals is, therefore, of great practical importance.

## **1.5 HETEROGENEOUSLY CATALYZED REACTIONS FOR THE SYNTHESIS OF FINE CHEMICALS.**

### **1.5.1 Friedel-Crafts Type Alkylation and Acylation Reactions**

Friedel-Crafts reactions are characterized by an extremely broad and difficult to define range of chemistries. One of the best definitions is given by Nobel Prize laureate G. A. Olah in the classical series 'Friedel-Crafts Related Reactions' [6] in which he defines these reactions 'to be any substitution, isomerization, elimination, cracking, polymerization or addition reactions taking place under the catalytic effect of Lewis acidic type acid halides or protonic acids'.

Friedel-Crafts reactions are electrophilic in nature and can be divided into two main categories – alkylations and acylations. The essential feature of the reaction consists in the replacement of a hydrogen atom of an aromatic compound by an alkyl or acyl group derived from an alkylating or acylating agent in the presence of Lewis acids (e.g.  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ , etc.) or protonic acids (e.g.  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ , etc.). Among all the catalysts,  $\text{AlCl}_3$  is commonly used for the Friedel-Crafts type reactions. The overall reaction scheme for the aromatic alkylations or acylations is written as follows:



[where ArH = aromatic compound; RX = alkylating or acylating agent, X = Cl, Br, I, OH, COCl, COBr, COI, COOH, O(CO)<sub>2</sub>R]

The primary function of the catalyst is to generate an alkyl or acyl carbocation. A disadvantage of classical Friedel-Crafts chemistry with Lewis acids (metal halides) is that the catalyst coordinates strongly to the basic compounds and eventually becomes exhausted and cannot readily be regenerated. Other drawbacks are during alkylations several reactions can take place concurrently (e.g. polymerization, polyalkylation, isomerization, transalkylation, cracking, etc.) which reduce selectivity for the desired compound.

Shape selective solid catalysts are very capable of replacing traditional Friedel-Crafts catalysts. Besides providing an environmental advantage, the higher selectivity can have economic advantages also. Often separation of the desired product from the product mixture is easier, resulting in lower energy costs. Solid acid catalysts in heterogeneous Friedel-Crafts reactions is rapidly expanding field for the synthesis of fine chemicals.

#### ***1.5.1.1 Friedel-Crafts Type Alkylation Reactions***

Friedel-Crafts alkylation of aromatic compounds is widely used in the large scale synthesis of petrochemicals and a great variety of fine chemicals and intermediates. Benzylation is an important class of Friedel-Crafts type alkylation reaction used for the synthesis of cosmetics, dyes, pharmaceuticals and a variety of fine chemicals and intermediates. Benzene and other aromatic compounds can be benzylated by different benzyl derivatives (e.g. benzyl chloride, bromide, iodide or alcohol), however, benzyl chloride is a commonly used benzylating agent for the benzylation reaction. A number of solid acid catalysts, such as heteropoly acids and their salts [7-13], super acids [14-19], zeolites [20-26], mesoporous MCM-41 type catalysts [27-31], metal chloride and clay based catalysts [32-60], metal oxides [61-63], spinel [64], metal sulfates [65], alumina or silica-alumina [66-68], carbon [69] and hydrotalcite [70] for the benzylation of benzene and other aromatic compounds by benzyl chloride are reported earlier. The benzylation of aromatic compounds containing electron donating group (e.g. alkyl, alkoxy, OH) can be accomplished with ease, but in the absence of such an aromatic ring activating group (e.g. benzene) is relatively difficult [6]. The relatively small number of data of the important catalysts for the benzylation of benzene by benzyl chloride (which is relatively difficult to benzylate) is a reflection of the fact that the number of catalysts evaluated so

far is limited. The studies for the benzylation of benzene and other aromatic compounds by benzyl chloride, reported so far, are summarized in Table 1.2.

#### ***1.5.1.2 Friedel-Crafts Type Acylation Reactions***

Friedel-Crafts type acylation of aromatic compounds to aromatic ketones (important intermediates for the production of fine chemicals) is one of the most important synthesis methods in organic chemistry. Benzene and other aromatic compounds can be acylated by different carboxylic acid derivatives (e.g. carboxylic acid halide, carboxylic acid anhydride, carboxylic acid), however, carboxylic acid chloride is a commonly used acylating agent for the acylation reaction. In the last 15 to 20 years, worldwide efforts have been made to replace homogeneous acid catalysts by heterogeneous solid acid catalysts, such as: heteropoly acids and salts [7,8,12,13,71], resins [72], modified  $ZrO_2$  [73-77], zeolites [78-93], metal chloride and clay based catalysts [59,94-101], metal oxides [31,63], hydrotalcite [70], metal sulfate [65] and graphite [102] for the acylation of benzene and other aromatic compounds by different acyl halides. The very small number of literature of the important catalysts for the industrially important acylation reactions, is largely a reflection of the fact that the number of catalysts evaluated so far is very limited, the list of active catalysts is likely to grow as a result of the future research efforts. The studies for the acylation of aromatic compounds by different acyl halides, reported so far, are summarized in Table 1.3.

**Table 1.2** Summary of work on the benzylation of aromatic compounds by benzyl chloride (BnCl).

Catalyst	Reaction conditions		Conversion of benzyl chloride (%) /Reaction period (min)	Remarks, if any	Investigators (Year)	Ref.
	Temp.	Reaction mixture				
I	II	III	IV	V	VI	VII
<b>Heteropoly acids and their salts:</b>						
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , Rb <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , (NH <sub>4</sub> ) <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , K <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , Cs <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , Rb <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , (NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , K <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	Reflux	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (0.02 mmol)	75 (120) 49 (120) 53 (120) 75 (120) 99 (120) 43 (120) 26 (120) 72 (120)	The selectivity for the major mono-alkylated product of diphenyl methane (DPM) was 63 %. Dissolution of any active catalyst species from Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> was not observed, since the alkylation did not proceed if the solid catalyst was removed from the reactor on the way of the reaction.	Izumi et al (1992)	7
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> Cs <sub>2.5</sub> H <sub>0.5</sub> PMo <sub>12</sub> O <sub>40</sub> , HY, LaY Nafion H Zn-Mont.	Reflux	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (65 mg)	41 (120) 93 (120) 36 (120) 50 (120) 24 (120) 100 (120)	The salt catalyst was much more active than the free acid for the benzylation with benzyl chloride and the salt catalysts could be repeatedly used without deactivation.	Izumi et al (1995)	8
Cs <sub>x</sub> H <sub>3-x</sub> (PW <sub>12</sub> O <sub>40</sub> ) (x = 2.0, 2.5 and 2.9)	-	Benzene + BnCl + Catalyst	-	Immobilization of heteropoly acid on oxide support (especially SiO <sub>2</sub> and Si-MCM-41) reduced the problem of dissolution into an aqueous phase.	Molnar et al (1998)	9
H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	-	Anisole + BnCl + Catalyst	-	The reaction proceeds via carbocation-generation mechanism brought about by the strong Bronsted acid.	Nomiya et al (1980)	10
Tetra-butyl ammonium cation exchanged H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	-	Toluene + BnCl + Catalyst	-	Only tri-protonated forms of tetra-butyl ammonium cation-exchanged H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub> showed activity comparable with that of the parent catalyst.	Nomiya et al (1980)	11

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> (15 wt%) /Silica B, H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (15 wt%) / Silica B,	80 <sup>0</sup> C	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (acid = 0.02 mmol, loading 15 wt%)	72.2 (120) 27.2 (120)	Supported heteropoly acids are highly active and reusable catalysts for the benzylation reaction.	Izumi et al (1987)	12
<b>Super Acid Catalysts:</b>						
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> , Filtro-24, Dodeca-tungsto phosphoric acid	-	Toluene + BnCl + Catalyst	-	Benzyl chloride is more reactive than benzyl alcohol, in the mixture benzyl alcohol reacts first and after it is completely consumed, BnCl begins to react, this is due to preferential adsorption of benzyl alcohol.	Yadav et al (1994)	15
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> , SO <sub>4</sub> <sup>2-</sup> /heteropoly acids	80 <sup>0</sup> C, 100 <sup>0</sup> C	Toluene + BnCl + Catalyst	-	Alkylation of toluene with benzyl chloride and benzyl alcohol in the presence of different solid acid catalysts has been studied.	Yadav et al (1996)	17
So <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> , So <sub>4</sub> <sup>2-</sup> /Fe <sub>2</sub> O <sub>3</sub> , So <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub>	80 <sup>0</sup> C	Benzene + BnCl + Catalyst	-	Among the catalysts, SO <sub>4</sub> <sup>2-</sup> /Fe <sub>2</sub> O <sub>3</sub> shows highest activity; however, SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> shows better reusability.	Koyande et al (1998)	18
Ion-exchange resins (Lewatit & Amberlist-15)	80 <sup>0</sup> C	Benzene (10 mmol) + BnCl (1 mmol) + Catalyst	-	The yield of DPM was low when BnCl was used as benzylating agent instead of benzyl alcohol. Among the ion-exchange resin Amberlyst-15 is most active catalyst.	Marques da Silva et al (1995)	19
<b>Zeolites:</b>						
HSY type zeolite	80 <sup>0</sup> C	Toluene (355.5 g) + BnCl (66.2 g) + Catalyst (20 g)	100 (-)	100% conversion with 95.4% selectivity. Under similar conditions NaY give 68.96% conversion with 81% selectivity.	Akatsu et al (1991)	20
H-ZSM-5 (Si/Al = 60) H-Beta (Si/Al = 27.5) HY <sub>2.5</sub> (Si/Al = 2.5) HY <sub>10</sub> (Si/Al = 10) HY <sub>20</sub> (Si/Al = 20)	110 <sup>0</sup> C	Toluene (25 mmol) + BnCl (5 mmol) + Catalyst (0.5 g)	50 (>1200) 50 (370) 50 (1100) 50 (370) 50 (42)	Protonic zeolites are active and regio-selective catalysts for the benzylation reaction.	Coq et al (1993)	21

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
HY	50-100 <sup>0</sup> C	Biphenyl + BnCl + Catalyst	-	Solvent effect studied. Mono-benzyl biphenyl with appreciable quantity of di-benzyl derivatives was obtained. Within the mono-benzylated fraction 65-70% p-product is observed.	Beltrame et al (1997)	22
H-Beta, HY	40-70 <sup>0</sup> C	Naphthalene + BnCl + Catalyst	-	H-Beta shows high activity and selectivity towards 2-benzyl naphthalene.	Bhattacharaya et al (1998)	23
H-Beta	93 <sup>0</sup> C	O-Xylene + BnCl + Catalyst	33.5 (60)	H-Beta is recycled 4 times and a decrease in BnCl conversion is observed after each cycle, which is related to the minor dealumination of zeolite catalyst by HCl formed during the reaction.	Singh et al (1998)	24
H-AIMFI H-FeMFI H-FeAIMFI H-GaMFI H-GaAIMFI	80 <sup>0</sup> C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	0 (90) 90 (25) 90 (104) 90 (82.5) 90 (56.2)	H-AIMFI zeolite (having high acidity) shows almost no activity in the benzylation of benzene, but its benzylation activity is increased drastically because of partial or complete substitution of its framework Al by Fe or Ga.	Choudhary et al (1999)	25*
ZnO/H-ZSM-5 Fe <sub>2</sub> O <sub>3</sub> /H-ZSM-5 Ga <sub>2</sub> O <sub>3</sub> /H-ZSM-5 In <sub>2</sub> O <sub>3</sub> /H-ZSM-5	80 <sup>0</sup> C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	50 (183) 90 (8.5) 90 (17.6) 90 (17.0)	The impregnation of the zeolite by Fe <sub>2</sub> O <sub>3</sub> , ZnO, Ga <sub>2</sub> O <sub>3</sub> and In <sub>2</sub> O <sub>3</sub> makes the zeolite highly active for the benzylation reaction. The redox function created due to the modification of the H-ZSM-5 by Fe, Zn, Ga or In seems to play very important role in the benzylation process.	Choudhary et al (1999)	26*
<b>Mesoporous MCM-41 type Catalysts:</b>						
MCM-41	-	Biphenyl + BnCl + Catalyst	-	The mesoporous MCM-41 are only slightly less stable than amorphous silica-alumina and HY zeolite but are more active than them and about as selective as they are.	Beltrame et al (2000)	27
Fe-MCM-41, Zn-MCM-41, Cr-MCM-41, Ni-MCM-41, Al-MCM-41	-	Benzene + BnCl + Catalyst	-	Fe-Containing molecular sieve shows high activity and no relationship between activity and acidity of different metal containing (e.g. Zn, Cr, Ni, Al, Co) catalysts was found.	Cao et al (1998)	28

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
Fe-Si-MCM-41, La-Si-MCM-41, Al-Si-MCM-41, Fe/Si-MCM-41	60 <sup>0</sup> C	Benzene + BnCl + Catalyst	-	Both Fe-Si-MCM-41 and Fe/Si-MCM-41 show very high activity with 100% selectivity of DPM. Temperature greatly influences the activity of Fe-containing zeolite samples. After H <sup>+</sup> is exchanged by Na <sup>+</sup> , the conversion of BnCl on Fe/Si-MCM-41 is decreased, indicating H <sup>+</sup> may enhance the activity of the Fe (III) species deposited samples for the above reaction.	He et al (1998)	<b>29</b>
AlSiMCM41, LaSiMCM-41, Si-MCM-41, Fe(6.2)/Si-MCM-41, Fe-MCM-41 (7.7), FeUSY (13), Fe-Y (6), FeKL (6.5)	60 <sup>0</sup> C	Benzene (20 mol) + BnCl (1 mol) + Catalyst ( 60 mg)	3 (120) 1 (120) 0 (120) 91 (120) 99 (120) 90 (120) ~ 0 (120) < 1 (120)	Fe-containing mesoporous materials are very active and selective benzylation catalyst. Pore size is a critical function influence the activity of the catalyst. Fe/KL and Fe/Y , which only show a pore size of 0.7 nm and a super cage of 1.36 nm diameter, respectively, exhibit little activity.	He et al (1998)	<b>30</b>
Ga <sub>2</sub> O <sub>3</sub> /Si-MCM-41 In <sub>2</sub> O <sub>3</sub> /Swi-MCM-41	80 <sup>0</sup> C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	90 (7.8) 90 (7.5)	Ga <sub>2</sub> O <sub>3</sub> and In <sub>2</sub> O <sub>3</sub> supported on Si-MCM-41 are highly active and reusable catalysts for the benzylation reactions.	Choudhary et al (2000)	<b>31*</b>
<b><i>Metal Chlorides and Clay based Catalysts:</i></b>						
ZnCl <sub>2</sub> (or NiCl <sub>2</sub> )/Mont.- K10		Benzene (1.6 mol) + BnCl (0.9 mol) + Catalyst (8 g)	80 (15)	Mont.-K10 day supported ZnCl <sub>2</sub> and NiCl <sub>2</sub> are highly active for Friedel-Crafts alkylation reaction.	Clark et al (1989)	<b>33</b>
Zn, Ni, Al, Cu, Cd, Co or Mg deposited on clay or hydrous silicate		Benzene (140 ml) + Bncl (10 ml) + Catalyst (8 g)	99 (15)	-	Brown et al (1990)	<b>34</b>
ZnCl <sub>2</sub> (or CuCl <sub>2</sub> or MgCl <sub>2</sub> )/Mont.-K10	-	Benzene (or Chlorobenzene) + BnCl + Catalyst	-	The alkylation of benzene with BnCl using ZnCl <sub>2</sub> /Mont.-K10 gave 80% DPM and chlorobenzene using CuCl <sub>2</sub> /Mont.-K10 gave 2- and 4-chloro-diphenylmethane (30 : 70) in 70% yield.	Barlow et al (1991)	<b>35</b>
Zn (II) substituted Smectite clay	-	Benzene + BnCl + Catalyst	-	Maximum catalytic activity in the benzylation of benzene was achieved after 150 <sup>0</sup> C activation.	Luca et al (1992)	<b>36</b>

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
ZnCl <sub>2</sub> /(acid treated Mont.-K10 or high porosity silica)	-	Aromatic compounds + BnCl + Catalyst	-	Maximum activity is associated with long acid treatment times. After acid treatment there was a little residual clay structure in the most active supports. High porosity silicas were more active supports than acid treated clays. Porosimetry measurements indicate that the presence of mesopores is important for an effective ZnCl <sub>2</sub> catalyst supports.	Rhodes et al (1992)	<b>37</b>
Acid treated Kaolinite	-	Benzene + BnCl + Catalyst	-	Natural Kaolinitic clays having transition metals in their lattice possess disorder structure, acid activation results in the generation of larger amounts of relocable cations, higher surface area and higher acidity compared to the ideal Kaolinites. These acid treated Kaolinites show high catalytic activity and selectivity for the conversion of BnCl to DPM.	Sabu et al (1993)	<b>38</b>
Clayzic	-	Benzene (or halobenzene) + BnCl + Catalyst	-	Effect of activation of clayzic has been studied. There is an optimum temperature for thermal activation in air at which point a rate enhancement, compared to unactivated clayzic, in the benzylation of benzene of greater than 30 has been achieved. Activation of clayzic is believed to reduce the polar nature of the pores, so aiding partitioning of the substrate into the catalyst.	Barlow et al (1994)	<b>39</b>
Fe-Pillared clay	-	Aromatic hydrocarbons + BnCl + Catalyst	-	The high activity of the catalyst is attributed to the higher Fe <sup>3+</sup> contents in the catalyst and the pillaring effect.	Choudary et al (1997)	<b>40</b>
FeCl <sub>3</sub> /Mont.-K10	-	Benzene (or other aromatics) ( 10 ml) + BnCl (2 mmol) + Catalyst (0.1 g)	100 (15) in case of benzene	Complete conversion of BnCl within 5 min. for benzene and toluene.	Pai et al (1997)	<b>41</b>
ZnCl <sub>2</sub> (or FeCl <sub>3</sub> or MnCl <sub>2</sub> or SnCl <sub>2</sub> or AlCl <sub>3</sub> )/Kaoline	-	Benzene (2ml) + BnCl (0.1 ml) + Catalyst (FeCl <sub>3</sub> /Kaoline, 0.1 g)	86 (-)	Ideal Kaolinites are ineffective as solid catalyst even after thermal and acid activation. It becomes activated after impregnation with ZnCl <sub>2</sub> , FeCl <sub>3</sub> , MnCl <sub>2</sub> , SnCl <sub>2</sub> or AlCl <sub>3</sub> . FeCl <sub>3</sub> catalyst shows maximum activity. Supported AlCl <sub>3</sub> catalyst proved to be the less effective for alkylation reaction.	Sukumar et al (1998)	<b>42</b>



Table 1.2 (continued)

I	II	III	IV	V	VI	VII
ZnCl <sub>2</sub> / Mesoporous Silica	-	Benzene + BnCl + Catalyst	-	Incorporation of ZnCl <sub>2</sub> by sol-gel synthesis gives a range of mesoporous materials with significantly higher catalytic activity than the commercially available catalyst 'clayzic' in the Friedel-Crafts benzylation of benzene.	Miller et al (1998)	<b>43</b>
H <sub>2</sub> SO <sub>4</sub> / Kaolinite, HNO <sub>3</sub> / Kaolinite, HClO <sub>4</sub> / Kaolinite	80 <sup>0</sup> C	Benzene (0.25 mol) + BnCl (0.025 mol) + Catalyst (1 g)	86.1 (45) 87 (30) 86.5 (240)	The acid treated clay was prepared by refluxing calcined clay (calcined at 550 <sup>0</sup> C for 5 h) with 4 M acid in the solid/liquid wt. ratio 1 : 4 for 45 min. The samples were then washed thoroughly with distilled water and then dried in air oven at 110 <sup>0</sup> C for 12 h and then calcined at 400 <sup>0</sup> C for 3 h.	Sabu et al (1999)	<b>44</b>
Fe (III) exchanged kaolinites	80 <sup>0</sup> C	Benzene (2 mol) + BnCl (0.1 mol) + Catalyst (2 g)	-	Modified Kaolinites containing Fe (III) ions exchanged for the interstitial cations are efficient catalysts for Friedel-Crafts benzene benzylation using BnCl give 80% conversion with 100% selectivity.	Sukumar et al (1996)	<b>45</b>
ZnCl <sub>2</sub> - Aluminosilicate	Room temp.	Benzene (22 ml) + BnCl (5.8 ml) + Catalyst (0.5 g)	97 (15)	Zn-aluminosilicate is an effective Friedel-Crafts catalyst.	Miller et al (1999)	<b>46</b>
FeCl <sub>3</sub> /Mont.-K10	80 <sup>0</sup> C	Benzene (10 ml) + BnCl (0.23 ml), Catalyst (0.1 g)	100 (5)	The maximum catalytic activity was associated with Mont.-K10 modified by FeCl <sub>3</sub> in acetonitrile solution and activated at 120 <sup>0</sup> C.	Pai et al (2000)	<b>47</b>
ZnCl <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	Room temp.	Benzene (22 ml) + BnCl (5.8 ml) + Catalyst (0.5 g)	98 (15)	Alumina was synthesized by a sol-gel method using modifying agent such as 2,4-pentanedione, acetophenone, benzophenone and dibenzoyl methane. The acetophenone and benzophenone modified alumina supported ZnCl <sub>2</sub> were found to be effective catalyst for Friedel-Crafts alkylation.	Miller et al (2000)	<b>48</b>
Graphite-AlCl <sub>3</sub> intercalation compound	-	Aromatics + BnCl + Catalyst	-	Graphite-AlCl <sub>3</sub> intercalated compound is an active catalyst for the benzylation reaction.	Freeman et al (1974)	<b>49</b>
H <sub>2</sub> SO <sub>4</sub> (30%) treated clay supported ZnCl <sub>2</sub>	Room temp.	Benzene (0.2 mol) + BnCl (0.01 mol) + Catalyst (0.25 g)	92 (30)	Optimum activity for the clay supported ZnCl <sub>2</sub> is achieved after 20 h acid treatment.	Rhodes et al (1991)	<b>50</b>

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
Clayzic	-	Toluene (or Mesitylene) + BnCl + Catalyst	-	Toluene is more reactive than mesitylene when they are benzylated separately but one-pot reactions favor mesitylene, with high intermolecular selectivity.	Cornelis et al (1991)	51
Clayzic	-	Toluene + BnCl + Catalyst	-	In the benzylation of toluene with clayzic, the conversion of benzyl alcohol taking precedence over benzyl chloride.	Davister et al (1993)	52
Clayzic	40 <sup>0</sup> C	Aromatics + BnCl + Catalyst	-	Thermal treatment of clayzic results in a steady increase in the surface area likely due to partly dehydration forming mesoporous materials in which Zn ions largely reside. The high activity of clayzic may be due to the presence of high local concentration of Zn ions in the structural mesopores.	Clark et al (1994)	53
Zn (II) or Fe (III) modified Mont.-K10 clay	80 <sup>0</sup> C	Thiophene + BnCl + solvent (nitrobenzene) + Catalyst	80 (5)	2-isomer is the major mono-substituted product.	Clark et al (1994)	54
Acid treated clays - KSF, KSF/0, K0, KP10, K10, KS	-	Toluene + BnCl + Catalyst	-	The Fe-containing clays show high activity in spite of their low Lewis acidity. Amount of Fe <sup>3+</sup> of the clay controls the activity.	Cseri et al (1995)	55
AlCl <sub>3</sub> , FeCl <sub>3</sub> and ZnCl <sub>2</sub> doped Bentonite Clay	-	Activated arenes + BnCl + Catalyst	-	The doping of bentonite K10 with Lewis acids AlCl <sub>3</sub> , FeCl <sub>3</sub> and ZnCl <sub>2</sub> has been found to enhance the catalytic activity of clay remarkably.	Natekar et al (1995)	56
CuCl <sub>2</sub> /Alumina	-	Aromatics + BnCl + Catalyst	-	Alumina supported CuCl <sub>2</sub> effectively catalyzed Friedel-Crafts benzylation of aromatics with BnCl under mild condition.	Kodamari et al (1994)	57
Envirocrat EPZ 10	90 <sup>0</sup> C	Biphenyl + BnCl + Catalyst	> 99 (60)	Ortho/para selectivity = 1/3	Calvert et al (1992)	59
GaCl <sub>3</sub> /Mont.-K10 InCl <sub>3</sub> /Mont.-K10 GaCl <sub>3</sub> /Si-MCM-41 InCl <sub>3</sub> /Si-MCM-41	80 <sup>0</sup> C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	90 (14.9) 90 (6.2) 90 (26.8) 90 (8.9)	Mont.-K10 and Si-MCM-41 shows little or no activity in the benzylation of benzene; Mont.-K10 and Si-MCM-41 supported GaCl <sub>3</sub> and InCl <sub>3</sub> catalysts show very high benzylation activity. Supported AlCl <sub>3</sub> shows poor catalytic activity.	Choudhary et al (2000)	60*

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
<b>Metal Oxide Catalysts:</b>						
H <sub>2</sub> SO <sub>4</sub> treated SnO <sub>2</sub>	-	Aromatics + BnCl + Catalyst	-	The alkylation activity of SnO <sub>2</sub> was improved by acid treatment.	Jogalekar et al (1998)	<b>61</b>
Fe <sub>2</sub> O <sub>3</sub> / Al <sub>2</sub> O <sub>3</sub>	80 <sup>0</sup> C	Ethyl biphenyl + BnCl	-	Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> is an active solid catalyst for the benzylation reaction.	Nippon Steel Corp. (1984)	<b>62</b>
TiO <sub>x</sub> /silica-alumina (HS) TiO <sub>x</sub> /silica-alumina (LS) TiO <sub>x</sub> /Si-MCM-41 (HS) TiO <sub>x</sub> /silica (LS) TiO <sub>x</sub> /zirconia(HS) TiO <sub>x</sub> /zirconia (LS)	80 <sup>0</sup> C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	0 (150) 90 (10) 0 (150) 90 (19) 0 (150) 90 (8.2)	The supported TiO <sub>x</sub> prepared using high surface area supports are inactive in the benzylation of benzene. In contrast, the TiO <sub>x</sub> supported on low surface area sintered macroporous supports shows high benzene benzylation activity.	Choudhary et al (2001)	<b>63*</b>
<b>Spinel:</b>						
CuCr <sub>2-x</sub> Fe <sub>x</sub> O <sub>4</sub>	-	Benzene + BnCl + Catalyst	-	CuFe <sub>2</sub> O <sub>4</sub> gives the high benzene benzylation yield. The Lewis surface acidity of the catalysts was mainly responsible for the good catalytic performance.	Ghorpade et al (1998)	<b>64</b>
<b>Metal Sulfates:</b>						
FeSO <sub>4</sub> , Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	45 <sup>0</sup> C	Toluene + BnCl + Catalyst	-	Both the catalysts calcined at 700 <sup>0</sup> C showed maximum catalytic activity . The catalysts calcined at 700 <sup>0</sup> C containing 0.15% sulfur.	Arata et al (1976)	<b>65</b>
<b>Silica-alumina and alumina:</b>						
Amorphous Silica-alumina	80 <sup>0</sup> C	Biphenyl + BnCl + Catalyst	-	Amorphous silica-alumina catalyst was found to be less active than zeolites, however, it has the advantage of being stable and as a consequence, in some cases it could be more active than zeolite catalyst in a long reaction time.	Beltrame et al (1998)	<b>66</b>

Table 1.2 (continued)

I	II	III	IV	V	VI	VII
Silica-alumina	160 <sup>0</sup> C	Biphenyl + BnCl + Catalyst	15 to 16 (-)	Silica-alumina shows high activity in the benzylation reaction.	Sakura et al (1991)	67
KF-Al <sub>2</sub> O <sub>3</sub>	160 <sup>0</sup> C	PhNH <sub>2</sub> + BnCl + DMF + Catalyst	88.4 (840)	KF-Al <sub>2</sub> O <sub>3</sub> is an active catalyst for the benzylation of aniline.	Wang et al (1992)	68
<b>Carbon Catalyst:</b>						
Carbon	170 <sup>0</sup> C	Naphthalene (1 mol) + BnCl (1 mol) + Catalyst	11.6 (30)	Selectivity of mono-benzyl naphthalene, di-benzyl naphthalene and tri-benzyl naphthalene were 46.5%, 29.4% and 6.8%, respectively.	Staeglich et al (1992)	69
<b>Hydrotalcite Catalysts:</b>						
Fresh Ga-Mg HT HCl treated Ga-Mg HT Used Ga-Mg HT	110 <sup>0</sup> C	Toluene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	90 (44) 90 (5.75) 90 (3.0)	Ga-Mg HT (calcined at 200 <sup>0</sup> C), a basic anionic clay, shows very large induction period in the benzylation of toluene. But after its use in the reaction or HCl pretreatment, the hydrotalcite derived catalysts shows very high activity in the benzylation of toluene, with a drastic reduction in the induction period, even in the presence of moisture in the reaction mixture.	Choudhary et al	70*

\*Present work.

**Table 1.3** Summary of work on the acylation of aromatic compounds by acyl halides.

Catalyst	Reaction conditions		Conversion of acyl chloride (%) /Reaction Period (min)	Remarks, if any	Investigators (year)	Ref.
	Temp.	Reaction mixture				
I	II	III	IV	V	VI	VII
<b>Heteropoly Acids and Salts :</b>						
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , Rb <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , (NH <sub>4</sub> ) <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , K <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> , Cs <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , Rb <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , (NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> , K <sub>2</sub> H <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	Reflux	p-Xylene (100 mmol) + PhCOCl (5 mmol) + Catalyst (0.01 mmol)	57 (120) 64 (120) 46 (120) 18 (120) 12 (120) - - -	Dissolution of any active catalyst species from Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> was not observed.	Izumi et al (1992)	7
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> Cs <sub>2.5</sub> H <sub>0.5</sub> PMo <sub>12</sub> O <sub>40</sub> , HY, LaY Nafion H Zn-Mont. (140mg)	Reflux	p-Xylene (100 mmol) + PhCOCl (5 mmol) + Catalyst (35 mg)	39 (120) - 9 (120) 9 (120) 48 (120) 35 (120)	The salt catalyst was much more active than the free acid.	Izumi et al (1995)	8
Tungstosilicic acid / Silica B, Tungstophosphoric acid / Silica B	138 <sup>0</sup> C	p-Xylene (30 mmol) + PhCOCl (3 mmol) + Catalyst (loading = 15 wt%, net amount of heteropoly acid = 0.01 mmol, calcined at 300 <sup>0</sup> C)	46 (60) 33.2 (60)	Supported acid proved to be effectively catalyze the acylation as heterogeneous and insoluble catalysts particularly when calcined at 200-500 <sup>0</sup> C.	Izumi et al (1987)	12

Table 1.3 (continued)

I	II	III	IV	V	VI	VII
<b>Resin Based Catalyst:</b>						
Silane modified perfluorosulfonic acid, Nafion resin	140 <sup>0</sup> C	m-Xylene (21.2g) + PhCOCl (14g) + Catalyst (1g)	99 (360) 99 (360)	Surface modified catalyst and Nafion resin are very effective heterogeneous catalysts for Friedel-Crafts acylation.	Harmer et al (1997)	<b>72</b>
<b>ZrO<sub>2</sub> based Catalysts :</b>						
Zr/c1 [ZrO <sub>2</sub> ( from ZrOCl <sub>2</sub> , 500 <sup>0</sup> C)] Zr/amSO <sub>4</sub> [Zr/1, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ] Zr/SOCl <sub>2</sub> [Zr/1, SOCl <sub>2</sub> ] Zr/SF <sub>4</sub> [Zr/1, SF <sub>4</sub> ] A/c [ZrO <sub>2</sub> aerogel, 300 <sup>0</sup> C] A/c-SO <sub>4</sub> [A/c-H <sub>2</sub> SO <sub>4</sub> ] A/c-PO <sub>4</sub> [A/c-H <sub>3</sub> PO <sub>4</sub> ] Zr/com [SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> , commer.] β AlF <sub>3</sub> γ Al <sub>2</sub> O <sub>3</sub>	140 <sup>0</sup> C	Anisole (12 ml) + PhCOCl (0.00265 mol) + Catalyst (0.2g)	0 (420) 76 (420) 1 (420) 12 (420) 0 (420) 86 (420) 57 (420) 57 (420) 0 (420) 2 (420)	Acylation of anisole over sulfated ZrO <sub>2</sub> prepared by different methods has been studied.	Quaschnig et al (1998)	<b>73</b>
WO <sub>3</sub> /ZrO <sub>2</sub> WO <sub>3</sub> /TiO <sub>2</sub> WO <sub>3</sub> /SnO <sub>2</sub> WO <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> MoO <sub>3</sub> /ZrO <sub>2</sub> SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> Acidic zeolite Mordenite	100 <sup>0</sup> C	Toluene (15 ml) + PhCOCl (0.281 g) + Catalyst (0.5g)	19 (180) 20 (180) 14 (180) 74 (180) 18 (180) 0 (180) 0 (180) 1 (180)	These catalysts show satisfactory results in the benzylation of toluene, one of the difficult acylation because of the difficulty in the formation of an intermediate acyl cation from benzoyl chloride.	Arata et al (2000)	<b>76</b>

Table 1.3 (continued)

I	II	III	IV		VI	VII
<b>Zeolite based Catalysts :</b>						
$\gamma$ -alumina Modified zeolite Y Nafion	130 <sup>0</sup> C	m-Xylene (0.1 mol) + PhCOCl (0.05 mol) + solvent (sulfolane = 20 ml) + Catalyst (1.0 g)	96 (360) 94 (360) 80 (360)	Non-framework alumina in the zeolite Y is an active catalyst in the acylation of m-xylene with PhCOCl.	Fang et al (1995)	<b>78</b>
H-Al-Beta H-Ga-Beta H-Fe-Beta	80 <sup>0</sup> C	Benzene (0.1 mol) +PhCOCl (0.02 mol) + Catalyst (0.93 g)	54 (1080) 32.8 (1080) 19 (1080)	A higher yield of benzophenone was obtained by increasing the reaction temperature, catalyst concentration and mole ratios of benzene/PhCOCl. The isomorphous substitution of Al by Ga or Fe significantly decreases the yield of benzophenone probably due to the decrease in the acid strength in the order: H-Al-Beta > H-Ga-Beta > H-Fe-Beta.	Singh et al (1995)	<b>79</b>
HY	-	Thiophene + PhCOCl (or acetyl chloride) + Catalyst	-	Thiophene is slightly more adsorbed than acetyl chloride on catalyst. Kinetics follows Langmuir-Hinshelwood mechanism.	Finiels et al (1993)	<b>80</b>
H-ZSM-5	120 <sup>0</sup> C (bath temp.)	Activated arenes (0.01 mol) + PhCOCl (0.01 mol) + Cat. (0.1 g) + solvent (EDC = 25 ml)	50 (300) in case of anisole	Activated arenes underwent benzylation efficiently and the reaction is essentially regiospecific. Benzene, halo-benzenes and naphthalene failed to undergo benzylation under the reaction conditions.	Paul et al (1994)	<b>82</b>
H-ZSM-5 H-ZSM-12 H-Beta H-Mordenite HY NaY NaREY HREY SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	115 <sup>0</sup> C	Toluene (0.11 mol) + PhCOCl (0.022 mol) + Catalyst (0.93 g)	4.2 (1080) 41 (1080) 83.4 (1080) 19.5 (1080) 18.8 (1080) 3.8 (1080) 31.6 (1080) 61.7 (1080) 3.2 (1080)	Acidic zeolites are active in the benzylation of toluene with PhCOCl. H-beta shows high activity and selectivity among the zeolite catalysts.	Singh et al (1995)	<b>83</b>

Table 1.3 (continued)

I	II	III	IV	V	VI	VII
H-RE-Y H-Beta	85 <sup>0</sup> C	Naphthalene (0.039 mol) + PhCOCl (0.0195 mol), Catalyst (1.01 g) + Dichloroethane	7.2 (1080) 17.6 (1080)	H-beta catalyzes the benzylation of naphthalene with PhCOCl efficiently, which leads to the formation of 2-benzoyl naphthalene in high selectivity.	Bhattacharya et al (1997)	<b>86</b>
H-Beta In-H-Beta	70 <sup>0</sup> C	Naphthalene (0.023 mol) + PhCOCl (0.011 mol) + Catalyst (1 g)	30.3 (-) 25.4 (-)	The yield of benzyl naphthalene is decreased in case of In-H-beta as compared to H-beta.	Chatterjee et al (1998)	<b>87</b>
H-Beta	Reflux	Veratrole + Propionyl chloride + Catalyst	67.8 (180) (isolated yield)	H-beta shows high activity in the acylation of veratrole.	Myata et al (1992)	<b>89</b>
USY, ZSM-5	-	Anisole + Phenyl acetyl chloride + Catalyst	-	Zeolite catalysts are active in the acylation of anisole by phenyl acetyl chloride.	Harvey et al (1992)	<b>90</b>
H-Beta	270 <sup>0</sup> C	Chlorobenzene + Propionyl chloride + Catalyst	5.6 (240) (isolated yield)	H-beta is an active catalyst for the acylation reaction.	Morimoto et al (1997)	<b>92</b>
<b><i>Metal Chloride and Clay based Catalyst :</i></b>						
EPZG	130-140 <sup>0</sup> C	Benzene + PhCOCl + Catalyst	66 (1800)	EPZG is an supported active catalyst for the acylation reaction.	Calvert (1992)	<b>59</b>
Acid treated Mont.-FeCl <sub>3</sub>	-	Aromatics + Acyl chloride + Catalyst	-	Acid treated Mont.-FeCl <sub>3</sub> is an active catalyst for the acylation of aromatics with acyl chlorides.	Bastock et al (1994)	<b>94</b>



Table 1.3 (continued)

I	II	III	IV	V	VI	VII
FeCl <sub>3</sub> /silica gel	Reflux	Benzene (20 mmol) + benzotrichloride (40 mmol) + Catalyst (6 g) + Dichloroethane	72 (240)	Catalyst was prepared by co-grinding FeCl <sub>3</sub> and silica gel in an agate mortar and activating it at 80 <sup>0</sup> C for 3 h.	Khadilkar et al (1997)	<b>96</b>
K-10, KSF	-	Alcohol + Acylating agent + Catalyst	-	Mont.-K10 and KSF are good acylating catalyst for alcohols, phenols, thiols and amines with acetyl chloride and PhCOCl.	Li et al (1998)	<b>99</b>
InCl <sub>3</sub> /Mont.-K10 GaCl <sub>3</sub> /Mont.-K10 ZnCl <sub>2</sub> /Mont.-K10	80 <sup>0</sup> C	Benzene (13 ml) + PhCOCl (1 ml) + Catalyst (0.4 g)	50 (84) 50 (102) 50 (438)	Mont.-K10 supported InCl <sub>3</sub> and GaCl <sub>3</sub> are highly active catalysts for the acylation of benzene by acyl chlorides, even in the presence of moisture in the reaction mixture.	Choudhary et al	<b>101*</b>
<b>Metal Oxide Catalysts :</b>						
Ga <sub>2</sub> O <sub>3</sub> /Si-MCM-41 In <sub>2</sub> O <sub>3</sub> /Si-MCM-41	110 <sup>0</sup> C	Toluene (13 ml) + PhCOCl (1 ml) + Catalyst (0.4 g)	80 (182) 80 (130)	Supported Ga <sub>2</sub> O <sub>3</sub> and In <sub>2</sub> O <sub>3</sub> are highly active catalysts for the benzoxylation reactions.	Choudhary et al (2000)	<b>31*</b>
TiO <sub>x</sub> (20)/zirconia (LS) TiO <sub>x</sub> (20)/zirconia (HS) TiO <sub>x</sub> (40)/zirconia (HS)	80 <sup>0</sup> C	Benzene (13 ml) + PhCOCl (1 ml) + Catalyst (0.4 g)	50 (158) 0 (150) 50 (196)	TiO <sub>x</sub> supported on low surface area sintered macroporous catalyst carriers are active catalysts for the acylation reaction	Choudhary et al (2001)	<b>63*</b>
<b>Hydrotalcite Catalyst :</b>						
Fresh Ga-Mg HT HCl treated Ga-Mg HT Used Ga-Mg HT	110 <sup>0</sup> C	Toluene (13 ml) + PhCOCl (1 ml) + Catalyst (0.4 g)	0 (120) 90 (208) 90 (165)	Ga-Mg HT, a basic anionic clay is inactive in the acylation reaction. But after its use in the toluene benzylation or HCl pretreatment, the HT derived catalyst showed very high activity in the acylation reaction.	Choudhary et al	<b>70*</b>
<b>Metal Sulfate Catalyst :</b>						
FeSO <sub>4</sub> (700 <sup>0</sup> C) Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (700 <sup>0</sup> C)	110 <sup>0</sup> C	50 ml of 0.5 M PhCOCl in Toluene + Catalyst	7.7 (-) 10.1 (-)	Conversion of PhCOCl is calculated on the basis of initial rate x 10 <sup>3</sup> (mol/l.min.g)	Arata et al (1976)	<b>65</b>

Table 1.3 (continued)

I	II	III	IV	V	VI	VII
<b>Graphite Catalyst :</b>						
Graphite	120 <sup>0</sup> C	Anisole (2 mmol) + PhCOCl (3 mmol) + Catalyst (1 g) + Chlorobenzene	85 (480) isolated yield	Graphite was shown to have remarkably high acylation activity, without any environmental disadvantages of using toxic homogeneous catalyst such as AlCl <sub>3</sub> .	Kodamari et al (1997)	<b>102</b>

\* *Present work.*

### ***1.5.1.3 Polycondensation of Benzyl Chloride***

Benzyl chloride is a commonly used benzylating agent for the benzylation of aromatic compounds. However, in the presence of many Lewis acid catalysts, benzyl chloride undergoes a self-condensation reaction to form polybenzyl  $[(n+1)\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2(\text{C}_6\text{H}_4\text{CH}_2)_n\text{Cl} + n\text{HCl}]$ , which can be a predominant side reaction in the benzylation of aromatic compounds. It is, therefore, interesting to study the polycondensation of benzyl chloride over the solid catalysts to be used in the benzylation reactions. Heterogeneous solid catalysts, such as ferrous sulfate [103] and iron oxide [104] are reported earlier for the polycondensation of benzyl chloride.

### ***1.5.1.4 Esterification of tert-Butanol***

Esterification of alcohols, particularly normal alcohols, by carboxylic acids using homogeneous acid catalysts (viz. mineral acids) is very well known [105]. However, it is extremely difficult to prepare tert-butyl ester by the esterification of tert-butanol using an acid catalyst. This is because of the very high reactivity of tert-butanol in the presence of an acid, causing a rapid dehydration of the alcohol to iso-butylene, even at the room temperature. Recently, Nagasawa et. al. [106,107] used activated basic alumina at mild conditions (at room temperature under argon) for the esterification of tert-butanol by acid chlorides or acid bromides. They got a good yield of tert-butyl ester but the amount of catalyst relative to the reactants used by them was very large (catalyst/reactants wt. ratio =  $2.1 \pm 0.4$  and the reaction period was also very long (9 – 15 h). It is not of practical interest to use such a large amount of catalyst relative to the reactants, and moreover the removal of high molecular weight adsorbed products from the catalyst is quite difficult and expensive too. Other important drawback of their butyl ester synthetic method results from the use of an acid halide as esterification agent, because of which a highly toxic by-product, gaseous hydrogen halide, is produced in stoichiometric quantities. Hence, there is a need to develop an environmentally benign method for the esterification of tert-butanol using a highly active, selective and reusable solid catalyst having a little or no activity for the dehydration of tert-butanol.

## **1.6 OBJECTIVE AND SCOPE**

The present work for the Ph. D. thesis was undertaken as a part of the comprehensive R & D programme in our laboratory for replacing homogeneous catalysts

by reusable heterogeneous solid catalysts for the synthesis of fine chemicals, with the following objectives.

1. To study the benzylation (by benzyl chloride) or acylation (by benzoyl chloride or other acyl chloride) of benzene and other aromatic compounds over
  - Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts,
  - $\text{GaCl}_3$  and  $\text{InCl}_3$  supported on commercial clays and Si-MCM-41,
  - $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$  and  $\text{TlO}_x$  supported on micro-, meso- and macro-porous catalyst carriers, and
  - Ga-Mg-hydrotalcite anionic clay with or without its modifications by calcination and/or halogenation.
2. To study the effect of moisture on the rate of benzylation (by benzyl chloride) or acylation (by benzoyl chloride) of benzene or toluene over
  - Ga- modified ZSM-5 type zeolite catalysts,
  - $\text{GaCl}_3$  and  $\text{InCl}_3$  supported on Montmorillonite K10 and Si-MCM-41,
  - $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  supported on Si-MCM-41 and  $\text{TlO}_x$  supported on sintered low surface area zirconia, and
  - Ga-Mg-hydrotalcite anionic clay.
3. To study the strong thallium oxide-support hydroxyl interactions and their influence on the benzylation and benzoylation reactions.
4. To study the polycondensation of benzyl chloride over
  - Fe-containing micro-, meso- and macro-porous solid catalysts, and
  - Ga- and In-modified ZSM-5 type zeolites and Si-MCM-41 or Montmorillonite-K10 supported  $\text{GaCl}_3$  and  $\text{InCl}_3$  catalysts.
5. To study the esterification of tert-butanol by acetic anhydride over clay supported  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  catalysts.

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***CHAPTER-2***  
***EXPERIMENTAL***

## Chapter 2

### EXPERIMENTAL

#### 2.1 GASES AND CHEMICALS

The following gases and chemicals have been used.

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Helium	-	High purity IOLAR-II Grade (99.99%) obtained from Indian Oxygen Ltd., Mumbai
Hydrogen	-	IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Nitrogen	-	IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Na-trisilicate	-	Fluka, Switzerland
Tetra-propyl-ammonium bromide (TPA Br)	-	(20% in water) Fluka, Switzerland
Tetra-propyl-ammonium hydroxide (TPA OH)	-	(20% in water) Fluka, Switzerland
Tetra-methyl-ammonium hydroxide (TMA OH)	-	(25% in water) Aldrich, USA
Cetyl trimethyl-ammonium bromide (CTAB)	-	Lancaster, UK
Tetra-ethyl orthosilicate (TEOS)	-	(98+%) Aldrich, USA
Aluminium nitrate	-	(EP Grade), s. d. FINE CHEMICALS, Mumbai
Magnesium nitrate	-	(AR Grade), s. d. FINE CHEMICALS, Mumbai
Potassium nitrate	-	Qualigens Fine Chemicals, Mumbai
Ferric nitrate	-	Qualigens Fine Chemicals, Mumbai
Zinc nitrate	-	Loba Chemie Lab. Pvt. Ltd., Mumbai
Gallium (III) nitrate, hydrate	-	(99.9%) Aldrich, USA
Indium nitrate pentahydrate	-	(99.9%) Aldrich, USA
Thallium nitrate	-	(99.999%) Aldrich, USA
Aluminium chloride	-	(Anhydrous) Aldrich, USA
Ferric chloride	-	(97%) Aldrich, USA
Zinc chloride	-	(Anhydrous 99.99 %) Aldrich, USA
Gallium chloride	-	(Anhydrous 99.99 %) Aldrich, USA
Indium chloride	-	(Anhydrous 99.999 %) Aldrich, USA

Thalious chloride	- (99%) BDH Chemicals Ltd., England
Potassium hydroxide	- (Pellets AR Grade), s. d. FINE CHEMICALS, Mumbai
Potassium carbonate	- (AR Grade) s. d. FINE CHEMICALS, Mumbai
Sodium hydroxide	- s. d. FINE CHEMICALS, Mumbai
Phenolphthalein	- Merck (India) Pvt. Ltd., Mumbai
Hydrochloric acid	- (32%) Merck (India) Pvt. Ltd., Mumbai
Sulfuric acid	- (98%) Merck (India) Pvt. Ltd., Mumbai
Silica gel	- (60-120 mesh) Sisco Research Laboratory Pvt. Ltd, Mumbai
Benzene	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
Toluene	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
p-Xylene	- (> 99%) Fluka, Switzerland
Mesitylene	- (99%) Fluka, Switzerland
Durene	- (98%) Aldrich, USA
Anisole	- (EP Grade) s. d. FINE CHEMICALS, Mumbai
Naphthalene	- (99%) Loba Chemie Lab. Pvt. Ltd., Mumbai
Methyl naphthalene	- Merck (India) Pvt. Ltd., Mumbai
Methoxy naphthalene	- Merck (India) Pvt. Ltd., Mumbai
Benzyl chloride	- (99%) Aldrich, USA
Benzoyl chloride	- (99%) Aldrich, USA
Phenyl acetyl chloride	- (98%) Aldrich, USA
Butyryl chloride	- (EP Grade) Sisco Research Laboratory Pvt. Ltd, Mumbai
Acetic anhydride	- Lancaster, UK
Dichloroethane	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
Acetonitrile	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
n-Hexane	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
n-Heptane	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai
n-Octane	- (HPLC and Spectroscopic Grade) s. d. FINE CHEMICALS, Mumbai

Ethanol	- (99.7%) Merck (India) Pvt. Ltd., Mumbai
Tert-butanol	- (GR Grade) Loba Chemie Lab. Pvt. Ltd., Mumbai
Petroleum ether	- (AR Grade) s. d. FINE CHEMICALS, Mumbai
Ethyl acetate	- (AR Grade) s. d. FINE CHEMICALS, Mumbai

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## 2.2 CATALYST PREPARATION

### 2.2.1 H-ZSM-5

The H-ZSM-5 with different Si/Al ratios were prepared and characterized earlier [1]. They were prepared by hydrothermal crystallization from a gel (pH = 11-12) consists of Na-trisilicate, aluminium nitrate, TPA Br, sulfuric acid and deionized water in a stainless steel autoclave at 180<sup>0</sup>C for 96 h, washing, drying and calcining the resulting zeolite crystals at 550<sup>0</sup>C in static air for 15 h to remove the occluded organic template, exchanging with 1 M ammonium nitrate at 80<sup>0</sup>C for 4 times and drying and again calcining the zeolite under static air at 550<sup>0</sup>C for 4 h to convert its NH<sub>4</sub>-form to H-form.

### 2.2.2 H-FeMFI and H-FeAlMFI

The H-FeMFI and H-FeAlMFI catalysts were prepared by hydrothermal crystallization from a gel (pH = 9-10) consisting of Na-trisilicate, ferric nitrate, with or without aluminium nitrate, TPA OH, sulfuric acid and deionized water in a stainless steel autoclave at 180<sup>0</sup>C for 96 h, washing, drying and calcining the resulting zeolite crystals at 550<sup>0</sup>C in static air for 15 h to remove the occluded organic template, exchanging with 1 M ammonium nitrate at 80<sup>0</sup>C for 4 times and drying and again calcining the zeolite under static air at 550<sup>0</sup>C for 4 h to convert its NH<sub>4</sub>-form to H-form.

### 2.2.3 H-GaMFI and H-GaAlMFI

The H-GaMFI and H-GaAlMFI catalysts were prepared and characterized earlier [2-4]. These were prepared by hydrothermal crystallization from a gel (pH = 9-10) consisting of Na-trisilicate, gallium nitrate, with or without aluminium nitrate, TPA Br, sulfuric acid and deionized water in a stainless steel autoclave at 180<sup>0</sup>C for 96 h, washing, drying and calcining the resulting zeolite crystals at 550<sup>0</sup>C in static air for 15 h to remove the occluded organic template, exchanging with 1M ammonium nitrate at 80<sup>0</sup>C for 4 times and drying and again calcining the zeolite under static air at 550<sup>0</sup>C for 4 h to convert its NH<sub>4</sub>-form to H-form.

#### 2.2.4 Si-MCM-41

It was prepared by the procedures given elsewhere [5]. A mixture of sodium hydroxide (1.7 g in 30 g of water) and tetramethyl ammonium hydroxide (2 ml of 25 wt% TMA OH) solution was added to an aqueous solution of CTAB (14.6 g in 100 g of water) with continuous stirring. 210 g of water was added to the solution. After allowing the solution to stir for 10 min, tetra-ethylorthosilicate (TEOS, silica source) was combined with resulting solution at room temperature under stirring and kept for 24 h. The final gel composition of the mixture was 0.17 TEOS : 0.04 NaOH : 0.02 TMA OH : 0.04 CTAB : 18.9 H<sub>2</sub>O. The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and finally calcined at 550<sup>0</sup>C for 16 h.

#### 2.2.5 Al-Si-MCM-41

It was prepared by its hydrothermal synthesis as follows. (i) 10.4 ml (25 wt%) of solution of tetramethylammonium hydroxide was combined with 14.23 g of Na-trisilicate dispersed in 50 g of water with stirring, and 29.5 g of CTAB (in 75 g of water) (surfactant/silica mole ratio = 0.5) solution were added and stirred for 30 min. (ii) 2.3 g of Na-aluminate (Si/Al = 5.0) was dispersed or dissolved in 50 g of water and then added slowly to the gel. (iii) The pH was adjusted with dilute sulfuric acid to 11.5. The resulting gel composition was 1.0 SiO<sub>2</sub> : 0.097 Al<sub>2</sub>O<sub>3</sub> : 0.298 CTAB : 0.20 TMA OH : 0.41 Na<sub>2</sub>O : 75 H<sub>2</sub>O. The final gel was transferred into teflon-lined stainless steel autoclave and heated at 120<sup>0</sup>C for 120 h under autogeneous pressure. After cooling to room temperature, the resulting solid product was recovered by filtration on a Buchner funnel, washed with water, and dried in air at ambient temperature. Surfactant was removed by calcining the as-synthesized product at 540<sup>0</sup>C for 5 h.

#### 2.2.6 Supported Metal Oxide Catalysts

Supported metal oxide (e.g. B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and TiO<sub>x</sub>) catalysts with different metal oxide loading were prepared by impregnating fine particles of support [low surface area macroporous inert silica-alumina (LS) (SA-5205, surface area (sa) = < 0.05 m<sup>2</sup>.g<sup>-1</sup>, pore volume (pv) = 0.35 cm<sup>3</sup>.g<sup>-1</sup>), silica (LS) (SS-5231, sa ≈ 0.2 m<sup>2</sup>.g<sup>-1</sup>, pv = 0.25 cm<sup>3</sup>.g<sup>-1</sup>) and ZrO<sub>2</sub> (LS) (SZ-5564, sa ≈ 0.1 m<sup>2</sup>. g<sup>-1</sup>, pv = 0.15 cm<sup>3</sup>. g<sup>-1</sup>), all obtained from M/s NORTON Co. USA; silica gel (sa = 280 m<sup>2</sup>.g<sup>-1</sup>); alumina (sa = 151 m<sup>2</sup>.g<sup>-1</sup>); H-ZSM-5 (Si/Al = 30); silicalite-I (high silica ZSM-5 with Si/Al > 1000); Si-MCM-41 (Si/Al > 1000, sa = 1180 m<sup>2</sup>.g<sup>-1</sup>); silica-alumina (HS) (sa = 255 m<sup>2</sup>.g<sup>-1</sup>) and H-Al-Si-MCM-41 (Si/Al = 30, sa = 810 m<sup>2</sup>.g<sup>-1</sup>)] with corresponding metal nitrate from their

aqueous solution by incipient wetness technique, drying at 110<sup>0</sup>C for 6 h, and then calcining in static air at 500<sup>0</sup>C for 4 h.

### 2.2.7 Supported Metal Chloride Catalysts

Supported metal chloride (e.g. FeCl<sub>3</sub>, ZnCl<sub>2</sub>, GaCl<sub>3</sub>, InCl<sub>3</sub> and TiCl<sub>4</sub>) catalysts with different metal chloride loading were prepared by impregnating Mont.-K10 (Montmorillonite-K10, Aldrich), Mont.-KSF (Montmorillonite KSF, Aldrich), Kaolin (Aldrich) and Si-MCM-41 (high silica mesoporous MCM-41 having surface area of 1140 m<sup>2</sup>.g<sup>-1</sup>) with corresponding anhydrous metal chloride from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 120<sup>0</sup>C for 8 h.

### 2.2.8 Mg-Ga Hydrotalcite

Ga-Mg-hydrotalcite (Mg/Ga mole ratio = 3.0), having a formula:  $[\text{Ga}_{0.25}\text{Mg}_{0.75}(\text{OH})_2]^{+0.25}[\text{CO}_3^{2-}]_{0.125}.n\text{H}_2\text{O}$ , was synthesized by the co-precipitation method [6] as follows. First an aqueous solution containing 6.83 g (26.7 mmol) Ga(NO<sub>3</sub>)<sub>3</sub>.x H<sub>2</sub>O and 20.48 g (79.9 mmol) Mg(NO<sub>3</sub>)<sub>2</sub> . 6 H<sub>2</sub>O in 100 cm<sup>3</sup> of water was prepared. 2.76 g (20 mmol) K<sub>2</sub>CO<sub>3</sub> and 15.19 g (270.72 mmol) KOH in 300 cm<sup>3</sup> of water were dissolved to make a second solution. These two solutions were added dropwise into a flask containing 200 cm<sup>3</sup> of water at 40<sup>0</sup>C under vigorous stirring. The rate of addition of the two solutions was controlled in order to keep a constant pH of 11-12, which was monitored continuously throughout the co-precipitation procedure by means of a pH-meter. After completing the addition of the solutions, the white gel obtained was immediately washed with deionised water several times and separated in a centrifuge. After this, the white paste was dried in an oven in static air at 80<sup>0</sup>C for 24 h. Ga-Mg-HT-80 and Ga-Mg-HT-200 hydrotalcite samples were obtained by calcining the as synthesized hydrotalcite at 80<sup>0</sup>C (for 12 h) and 200<sup>0</sup>C (for 4 h)

## 2.3 CATALYST CHARACTERIZATION

### 2.3.1 X-Ray Diffraction (XRD)

The crystalline phase identification and phase purity of the catalysts were determined by X-ray powder diffraction method using a Holland Phillips, PW/1730 X-ray generator with CuK<sub>α</sub> radiation (λ = 1.5406 Å; 40 kV, 25 mA). The samples were prepared as thin layer on a glass slide.

### 2.3.2 Surface Area

The surface area of the catalysts was measured by single-point BET method by measuring the adsorption of nitrogen at liquid temperature and at N<sub>2</sub> concentration of 30 mol% (balance helium), using a Monosorb Surface Area Analyzer (Quantachrome Corp., USA) based on dynamic adsorption/desorption technique.

Before carrying out surface area measurement experiments, the catalyst (0.5-2.0 g) was pretreated in situ in the sample cell at 300°C for 1h in flow (30 cm<sup>3</sup>.min<sup>-1</sup>) of a mixture of helium and nitrogen to remove the traces of moisture and the analyzer was calibrated by injecting a known amount of air.

The surface area was calculated from the observed desorption counts instead of the adsorption ones, as follows:

Surface area (m<sup>2</sup>.g<sup>-1</sup>) = (Desorption counts x 2.84) / (Wt. of catalyst x Counts of 1 ml of air).

(2.84 m<sup>2</sup>.area = 1 cm<sup>3</sup> N<sub>2</sub> or air. Counts are expressed in terms of surface area, m<sup>2</sup>)

### 2.3.3 Scanning Electron Microscopy (SEM)

The crystal size and morphology of the catalysts were determined by using Leico Cambridge Stereoscan 440 Scanning Electron Microscope. The samples were sputtered with gold to prevent surface charging and to protect them from thermal damage from the electron beam.

### 2.3.4 Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of samples were recorded with a Shimadzu FTIR spectrometer (Model 8300). FTIR spectra of the catalysts in the framework region (450 cm<sup>-1</sup> to 40000 cm<sup>-1</sup>) were obtained in nujol or in the diffuse reflectance mode.

### 2.3.5 X-Ray Photoelectron Spectroscopy (XPS)

Surface chemical analysis of the catalyst was done by the X-ray photoelectron Spectroscopy (XPS) using a VG-scientific ESCA-3 MK II electron spectrometer (C1s with binding energy = 285.0 eV was used as internal standard).

The surface concentration of the elements present in the reduced and free catalysts has estimated as follows:

(Area under curve x Scale) / (Cross-sectional area of an element x Magnification).



### 2.3.6 Measurement of Acidity

The acidity of the catalysts was determined by the GC adsorption/desorption methods, using pyridine as an acid probe.

Gas chromatographic adsorption/desorption data were collected using a Perkin-Elmer Sigma 300 GC fitted with a flame ionization detector. Nitrogen, passed over catalysts to remove traces of moisture, was used as the carrier gas. The flow rate was about  $40 \text{ cm}^3 \text{ (NTP). min}^{-1}$  in all the experiments. The experimental set up is shown in Figure 2.1.

The catalyst column was prepared by packing about 0.5 g of the adsorbent particles (particle size: 0.3 - 0.4 mm) in a stainless steel tube (length = 5.5 cm, i.d. = 1.5 mm and o.d. = 3.0 mm). In order to minimize the dead volume, one end of the column was directly connected to the detector and the other end to the injector through a 40 cm long stainless steel capillary (about 1.5 mm o.d. and 0.7 mm i.d.), which acted as a pre-heater. The catalyst was calcined in situ by heating rate of  $20^\circ\text{C min}^{-1}$  and further at  $400^\circ\text{C}$  for 1 h.

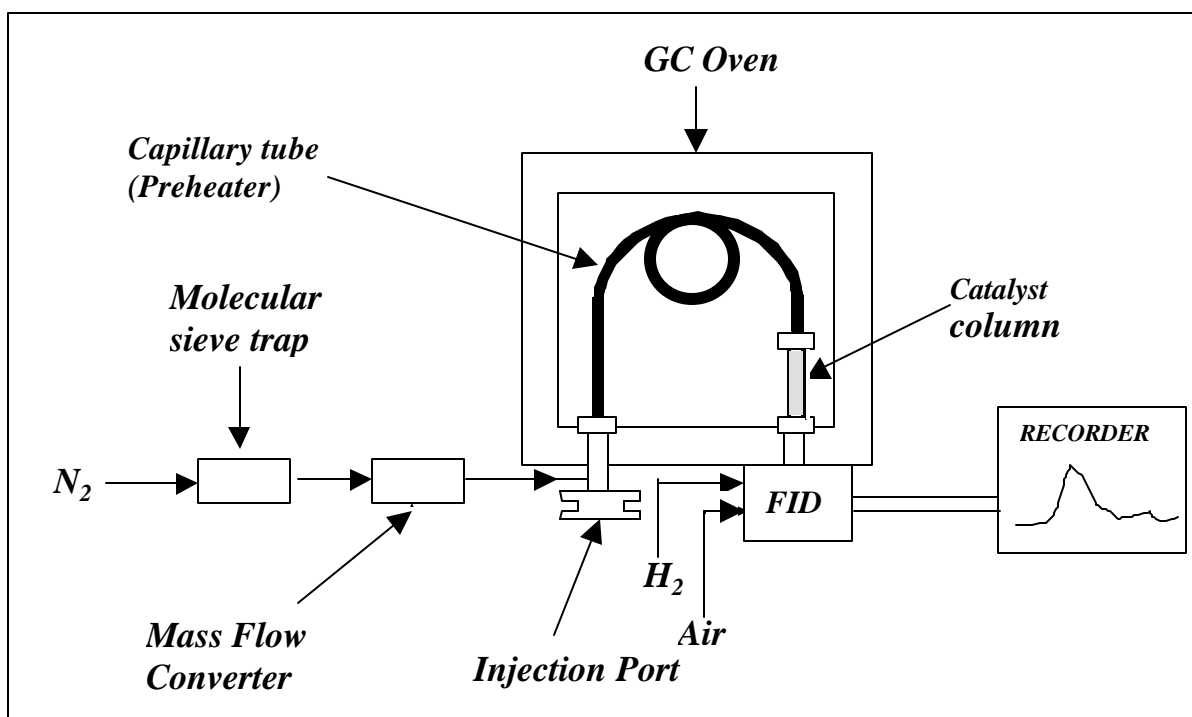


Figure 2.1 Experimental set-up for the acidity measurements.

The chemisorption of pyridine in the catalyst was measured by the GC pulse method [7] based on TPD under chromatographic conditions, as follows.

The initial temperature chosen for the TPD was 80°C. The catalyst was pretreated in situ in a flow of N<sub>2</sub> (carrier gas) for 1 h. After the pretreatment of the catalyst, the GC oven temperature was brought down to 80°C and a known amount of pyridine was injected into the catalyst column. After allowing redistribution of the adsorbed species in the column, the TPD was started at a linear heating rate of 20°C min<sup>-1</sup> in the flow of nitrogen. The final temperature chosen for the TPD (or the temperature at which the irreversible adsorption of the adsorbate was to be measured) was 400°C. After the final temperature was reached, the desorption of the reversibly adsorbed species was allowed to continue for a further period of 60 min isothermally at that temperature. At the end of the TPD, the catalyst retained only the adsorbate irreversibly adsorbed at 400°C.

After recording the first TPD chromatogram, the GC oven temperature was reduced to 80°C and the procedure was repeated to obtain the second TPD chromatogram by injecting the same amount of pyridine.

The amount of pyridine irreversibly adsorbed was calculated from the expression:

$$q_i = (A^* / s) / M$$

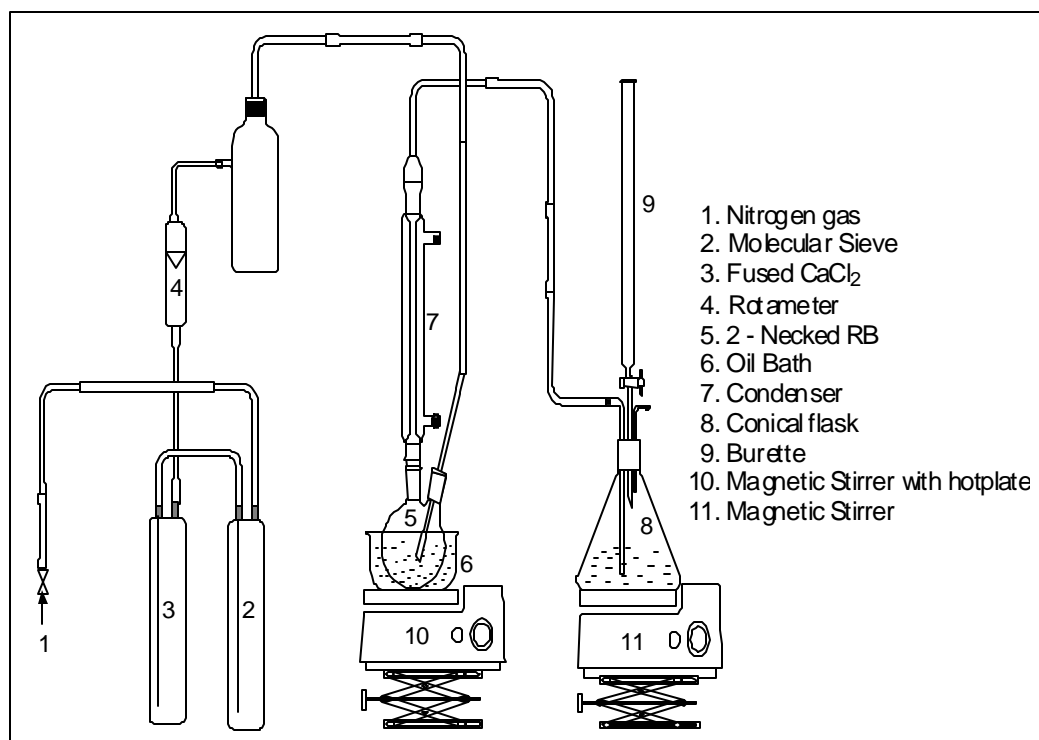
where A\* is the difference between the areas of the two chromatograms obtained by the superimposition of the two chromatograms and cutting and weighing, s is the detector sensitivity (area. mol<sup>-1</sup>) and M is the mass of the catalyst. The irreversible adsorption (or chemisorption) in the present study is defined as the amount of adsorbate retained by the presaturated catalyst after it was swept with pure nitrogen at the temperature of chemisorption for 1 h.

## 2.4 CATALYTIC REACTIONS

### 2.4.1 Benzylation and Acylation Reactions

The benzylation and acylation reactions over the catalysts were carried out in a magnetically stirred glass reactor (capacity 25 cm<sup>3</sup>) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N<sub>2</sub> (30 cm<sup>3</sup>.min<sup>-1</sup>) through the liquid reaction mixture as shown in Figure 2.2. The reaction was started by injecting benzyl chloride or acyl chloride in the reaction mixture, containing aromatic substrate with or without solvent and the catalyst, at the reaction temperature. 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<sub>2</sub> 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 or acyl chloride and benzylation or acylation product at the end of the experiment by gas chromatography. There was a good agreement between the benzyl or acyl chloride conversion obtained from the acid-base titration and that from the GC analysis. The conversion data were corrected for a small time lag between the evolution of HCl in the reaction and the analysis of the evolved HCl by the titration. In all the cases, the product formed was mainly mono-benzylated or acylated, and there was little no formation of poly-benzyl chloride or poly-acyl chloride. The amount of benzylation or acylation product formed was equivalent (within 2-5 % error) to the amount of benzylating or acylating agent consumed in the reaction.



**Figure 2.2** Typical liquid phase reaction setup for benzylation or acylation of aromatic compounds

The product of the acylation was isolated as follows. After the reaction, the catalyst was separated from the reaction mixture by filtration and the product from the filtrate was recovered by washing the filtrate with 0.1 M NaOH solution and removing the solvent and unconverted aromatic substrate by vacuum distillation. The product was then purified by column chromatography using silica gel (SRL 60-120 mesh) as the stationary phase and benzene as the eluent. The structure of the product was determined by  $^1\text{H}$  NMR spectroscopy. The isolated product yield was defined as follows: yield (%) = [(moles of isolated product) / (moles of acyl chloride used)] x 100.

In order to study the effect of moisture present in the reaction mixture, the catalyst stored over water at room temperature for 15 h and the aromatic substrate or solvent saturated with water at room temperature, respectively, were used for the benzylation or acylation reaction.

For studying the effect of HCl gas pretreatment to the catalyst on its performance in the benzylation or acylation reaction, a HCl (gas)- $\text{N}_2$  mixture (20 mol% HCl) was bubbled through a mixture of aromatic substrate and catalyst under stirring at the desired temperature for a period of 5 to 60 min. The aromatic substrate-catalyst mixture was flushed with pure  $\text{N}_2$  ( $30 \text{ cm}^3 \cdot \text{min}^{-1}$ ) for 30 min to remove physically adsorbed or absorbed HCl in the reaction mixture and then the reaction was started by injecting benzyl or acyl chloride in the reaction mixture.

In order to study the reuse of catalyst for the reaction, two different experiments were carried out. In the first experiment, 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. In the second experiment, after completion of the reaction on a fresh catalyst, a period of 10 min was allowed to lapse and then 1.0 ml benzyl (or acyl) chloride was introduced in the reaction mixture already containing excess of aromatic substrate at the reaction temperature to start the reaction.

#### **2.4.2 Polycondensation Reaction**

The polycondensation reaction was carried out in a magnetically stirred glass reactor (capacity:  $25 \text{ cm}^3$ ) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free  $\text{N}_2$  ( $30 \text{ cm}^3 \cdot \text{min}^{-1}$ ) through the liquid reaction mixture at the following reaction conditions: reaction mixture = 1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst at different

reaction temperature. The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by acid-base titration. The detailed experimental procedures are same as that described for the benzylation and acylation reactions (section 2.4.1).

After completing the reaction, the polymer was dissolved in benzene, separated from the catalyst by filtration, washed with water, dried and finally poured into excess methanol. The precipitated polymer was collected, washed with methanol for several times and dried in vacuum oven at 60<sup>o</sup>C for 24 h.

### 2.4.3 Esterification Reaction

Esterification of *tert*-butanol by acetic anhydride or dehydration of *tert*-butanol over the different clay supported metal chloride catalysts was carried out in a magnetically stirred glass reactor (capacity 25 cm<sup>3</sup>) fitted with a reflux condenser and a thermometer for measuring the reaction temperature and the outlet of the reflux condenser was connected to a constant pressure gas collector. The volume of the reaction mixture in the reactor was 10 cm<sup>3</sup>. The reactor was kept in a constant temperature water bath. The iso-butylene formed in the reaction was measured quantitatively by collecting it in the gas collector at the atmospheric pressure. The products of the esterification were analyzed by a gas chromatograph (with flame ionization detector and SE - 30 column), using n-hexane as an internal standard.

## 2.5 REFERENCE

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## ***CHAPTER-3***

### ***BENZYLATION OF BENZENE BY BENZYL CHLORIDE OVER Fe-, Zn-, Ga- AND In-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS***

## Chapter-3

# BENZYLATION OF BENZENE BY BENZYL CHLORIDE OVER Fe-, Zn-, Ga- AND In-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS.

### 3.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

A number of highly acidic solid catalysts, such as heteropolyacids [1-5] and sulfated  $ZrO_2$  or  $Fe_2O_3$  [6-7] and HY, H-beta and H-ZSM-5 zeolites [8] are reported earlier in the liquid phase alkylation of benzene [1-4,6] and toluene [5,7-8] by benzyl chloride. The alkylation of aromatic compound containing electron donating group (e.g. alkyl, alkoxy, OH, etc.) can be accomplished with ease but of that without such aromatic ring activating group (e.g. benzene) is relatively difficult [9]. The above mentioned acidic catalysts, except sulfated  $Fe_2O_3$ , show poor activity for the benzylation of benzene. Sulfated  $Fe_2O_3$  shows high activity but poor selectivity and also poor reusability in the benzylation of benzene [10].

It is interesting to note that, in spite of its very strong acidity, H-ZSM-5 zeolite shows almost no activity for the benzylation of benzene [8]. In the present investigation, we have observed that a complete or partial substitution of Al in H-ZSM-5 zeolite by Fe or Ga or an impregnation of the zeolite by  $Fe_2O_3$ , ZnO,  $Ga_2O_3$  or  $In_2O_3$  makes the zeolite highly active in the benzylation process. The redox function created due to the modification of the HZSM-5 zeolite by Fe, Zn, Ga and In seems to play a very important role in the benzylation process. In this investigation, liquid phase benzylation of benzene by benzyl chloride over different ZSM-5 type zeolites, such as HFeMFI, H-FeAlMFI, H-GaMFI, H-GaAlMFI,  $Fe_2O_3$ /H-ZSM-5, ZnO/H-ZSM-5,  $Ga_2O_3$ /H-ZSM-5 and  $In_2O_3$ /H-ZSM-5 catalysts at 80<sup>0</sup> and/or 60<sup>0</sup>C as a function of reaction time has been carried out and the catalysts are compared for their performance in the benzylation process. Influence of the presence of moisture in the catalyst and/or in the substrate and also of the HCl gas pretreatment to the catalyst on the reaction induction period and benzene benzylation activity of some of the zeolite catalysts and also their reusability in the benzene benzylation have also been investigated.

## 3.2 RESULTS AND DISCUSSION

### 3.2.1 *Composition and Properties of Modified ZSM-5 Type Zeolite Catalysts*

The modified ZSM-5 type zeolite catalysts were characterized for their bulk and non-framework compositions, crystal size and also for their strong acid sites (measured in terms of the pyridine chemisorbed on them at 400<sup>0</sup>C). The catalyst characterization data are presented in Table 3.1.

The GaMFI, GaAlMFI, FeMFI and FeAlMFI zeolites contain appreciable amounts of non-framework Ga- or Fe-species, which are produced by the degallation or deferritation of the corresponding zeolite during their pretreatment [11-13].

### 3.2.2 *Comparison of the Modified ZSM-5 Zeolite Catalysts for Benzene Benzylation*

The H-ZSM-5 and Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts are compared for their benzene benzylation activity (at 80<sup>0</sup>C) in Table 3.2. The benzyl chloride conversion vs. time plots for the benzylation of benzene over HZSM-5 (a and b) and Fe- or Ga-substituted ZSM-5 and Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5a, ZnO/H-ZSM-5a, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5a catalysts at 80<sup>0</sup>C are presented in Figures 3.1 and 3.2 and those at 60<sup>0</sup>C are presented in Figure 3.3. Turn-over rate (TOR) for half the benzene benzylation reaction (i.e. at 50% conversion of benzyl chloride) was estimated as the moles of benzyl chloride converted per gramme of catalyst per unit time.

From the comparison of results in Tables 3.1 and 3.2, following important observations can be made:

- In spite of its high acidity, the H-ZSM-5 zeolite is almost inactive in the benzylation of benzene but its benzylation activity is drastically increased because of a partial or complete substitution of its framework Al by Fe or Ga or even by the impregnation of the zeolite with Fe<sub>2</sub>O<sub>3</sub>, ZnO, Ga<sub>2</sub>O<sub>3</sub> or In<sub>2</sub>O<sub>3</sub>.
- Among the Ga- and Fe-substituted zeolites, the H-FeMFI zeolite showed highest activity but lowest selectivity for the benzene benzylation. Similarly, among the metal oxide impregnated zeolite catalysts, the Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5a showed highest activity but lowest selectivity for the reaction. The lower selectivity for diphenyl methane is because of the higher benzyl chloride polycondensation activity of the Fe-modified ZSM-5 zeolite catalysts [14].
- For the zeolites having same Si/Ga ratio but having different acidity (i.e. H.Na-GaMFI with different H<sup>+</sup> exchange or calcined at different temperatures), the benzylation activity of the zeolite is increased with increasing zeolite acidity.



Because of the dehydroxylation during the calcination at higher temperature (750°C), the acidity and consequently the benzylation activity of the H-GaMFI zeolite is decreased markedly.

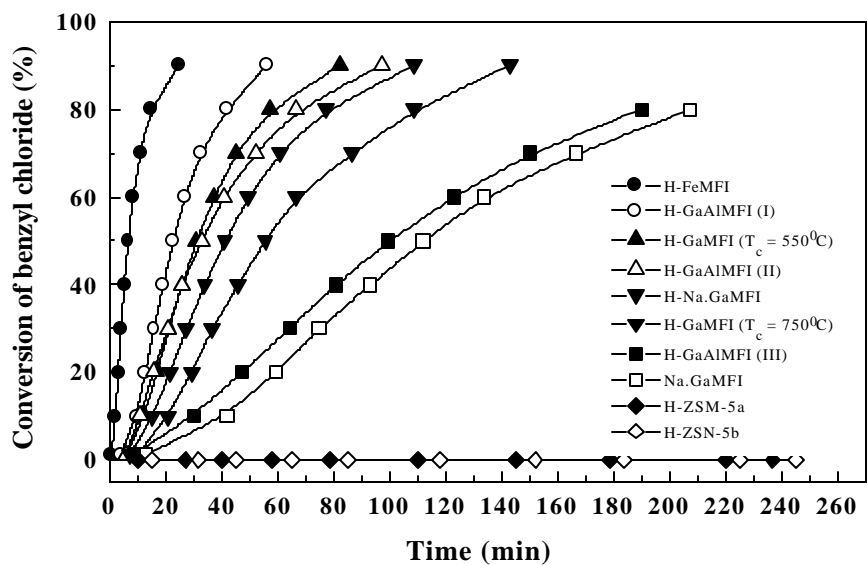
**Table 3.1** Composition and properties of Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolites.

Zeolite catalysts	H <sup>+</sup> exchange (%)	Bulk ratio (M=Al, Fe or Ga)	Si/M (M=Al, Fe, Zn, Ga or (wt %))	Non-FW or (wt %)	Crystal size (µm)	Strong acidity (mmol. g <sup>-1</sup> )
H-ZSM-5a	99	Si/Al = 31.1	-	-	4-6	0.26
H-ZSM-5b	99	Si/Al = 13.6	-	-	3-4	0.36
H-Ga MFI (T <sub>c</sub> = 550°C)	95	Si/Ga = 33	1.2 (Ga)	-	5-7	0.29
H-Ga MFI (T <sub>c</sub> = 750°C)	95	Si/Ga = 33	2.4 (Ga)	-	5-7	0.09
H-Na Ga MFI	55	Si/Ga = 33	1.2 (Ga)	-	5-7	0.16
Na-Ga MFI	5	Si/Ga = 33	1.2 (Ga)	-	5-7	0.04
H-Ga Al MFI(I)	99	Si/Al = 49.6 Si/Ga = 15.3	4.5 (Ga)	-	3-5	0.44
H-Ga Al MFI(II)	99	Si/Al = 37.5 Si/Ga = 24.3	2.2 (Ga)	-	4-6	0.46
H-Ga Al MFI(III)	99	Si/Al = 17.1 Si/Ga = 51.2	1.1 (Ga)	-	-	0.48
H-Fe MFI	99	Si/Fe = 16.5	2.2 (Fe)	-	3-5	0.29
H-FeAl MFI	99	Si/Al = 26.2 Si/Fe = 28.1	-	-	-	0.26
ZnO / H-ZSM-5a	99	Si/Al = 31.1	4.0 (Zn)	-	4-6	0.20
Fe <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	99	Si/Al = 31.1	3.5 (Fe)	-	4-6	0.24
Ga <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	99	Si/Al = 31.1	3.7 (Ga)	-	4-6	0.18
In <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	99	Si/Al = 31.1	4.1 (In)	-	4-6	0.23

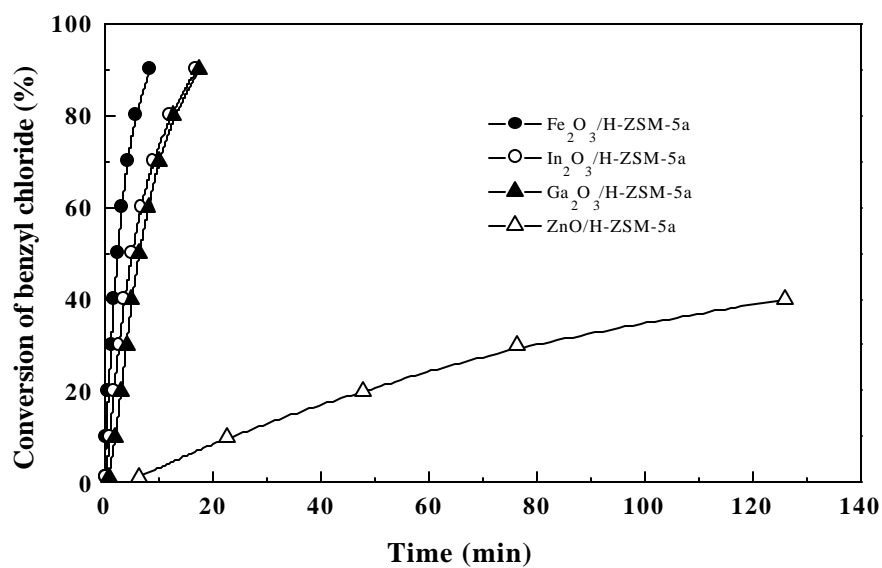
*T<sub>c</sub>* = calcination temperature.

**Table 3.2** Comparison of the Fe-, Zn-, Ga- and In-modified zeolites for their performance in the benzylation of benzene (at 80°C).

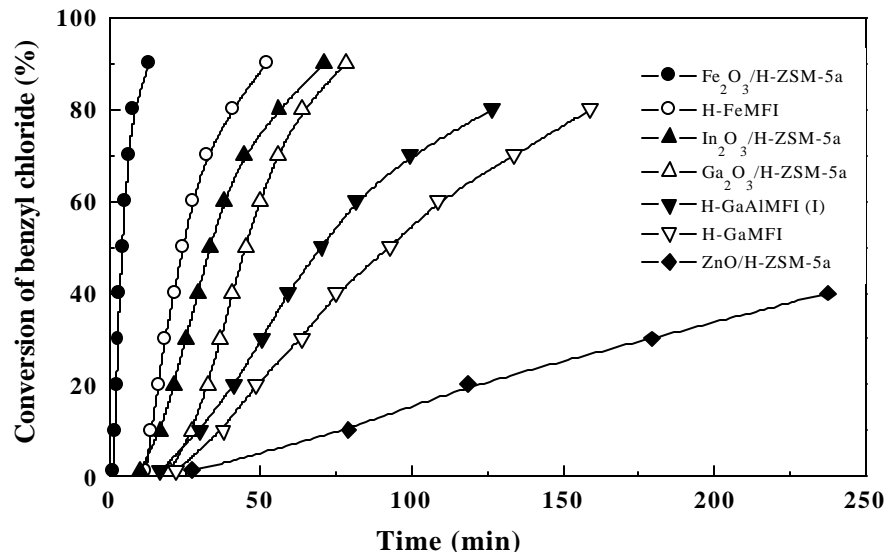
Zeolite catalysts	Induction period (min)	Time required for conversion of benzyl chloride		Apparent rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )	TOR ( $\mu\text{mol. g}^{-1} \text{s}^{-1}$ ) for half the reaction	Selectivity for diphenylmethane at complete conversion of benzyl chloride (%)
		50 %	90 %			
H-ZSM-5a	No conversion upto 2.0 h			≈ 0.0	≈ 0.0	-
H-ZSM-5b	No conversion upto 2.0 h			≈ 0.0	≈ 0.0	-
H-GaMFI ( $T_c = 550^\circ\text{C}$ )	6.1	31.2	82.5	34.4	23	> 98
H-GaMFI ( $T_c = 750^\circ\text{C}$ )	10.1	55.7	143.0	17.9	13	> 98
H-NaGaMFI	7.5	41.3	109.0	25.2	18	95
Na-GaMFI	13.1	112.0	-	8.8	7	93
H-GaAlMFI (I)	4.1	22.8	56.2	46.5	32	> 98
H-GaAlMFI (II)	5.8	33.0	97.2	26.8	21.9	> 98
H-GaAlMFI (III)	8.7	99.7	285	8.4	7.2	> 98
H-FeMFI	0.9	6.7	25.0	124.5	108	89
H-FeAlMFI	5.5	30.3	104	24.7	23.6	90
ZnO / H-ZSM-5a	6.5	183.0	-	4.4	4	92
Fe <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	0.1	2.5	8.5	271.0	290	85
Ga <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	0.8	6.5	17.6	148.6	111	> 98
In <sub>2</sub> O <sub>3</sub> / H-ZSM-5a	0.4	5.1	17.0	153.5	142	> 98



**Figure 3.1** Conversion vs. reaction time plots for the benzylation of benzene (at 80°C) over H-ZSM-5 zeolite with or without isomorphous substitution of their framework Al by Ga or Fe.



**Figure 3.2** Conversion vs. reaction time plots for the benzylation of benzene (at 80°C) over the H-ZSM-5 zeolite impregnated with ZnO, Fe<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> or In<sub>2</sub>O<sub>3</sub>.



**Figure 3.3** Conversion vs. reaction time plots for the benzylation of benzene (at 60°C) over the Zn-, Fe-, Ga- and In- modified ZSM-5 type zeolite.

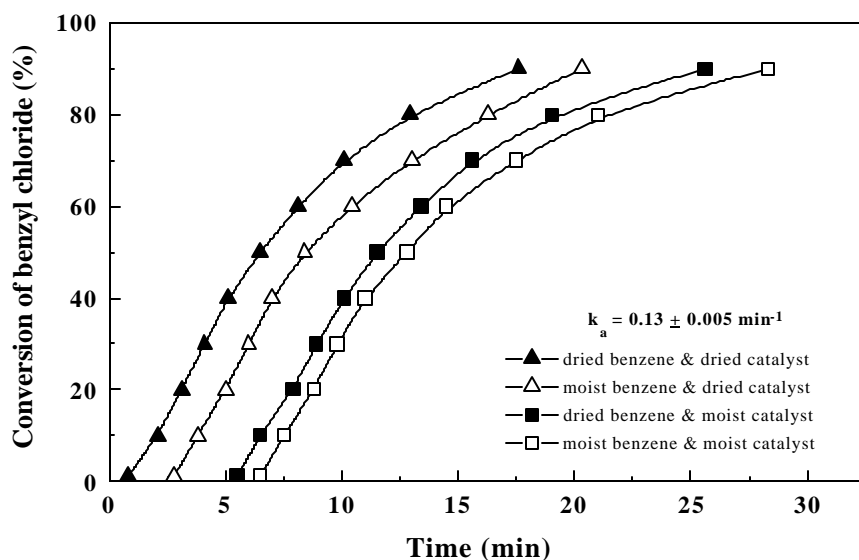
- Among the Ga-substituted zeolites, those having lower Si/Ga ratio showed higher benzylation activity, indicating the importance of Ga concentration in the zeolite for its benzylation activity; higher the Ga concentration higher is the benzylation activity.
- For the metal oxide impregnated zeolite catalysts having same metal oxide loading, there is no direct relationship between zeolitic acidity and benzylation activity; the benzylation activity of the zeolite catalysts is in the following order:  $\text{Fe}_2\text{O}_3/\text{H-ZSM-5a} > \text{In}_2\text{O}_3/\text{H-ZSM-5a} \approx \text{Ga}_2\text{O}_3/\text{H-ZSM-5a} \gg \text{ZnO}/\text{H-ZSM-5a}$ . It is interesting to note that the order of the redox potential for the metal oxides in these zeolite catalysts:  $E_{\text{Fe}^0/\text{Fe}^{+2}}^0 (+0.77 \text{ V}) > E_{\text{In}^0/\text{In}^{+1}}^0 (-0.44 \text{ V}) = E_{\text{Ga}^0/\text{Ga}^{+1}}^0 (-0.44 \text{ V}) > E_{\text{Zn}^0/\text{Zn}^{+2}}^0 (-0.74 \text{ V})$ , is very similar to the order of the zeolite catalysts for their benzene benzylation activity, indicating a close relationship between the redox potential and the catalytic activity.
- The benzene benzylation activity of the Fe- or Ga-substituted ZSM-5 zeolites is much lower than that of the  $\text{Fe}_2\text{O}_3$  or  $\text{Ga}_2\text{O}_3$  impregnated ZSM-5 zeolite catalysts. The lower activity of the former seems to be attributed to the lower concentration of non-framework Fe or Ga i.e.  $\text{Fe}_2\text{O}_3$  or  $\text{Ga}_2\text{O}_3$  in the zeolite channels.

The above observations clearly show that, although the zeolitic acidity is also important, the concentration of non-framework Fe, Ga or In in the zeolite is more important for its catalytic activity in the benzylation reaction.

### 3.2.3 Effect of Moisture on the Catalytic Activity/Reaction Induction Period

In order to study the effect of moisture present in the  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5a}$  catalyst and/or in the substrate, the catalyst stored over water at room temperature for 15 h (moist catalyst) and the benzene saturated with water at room temperature (moist benzene) were used for the benzylation of benzene. Results showing the effect of moisture present in the reaction mixture on the benzene benzylation over the  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5a}$  are presented in Figure 3.4.

Because of the presence of moisture in the reaction mixture, the reaction induction period is increased markedly, but without affecting significantly the reaction rate once the reaction started after the induction period. It is interesting to note that, even though both the substrate and catalyst are saturated with water, the catalyst showed high benzene benzylation activity. A similar observation was also made for the  $\text{In}_2\text{O}_3/\text{H-ZSM-5a}$  catalyst. Apart from their very high activity in the benzylation process, the low moisture sensitivity of these catalysts is of great practical importance. These catalysts do not demand stringent moisture-free conditions for them to be highly active/selective in the benzylation process.



**Figure 3.4** Effect of moisture in the catalyst and/or substrate on the conversion of benzyl chloride (at  $80^\circ\text{C}$ ) in the benzylation of benzene over  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5a}$ .

Also for studying the influence of traces of moisture present in the catalyst, the H GaMFI catalyst (which was pretreated under moisture-free N<sub>2</sub> at 450<sup>0</sup>C) was refluxed with moisture-free benzene for different periods and then its benzene benzylation activity was evaluated. Results showing the influence of the reflux period on the performance of the catalyst in the benzene benzylation are presented in Table 3.3. The reaction induction period is decreased appreciably with increasing the reflux period due to the increased removal of moisture from the catalyst. There is, however, only a small change in the value of the reaction rate constant, k<sub>a</sub> (Table 3.3). These results are complementary to the above ones

**Table 3.3** Reaction induction period and catalytic performance in the benzylation of benzene (at 80<sup>0</sup>C) of H-GaMFI pretreated with moisture-free benzene (13 ml benzene + 0.1 g catalyst) under reflux in the presence of moisture-free N<sub>2</sub> flow (30 cm<sup>3</sup>.min<sup>-1</sup>) for different periods.

Reflux period (h)	Reaction induction period (min)	Time required for 50 % conversion of benzyl chloride (min)	Apparent rate constant, k <sub>a</sub> x 10 <sup>3</sup> (min <sup>-1</sup> )
0.0	6.1	31.2	34.4
1.0	4.0	27.9	35.1
3.0	2.7	25.0	36.0

The above observations clearly show that the reaction induction period depends strongly on the moisture content of the reaction system; higher the moisture content, higher is the induction period.

#### 3.2.4 Effect of Catalyst Pretreatment by HCl

Results showing the influence of HCl gas pretreatment to the HGaMFI and Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a catalysts for their performance in the benzene benzylation are given in Table 3.4.

For both the catalysts, the HCl pretreatment resulted in a drastic reduction in the reaction induction period, which is almost reduced to zero. Accordingly, the time

required for half the reaction is also reduced. The disappearance of the induction period seems to be attributed to the displacement of adsorbed moisture from the catalyst by the strongly adsorbed HCl and/or to the creation of new catalytic active sites, such as surface metal chloride species, by the HCl pretreatment.

**Table 3.4** Effect of HCl gas pretreatment to the zeolite catalyst for its performance in the benzene benzylation (at 80°C).

Catalyst	HCl pretreatment (Yes/No)	Reaction induction period (min)	Time required for 50 % conversion of benzyl chloride (min)	Apparent rate constant, $k_a \times 10^3$ ( $\text{min}^{-1}$ )
H-GaMFI	No	6.1	31.2	34.4
H-GaMFI	Yes	0.0	25.5	34.7
Ga <sub>2</sub> O <sub>3</sub> /H-ZSM5a	No	0.8	6.5	148.6
Ga <sub>2</sub> O <sub>3</sub> /H-ZSM5a	Yes	0.0	5.8	150.1

### 3.2.5 Reusability of the Catalysts

Results in Table 3.5 reveal that the Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a, In<sub>2</sub>O<sub>3</sub>/H-ZSM-5a and H-GaAlMFI (I) zeolite catalysts can be reused in the benzylation process without a significant change in their catalytic activity. However, it is interesting to note that the reaction induction period for the used catalysts is much lower than the fresh ones. This is expected mostly because of the removal of moisture from the catalyst and/or the catalyst activation by the HCl produced in the reaction during the first use of the catalyst in the reaction. The observed small induction period (0.1- 0.2 min) for the reused catalysts, may be because of the moisture adsorbed on the catalyst before its reuse. No induction period was observed when the benzyl chloride was added to the reaction mixture immediately after the completion of the reaction on a fresh or reused catalyst (Table 3.5).

**Table 3.5** Data on the reuse of Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a, In<sub>2</sub>O<sub>3</sub>/H-ZSM-5a and H-GaAlMFI (I) zeolite catalysts in the benzylation of benzene (at 80<sup>o</sup>C).

Fresh / reused catalyst	Induction period (min)	Time for 50 % benzyl chloride conversion (min)	Apparent constant, $k_a \times 10^3$ (min <sup>-1</sup> )
<b>A) Catalyst: Ga<sub>2</sub>O<sub>3</sub> / H-ZSM-5a</b>			
Fresh	0.8	6.5	148.6
First reuse <sup>a</sup>	0.2	6.1	147.3
Second reuse <sup>a</sup>	0.2	6.1	148.0
Third reuse <sup>a</sup>	0.2	6.0	150.2
First/second reuse <sup>b</sup>	0.0	5.9	151.0
<b>B) Catalyst: In<sub>2</sub>O<sub>3</sub> / H-ZSM-5a</b>			
Fresh	0.5	5.1	153.5
First reuse <sup>a</sup>	0.1	4.8	151.2
Second reuse <sup>a</sup>	0.1	4.7	156.0
Third reuse <sup>a</sup>	0.1	4.7	159.0
First/second reuse <sup>b</sup>	0.0	4.6	158.1
<b>C) Catalyst: H-GaAlMFI (I)</b>			
Fresh	4.1	22.8	46.5
First reuse <sup>a</sup>	0.2	19.0	47.0

<sup>a</sup> The catalyst was reused after removing the supernatant liquid reaction mixture, while retaining the catalyst in the reactor and avoiding, the removal of catalyst fine particles.

<sup>b</sup> After completion of the reaction on fresh catalyst, a period of 10 min was allowed to lapse and then 1.0 ml benzyl chloride was introduced in the reaction mixture already containing excess of benzene at 80<sup>o</sup>C to start the reaction.



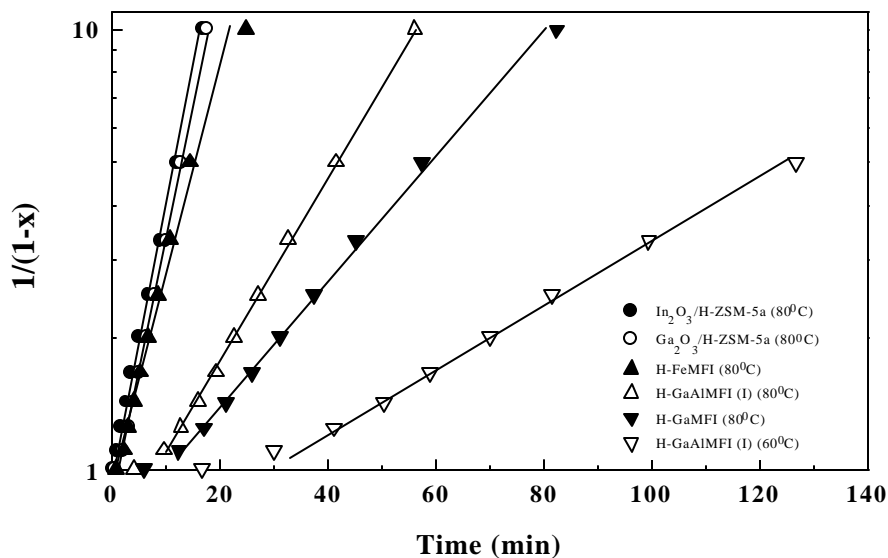
### 3.2.6 Reaction Kinetics

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

$$\log [1/(1-x)] = (k_a/2.303) (t-t_0) \quad (3.1)$$

where  $x$  is the fractional conversion of benzyl chloride,  $k_a$  is the apparent first order rate constant,  $t$  is the reaction time and  $t_0$  is the reaction induction period. Representative linear  $\log[1/(1-x)]$  against  $(t-t_0)$  plots, according to the above rate law, are given in Figure 3.5. The best fit of the rate data to the first order rate law could 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 3.2 – 3.6.

The values of the activation energy and frequency factor for the H-GaMFI, H-GaAlMFI (I), H-FeMFI,  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5a}$  and  $\text{In}_2\text{O}_3/\text{H-ZSM-5a}$  zeolite catalysts are included in Table 3.6. Among these zeolite catalysts, the H-FeMFI has the lowest activation energy but also has the lowest frequency factor. Whereas, the  $\text{Ga}_2\text{O}_3/\text{H-ZSM-5a}$  has the highest activation energy but also has the highest frequency factor.



**Figure 3.5** Representative pseudo-first order plots for the benzylation of benzene over different zeolite catalysts.

**Table 3.6** Kinetic parameters for the benzylation of benzene over different zeolite catalysts.

Zeolite catalyst	Apparent rate constant, $k_a \times 10^3$ ( $\text{min}^{-1}$ )		Activation energy, E ( $\text{kcal.mol}^{-1}$ ) <sup>a</sup>	Frequency factor, A ( $\text{min}^{-1}$ ) <sup>a</sup>
	60 <sup>o</sup> C	80 <sup>o</sup> C		
H-GaMFI	12.3	34.4	12.0	$7.6 \times 10^5$
H-GaAlMFI (I)	17.3	46.5	11.6	$6.6 \times 10^5$
H-FeMFI	31.6	124.5	9.1	$4.3 \times 10^4$
Ga <sub>2</sub> O <sub>3</sub> /H-ZSM-5a	37.9	148.6	16.1	$1.1 \times 10^9$
In <sub>2</sub> O <sub>3</sub> /H-ZSM-5a	40.1	153.5	15.8	$7.9 \times 10^8$

<sup>a</sup> Obtained from Arrhenius equation :  $k_a = A.exp.[-E/(RT)]$ , where R is a gas constant.

### 3.2.7 Reaction Mechanism

The observed very high benzene benzylation activity of the Fe-, Zn-, Ga- and In-modified H-ZSM-5 zeolites as compared to that of HZSM-5 is attributed to the presence of non-framework Fe-, Zn-, Ga- and In-oxide species most probably in combination with the zeolitic protons. The non-framework metal oxide species are known for their redox properties, which are expected to play a significant role in activating both the reactants in the benzene benzylation. A following probable mechanism for the activation of benzyl chloride by both the zeolitic protons and the metal oxide species, and the activation of benzene by the metal oxide species, is proposed.

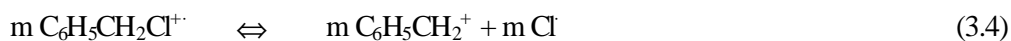
#### Activation of benzyl chloride



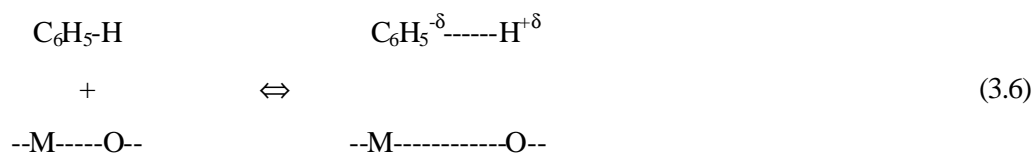
(wherein Z = tetrahedral Al<sup>-</sup>, Ga<sup>-</sup> or Fe<sup>-</sup>)



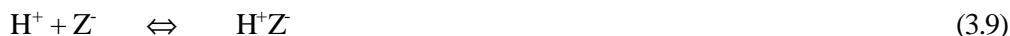
[where M = Fe, Zn, Ga or In, n = 3 (for Ga, In and Fe) or 2 (for Zn) and m = 2 (for Ga and In) and 1 (for Zn and Fe)]



### Activation of benzene



### Reaction between benzyl carbocation and activated benzene



The redox mechanism (equations 3.3 – 3.5) is similar to that proposed earlier [15]. The above redox mechanism is quite consistent with the observations; the order for the benzene benzylation activity of the Fe-, Zn-, Ga- and In-modified ZSM-5 zeolites is almost the same as that for the redox potential of the corresponding metal oxide. The activation of benzyl chloride can occur on both the protonic and redox sites of the zeolite catalysts. However, the activation of benzene according to equation 3.6 seems to be essential for the insertion of the benzyl carbonium ion into the benzene nucleus. It may be noted that, although H-ZSM-5 is capable of forming benzyl carbonium ion, yet it shows almost no benzene benzylation activity.

### **3.3 CONCLUSIONS**

From the present studies on the benzylation of benzene over the HZSM-5 and Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts, the following important conclusions can be made:

1. Fe-, Ga- and In-modified H-ZSM-5 type zeolites, particularly Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5a, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5a are highly active catalysts for the benzene benzylation reaction. The high catalytic activity of these zeolite catalysts is attributed to the presence of non-framework Fe-, Ga- or In-oxide species in combination with the zeolitic protons. These catalysts show high activity even in the presence of moisture in the reaction mixture and also have excellent reusability for the reaction.
2. For all the catalysts, a significant reaction induction period is observed. The induction period is found to depend strongly on the amount of moisture present in the catalyst and/or in the reaction mixture; it is increased with increasing the amount of moisture. It is drastically reduced (almost to zero) due to the pretreatment of the catalyst by HCl gas and also by the removal of traces of moisture from the catalyst.

3. The reaction with the excess of benzene follows a pseudo-first order rate law for the benzyl chloride conversion in the range from 10 to 90%. Among the HGaMFI, H-GaAlMFI (I), H-FeMFI, Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5a zeolite catalysts, the H-FeMFI showed the lowest activation energy (9.1 kcal.mol<sup>-1</sup>) but also the lowest frequency factor (4.3 x 10<sup>4</sup> min<sup>-1</sup>); whereas the Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5a showed the highest activation energy (16.1 kcal.mol<sup>-1</sup>) but also the highest frequency factor (1.1 x 10<sup>9</sup> min<sup>-1</sup>) for the benzene benzylation process.
4. There exists a close relationship between the redox potential and the benzene benzylation activity of the Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts. In the catalytic process, the activation of benzyl chloride seems to occur on both the zeolitic protons and the redox sites and that of benzene on the redox sites (non-FW Fe-, Zn-, Ga- or In-oxide species).

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## **CHAPTER-4**

***BENZYLATION AND ACYLATION  
OF BENZENE OR OTHER  
AROMATIC COMPOUNDS OVER  
GaCl<sub>3</sub> AND InCl<sub>3</sub> SUPPORTED ON  
COMMERCIAL CLAYS AND Si-  
MCM-41***

## Chapter-4

### 4.1 BENZYLATION OF BENZENE AND SUBSTITUTED BENZENES BY BENZYL CHLORIDE OVER $\text{InCl}_3$ , $\text{GaCl}_3$ , $\text{FeCl}_3$ AND $\text{ZnCl}_2$ SUPPORTED ON CLAYS AND Si-MCM-41.

#### 4.1.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

Heterogeneous solid acid catalysts, such as heteropoly acid salts [1,2], sulfated  $\text{ZrO}_2$  or  $\text{Fe}_2\text{O}_3$  [3,4], Fe/MCM-41 [5], cation exchanged clays [6,7],  $\text{FeCl}_3/\text{Mont. K10}$  [8], clayzic [9,10], acid treated clays [11,12], HY, H-beta and H-ZSM-5 zeolites [13-15] and Ga- or Fe-substituted H-ZSM-5 [16,17] are reported earlier for the benzylation of benzene and other aromatic compounds.

In our earlier studies [16,17], we have observed that a complete or partial substitution of Al in H-ZSM-5 zeolite by Fe or Ga or an impregnation of the zeolite by  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{Ga}_2\text{O}_3$  or  $\text{In}_2\text{O}_3$  makes the zeolite highly active in the benzylation process. The high catalytic activity of these zeolite catalysts is attributed to the presence of non-framework Fe, Zn, Ga or In oxide species, having redox function, in combination with the zeolitic protons. 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  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  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.

#### 4.1.2 RESULTS AND DISCUSSION

##### 4.1.2.1 Comparison of the Supported Metal Chloride Catalysts for Benzene Benzylation

The  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  supported metal chloride catalysts are compared for their performance in the benzene benzylation (at  $80^\circ\text{C}$ ) in Table 4.1.1. Kinetic curves (benzyl chloride conversion vs. time plots) for the benzylation of benzene over the supported metal chloride catalysts at  $80^\circ\text{C}$  are presented in Figure 4.1.1.

From the comparison of results in Table 4.1.1, following important observations can be made:

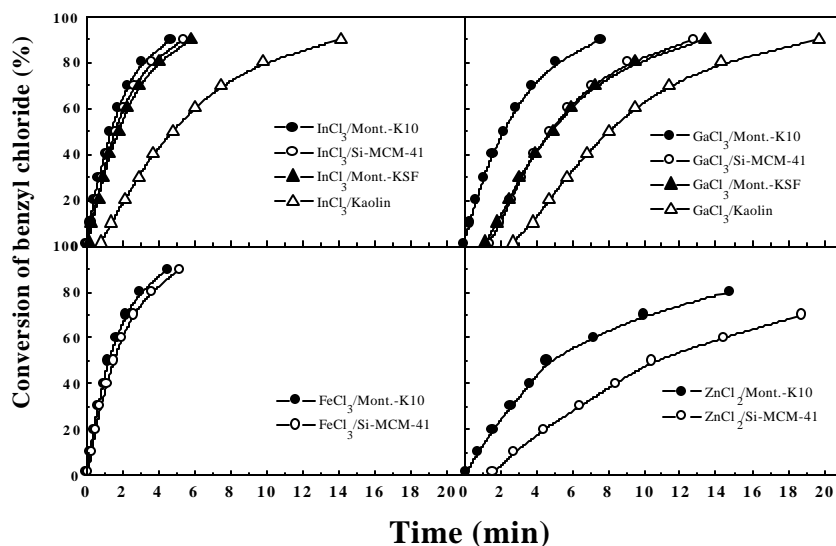
**Table 4.1.1** Comparison of the supported  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  (metal chloride loading =  $1.13 \text{ mmol.g}^{-1}$ ) catalysts for their performance in the benzylation of benzene (at  $80^\circ\text{C}$ ).

Catalyst	Time (min) required for benzyl chloride conversion		Reaction induction period (min)	Apparent reaction rate constant, $k_a \times 10^3 \text{ (min}^{-1}\text{)}$	Selectivity <sup>a</sup>
	50 %	90 %			
$\text{InCl}_3/\text{Mont.-K10}$	1.3	4.7	0.0	523.0	> 98
$\text{InCl}_3/\text{Mont.-KSF}$	1.8	5.8	0.1	418.7	> 98
$\text{InCl}_3/\text{Kaolin}$	4.8	14.1	0.8	180.0	96
$\text{InCl}_3/\text{Si-MCM-41}$	1.6	5.4	0.1	460.6	> 98
$\text{GaCl}_3/\text{Mont.-K10}$	2.2	7.6	0.0	320.0	> 98
$\text{GaCl}_3/\text{Mont.-KSF}$	4.9	13.4	1.2	198.5	> 98
$\text{GaCl}_3/\text{Kaolin}$	8.0	19.7	2.7	143.9	97
$\text{GaCl}_3/\text{Si-MCM-41}$	4.8	12.9	1.4	215.3	> 98
$\text{FeCl}_3/\text{Mont.-K10}$	1.2	4.5	0.0	548.0	91
$\text{FeCl}_3/\text{Si-MCM-41}$	1.5	5.2	0.1	470.0	92
$\text{ZnCl}_2/\text{Mont.-K10}$	4.5	23.1	0.1	126.0	82
$\text{ZnCl}_2/\text{Si-MCM-41}$	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		-	-	-

<sup>a</sup> With respect to diphenyl-methane at complete conversion of benzyl chloride (%).

- The catalyst support itself (Montmorillonite-K10, Montmorillonite-KSF and 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  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  or  $\text{ZnCl}_2$ .

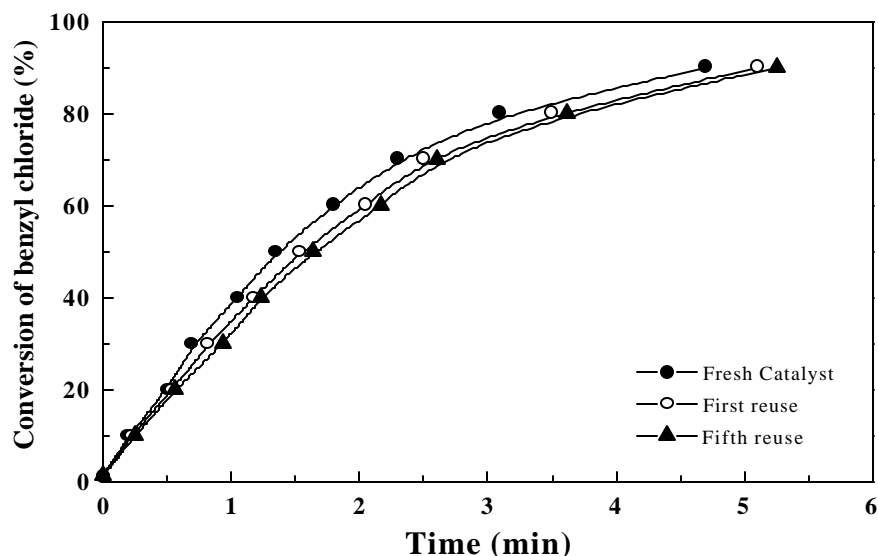




**Figure 4.1.1** Conversion vs. reaction time plots for the benzylation of benzene (at 80°C) over supported  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  catalysts.

- Among the different supported metal chloride catalysts, the supported  $\text{FeCl}_3$  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 [18].
- The benzylation activity of the supported metal chloride catalysts is in the following order: supported  $\text{FeCl}_3$  > supported  $\text{InCl}_3$  > supported  $\text{GaCl}_3$  > supported  $\text{ZnCl}_2$ . It is interesting to note that this order for the benzylation activity is quite similar to that for the redox potential of the metal in the supported metal chloride catalysts [ $E_{\text{Fe}}^0 \text{ } ^{3+}/\text{Fe}^{2+}$  (+ 0.77 V) >  $E_{\text{In}}^0 \text{ } ^{3+}/\text{In}^{1+}$  (- 0.44 V) =  $E_{\text{Ga}}^0 \text{ } ^{3+}/\text{Ga}^{1+}$  (- 0.44 V) >  $E_{\text{Zn}}^0 \text{ } ^{2+}/\text{Zn}$  (- 0.74 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 for the choice for the support is Mont.-K10 > Si-MCM-41 > Mont.-KSF > Kaolin.

- Among the supported metal chloride catalysts, the  $\text{InCl}_3/\text{Mont-K10}$  showed both high activity and high selectivity in the benzylation (Table 4.1.1). This catalyst can also be reused for the benzylation several times (Figure 4.1.2).

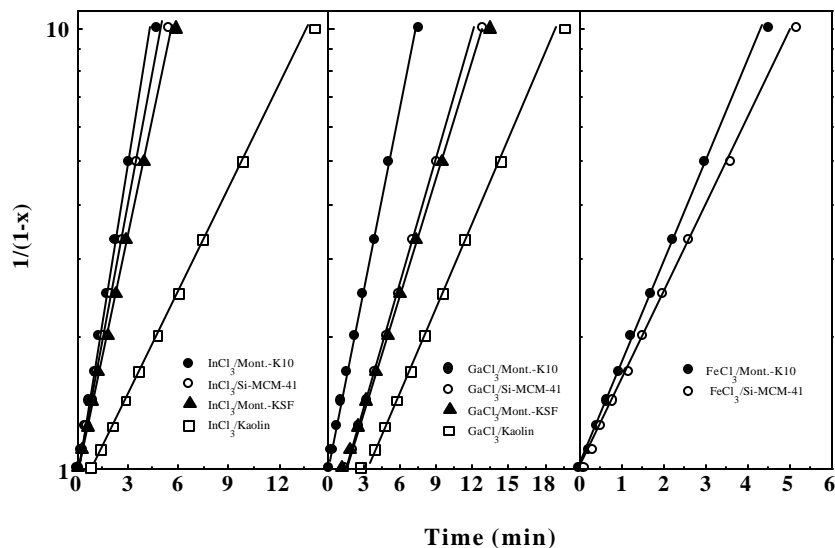


**Figure 4.1.2** Reusability of  $\text{InCl}_3/\text{Mont-K10}$  catalyst in the benzylation of benzene (at  $80^\circ\text{C}$ ).

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:

$$\log [1/(1-x)] = (k_a/2.303) (t-t_0) \quad (4.1.1)$$

where  $x$  is the fractional conversion of benzyl chloride,  $k_a$  is the apparent first order rate constant,  $t$  is the reaction time and  $t_0$  is the reaction induction period. Representative linear  $\log[1/(1-x)]$  against  $(t-t_0)$  plots, according to the above rate law, are given in Figure 4.1.3. 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 4.1.1 and 4.1.2.



**Figure 4.1.3** Representative pseudo-first order plots for the benzylation of benzene over the different supported metal chloride catalysts.

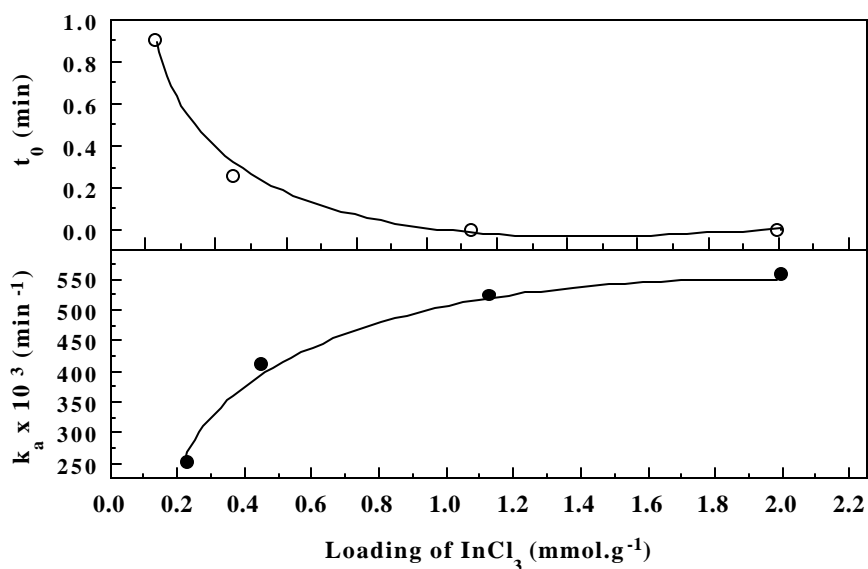
**Table 4.1.2** Kinetic parameters for the benzylation of benzene over different supported metal chloride catalysts.

Catalyst	Apparent rate constant, $k$ $\times 10^3$ ( $\text{min}^{-1}$ )			Activation energy, $E$ ( $\text{kcal.mol}^{-1}$ )	Frequency factor, $A$ ( $\text{min}^{-1}$ )
	$80^\circ\text{C}$	$70^\circ\text{C}$	$60^\circ\text{C}$		
InCl <sub>3</sub> /Mont.-K10	523.0	274.0	152.0	14.52	$4.16 \times 10^{11}$
InCl <sub>3</sub> /Mont.-KSF	418.7	224.9	115.0	15.10	$7.7 \times 10^{11}$
InCl <sub>3</sub> /Kaoline	180.0	85.0	45.2	16.2	$1.58 \times 10^{12}$
InCl <sub>3</sub> /Si-MCM-41	460.6	225.0	123.8	15.4	$1.32 \times 10^{12}$
GaCl <sub>3</sub> /Mont.-K10	320.0	171.0	89.0	15.05	$5.62 \times 10^{11}$
GaCl <sub>3</sub> /Si-MCM-41	215.3	111.0	54.7	16.1	$1.7 \times 10^{12}$
FeCl <sub>3</sub> /Mont.-K10	548.0	289.2	203.8	11.62	$7.2 \times 10^9$
FeCl <sub>3</sub> /Si-MCM-41	470.0	287.1	139.5	14.28	$2.89 \times 10^{11}$
ZnCl <sub>2</sub> /Mont.-K10	126.0	59.2	30.1	16.8	$2.6 \times 10^{12}$
ZnCl <sub>2</sub> /Si-MCM-41	72.0	31.8	14.7	18.7	$2.05 \times 10^{13}$

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 4.1.2. Among the supported metal chloride catalysts, the  $\text{FeCl}_3/\text{Mont.-K10}$  has the lowest activation energy but also the lowest frequency factor. Whereas, the  $\text{ZnCl}_2/\text{Si-MCM-41}$  has the highest activation energy but also the highest frequency factor.

#### 4.1.2.2 Effect of Metal Chloride Loading

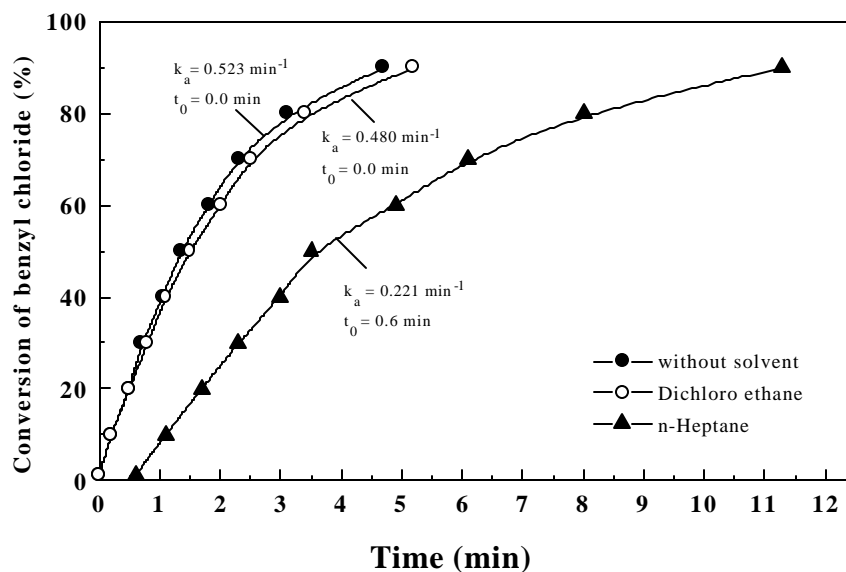
Figure 4.1.4 shows the influence of metal chloride loading on the reaction rate constant and induction period in the benzylation of benzene over the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst. The induction period is decreased and the rate constant is increased with increasing the metal chloride loading on Mont.-K10 support. At the lower metal chloride loading (below  $1.1 \text{ mmol.g}^{-1}$ ), 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.



**Figure 4.1.4** Effect of  $\text{InCl}_3$  loading in the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst on the conversion of benzyl chloride (at  $80^\circ\text{C}$ ) in the benzylation of benzene.

#### 4.1.2.3 Effect of Solvent

Results showing the effect of solvent on the rate of benzylation of benzene over  $\text{InCl}_3/\text{Mont.-K10}$  are presented in Figure 4.1.5. 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



**Figure 4.1.5** Effect of solvent on the conversion of benzyl chloride (at  $80^{\circ}\text{C}$ ) in the benzylation of benzene over  $\text{InCl}_3/\text{Mont.-K10}$ .

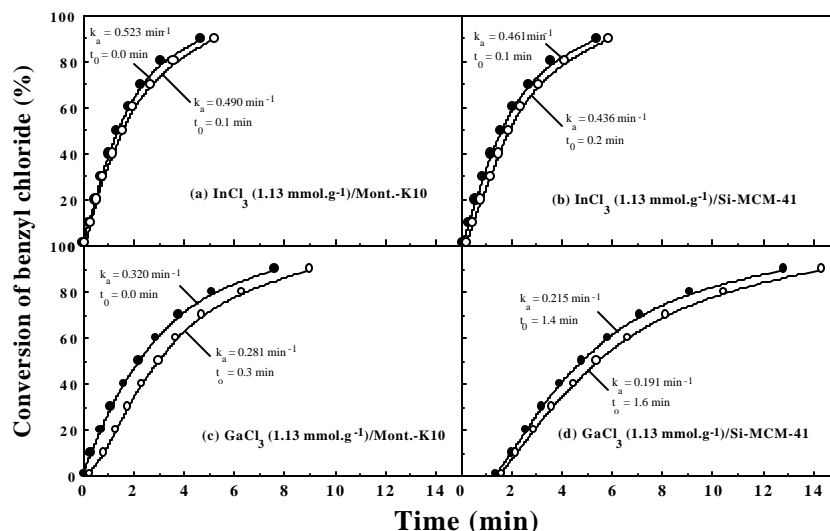
dichloroethane as a solvent. The reaction induction period is increased when n-heptane was used as a solvent. The observed solvent effect on the reaction rate is expected because of the competitive adsorption of both the reactants and the solvent on the catalyst. The results show that among the two solvents, dichloroethane is a better solvent for the benzylation reaction.

#### 4.1.2.4 Effect of Moisture

In order to study the effect of moisture present in the reaction mixture, benzene saturated with water at room temperature was used for the benzylation of benzene. Results showing the effect of moisture present in the reaction mixture on the benzene

benzylation over the  $\text{InCl}_3$  (or  $\text{GaCl}_3$ )/Mont.-K10 (or Si-MCM-41) are presented in Figure 4.1.6.

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. These catalysts do not demand stringent moisture-free conditions for them to



**Figure 4.1.6** Effect of moisture in the reaction mixture on the conversion of benzyl chloride (at  $80^{\circ}\text{C}$ ) in the benzylation of benzene over  $\text{InCl}_3$  (or  $\text{GaCl}_3$ )/Mont.-K10 (or Si-MCM-41) catalyst.

be highly active/selective in the benzylation process.

#### 4.1.2.5 Effect of Electron Donating Substituent Group(s)

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  $80^{\circ}\text{C}$ ) over the  $\text{InCl}_3$ /Mont.-K10 catalyst are presented in Figure 4.1.7. The first order rate constants ( $k_a$ ) and induction period for the benzylation reactions are as follows:

Substrate	:	Benzene	Toluene	Mesitylene	Anisole
$k_a$ ( $\text{min}^{-1}$ )	:	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. Hence, the order for the rate of benzylation for the aromatic compound is expected as follows: Anisole > Mesitylene >

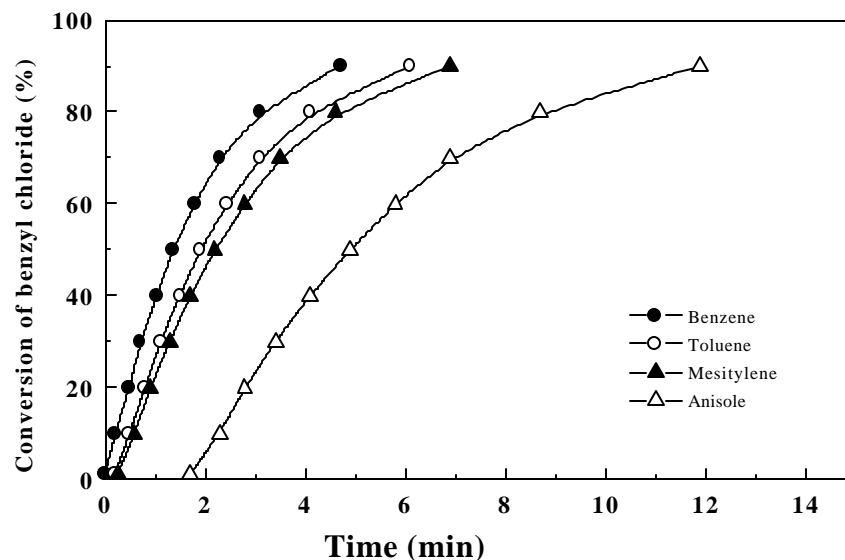


Figure 4.1.7 Effect of substituents present in the benzene ring on the conversion of benzyl chloride (at 80°C) in the benzylation over  $InCl_3/Mont.-K10$ .

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 >

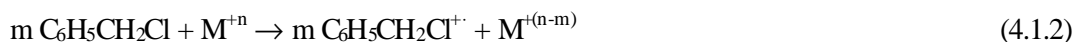
methyl benzene > tri-methyl benzene > methoxy benzene. This indicates that, for this catalyst, the reaction mechanism is different from that for the classical acid catalyzed benzylation reactions.

#### 4.1.2.6 Reaction Mechanism

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

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

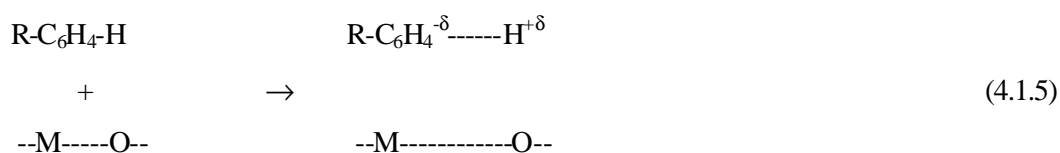
#### Activation of benzyl chloride



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



#### Activation of aromatic compound



#### Reaction between benzyl carbocation and activated aromatic compound



The above redox mechanism is similar to that proposed earlier for the alkylation reactions [6,17]. This mechanism is quite consistent with the observations; the order for the benzene benzylation activity of the  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  supported catalysts is almost same as that for the redox potential of metal in the corresponding supported metal chloride catalyst (section 4.1.2.1).

### 4.1.3 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  $\text{FeCl}_3$  > supported  $\text{InCl}_3$  > supported  $\text{GaCl}_3$  > supported  $\text{ZnCl}_2$ .
2. Among the different supports employed, Mont.-K10 is found to be the best support for all the supported metal chloride catalysts.
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  $\text{InCl}_3$  or  $\text{GaCl}_3$  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<sub>3</sub>/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<sub>3</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub> and ZnCl<sub>2</sub> catalysts is found to be same as that for the redox potential of the metal present in the corresponding supported metal chloride catalyst, indicating the operation of redox mechanism in the benzylation process.

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## 4.2 ACYLATION OF BENZENE OVER CLAY AND MESOPOROUS Si-MCM-41 SUPPORTED $\text{InCl}_3$ , $\text{GaCl}_3$ AND $\text{ZnCl}_2$ CATALYSTS.

### 4.2.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

A number of solid acid catalysts, such as: heteropoly acids [1-5], modified  $\text{ZrO}_2$  [6-7], H-beta and Ga-, Fe- or In substituted H-beta [8-10], H-ZSM-5, H-mordenite, HY and H-RE-Y [11-14], Montmorillonite K10 or KSF clay [15] and EPZG [16] for the acylation of benzene [8,16] and other aromatic compounds [1-7,9-15] by different acyl chlorides. In this investigation, we have observed the high activity of Mont.-K10 and Si-MCM-41 supported  $\text{InCl}_3$  and  $\text{GaCl}_3$  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  $\text{InCl}_3$ ,  $\text{GaCl}_3$  and  $\text{ZnCl}_2$  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.

### 4.2.2 RESULTS AND DISCUSSION

Results on the  $\text{InCl}_3$ ,  $\text{GaCl}_3$  and  $\text{ZnCl}_2$  catalysts supported on Si-MCM-41 and different clays on their performance in the acylation of benzene by benzoyl chloride (at  $80^\circ\text{C}$ ) are presented in Table 4.2.1. Kinetic curves (benzoyl chloride conversion vs. time plots) for the benzylation of benzene over the supported metal chloride catalysts (at  $80^\circ\text{C}$ ) are presented in Figure 4.2.1.

From the comparison of results in Table 4.2.1, 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 benzylation of benzene. However, its catalytic activity is increased drastically after its impregnation with  $\text{InCl}_3$ ,  $\text{GaCl}_3$  or  $\text{ZnCl}_2$ .
- Among the metal chloride catalysts deposited on the same support, the supported  $\text{InCl}_3$  catalyst showed highest activity. The acylation activity of the catalysts is in the following order: supported  $\text{InCl}_3$  > supported  $\text{GaCl}_3$  >> supported  $\text{ZnCl}_2$ .
- 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 >> Kaolin.

**Table 4.2.1** Results on the acylation of benzene by benzoyl chloride (at 80°C) over the supported InCl<sub>3</sub>, GaCl<sub>3</sub> and ZnCl<sub>2</sub> (metal chloride loading = 20%) catalysts.

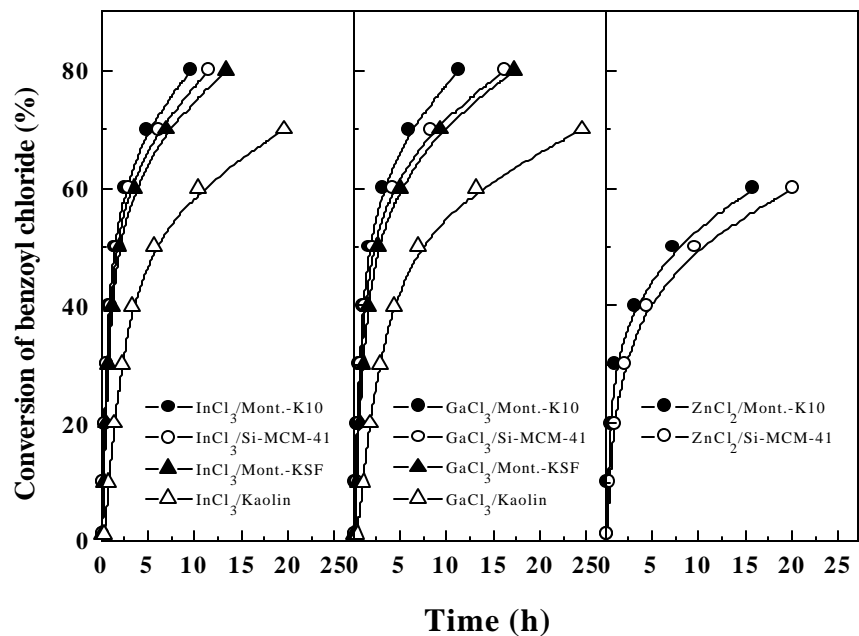
Supported catalysts	Reaction induction period, $t_0$ (min)	Time required for half the reaction <sup>b</sup> , $t_{1/2}$ (h)	TON (h <sup>-1</sup> ) for half the reaction
InCl <sub>3</sub> /Mont.-K10	4.5	1.4	8.5
InCl <sub>3</sub> /Mont.-KSF	5.4	2.0	6.0
InCl <sub>3</sub> /Kaolin	7.7	7.9	1.5
InCl <sub>3</sub> /Si-MCM-41	4.9	1.6	7.4
GaCl <sub>3</sub> /Mont.-K10	5.6	1.7	5.5
GaCl <sub>3</sub> /Mont.-KSF	6.8	2.6	3.6
GaCl <sub>3</sub> /Kaolin	8.5	10.4	0.9
GaCl <sub>3</sub> /Si-MCM-41	5.9	1.9	5.0
ZnCl <sub>2</sub> /Mont.-K10	7.0	7.3	1.0
ZnCl <sub>2</sub> /Si-MCM-41	7.8	8.4	0.9
Catalyst support <sup>a</sup>	No reaction for 2 h		-

<sup>a</sup> *Mont.-K10, Mont.-KSF, Kaolin or Si-MCM-41.*

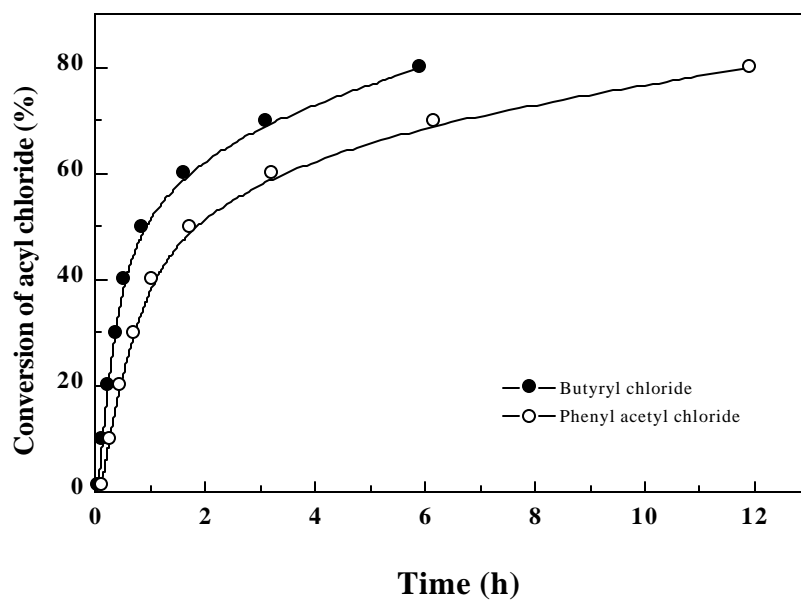
<sup>b</sup> *50% conversion of the acylating agent.*

Results showing high activity of the InCl<sub>3</sub>/Mont.-K10 catalyst in the acylation of benzene by other acyl chlorides (viz. butyryl chloride and phenyl acetyl chloride) at 80°C are presented in Figure 4.2.2. 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).

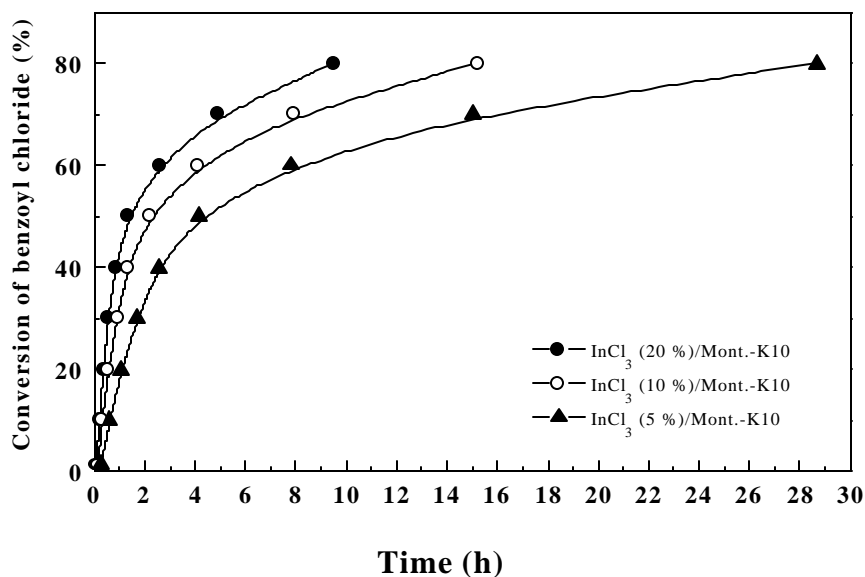
The influence of metal chloride loading on the conversion of benzoyl chloride in the acylation of benzene over the InCl<sub>3</sub>/Mont.-K10 catalyst is shown in Figure 4.2.3. The time required for half the acylation reaction ( $t_{1/2}$ ) and the reaction induction period ( $t_0$ ) are decreased markedly 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).



**Figure 4.2.1** Conversion vs. reaction time plots for the acylation of benzene by benzoyl chloride (at 80<sup>0</sup>C) over supported InCl<sub>3</sub>, GaCl<sub>3</sub> and ZnCl<sub>2</sub> (metal chloride loading = 20%) catalysts.



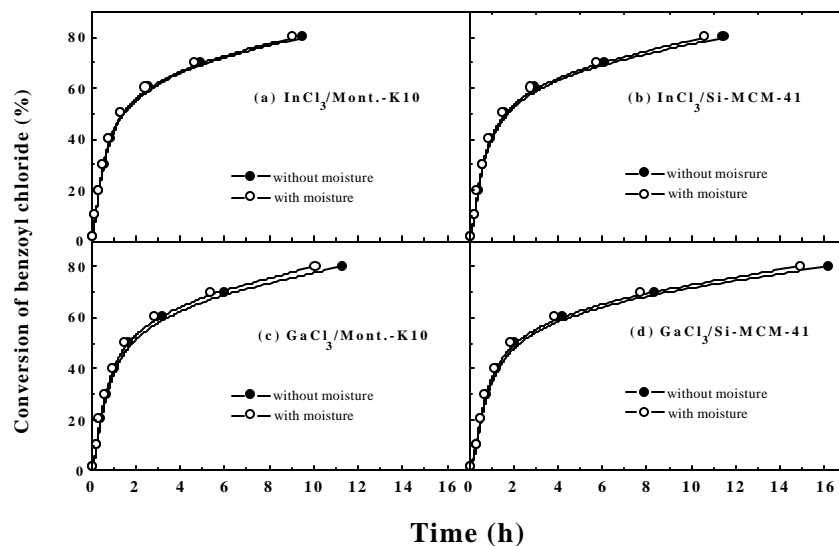
**Figure 4.2.2** Conversion vs. reaction time plots for the acylation of benzene by butyryl chloride and phenyl acetyl chloride (at 80<sup>0</sup>C) over InCl<sub>3</sub> (20%)/Mont.-K10 catalyst.



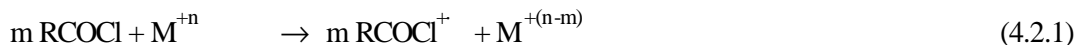
**Figure 4.2.3** Effect of metal chloride loading in the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst on the conversion of benzoyl chloride in the acylation of benzene (at  $80^\circ\text{C}$ ).

Results showing the effect of moisture present in the reaction mixture on the acylation of benzene by benzoyl chloride over the  $\text{InCl}_3$  (or  $\text{GaCl}_3$ )/Mont.-K10 (or Si-MCM-41) catalyst are presented in Figure 4.2.4. The acylation activity of the supported  $\text{InCl}_3$  and  $\text{GaCl}_3$  catalysts is increased slightly due to the presence of moisture in the reaction mixture. The observed high acylation activity of the supported  $\text{InCl}_3$  or  $\text{GaCl}_3$  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.

The metal chloride species present in the catalysts have redox properties, which are expected to play 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 ( $\text{InCl}_3 > \text{GaCl}_3 \gg \text{ZnCl}_2$ ) is quite similar to that for the redox potential of the metal in the catalysts [ $E_{\text{In}^{3+}/\text{In}^{1+}}^0$  or  $E_{\text{Ga}^{3+}/\text{Ga}^{1+}}^0$  (- 0.44 V)  $>$   $E_{\text{Zn}^{2+}/\text{Zn}}^0$  (- 0.74 V) and  $E_{\text{In}^{3+}/\text{In}}^0$  (- 0.34 V)  $>$   $E_{\text{Ga}^{3+}/\text{Ga}}^0$  (- 0.53 V)  $>$   $E_{\text{Zn}^{2+}/\text{Zn}}^0$  (- 0.74 V)]. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal chlorides. A following probable redox mechanism for the acylation reaction over the catalyst is proposed.



**Figure 4.2.4** Effect of moisture in the reaction mixture on the conversion of benzoyl chloride in the acylation of benzene over  $\text{InCl}_3$  or  $\text{GaCl}_3$  (20%)/Mont.-K10 or Si-MCM-41 catalyst (at  $80^\circ\text{C}$ ).



[where  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{CH}_2$  or  $\text{C}_3\text{H}_7$ ,  $\text{M} = \text{In}$ ,  $\text{Ga}$  or  $\text{Zn}$ ,  $n = 3$  (for  $\text{In}$  and  $\text{Ga}$ ) or  $2$  (for  $\text{Zn}$ ) and  $m = 2$  (for  $\text{In}$  and  $\text{Ga}$ ) and  $1$  (for  $\text{Zn}$ )]



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

In summary, the Mont.-K10 and Si-MCM-41 supported  $\text{InCl}_3$  and  $\text{GaCl}_3$  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  $\text{InCl}_3$ /Mont.-K10 shows best performance in the benzene acylation.

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## **CHAPTER-5**

### **BENZYLATION AND BENZOYLATION OF BENZENE AND OTHER AROMATIC COMPOUNDS OVER SUPPORTED $Ga_2O_3$ AND $In_2O_3$ CATALYSTS IN THE PRESENCE OR ABSENCE OF MOISTURE**

## Chapter-5

### 5.1 BENZYLATION OF BENZENE AND OTHER AROMATIC COMPOUNDS BY BENZYL CHLORIDE OVER Si-MCM-41 SUPPORTED Ga<sub>2</sub>O<sub>3</sub> AND In<sub>2</sub>O<sub>3</sub> CATALYSTS.

#### 5.1.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

A number of highly acidic solid acid catalysts, such as heteropolyacids [1-3], sulfated ZrO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> [4], Nafion-H [2], and Fe- or Ga-substituted H-ZSM-5 [5] for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites [6] for benzylation of toluene, are reported earlier.

It is interesting to note that, in spite of their high acidity, the H-ZSM-5, HY and H-beta zeolites and sulfated ZrO<sub>2</sub> show very low activity, even for the benzylation [4,6] of toluene. In the present study, we have, here shown that Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts supported on mesoporous Si-MCM-41, which are amphoteric and basic [7], respectively, in nature, are very active in the benzylation (by benzyl chloride) of benzene and other aromatic compounds, even in the presence of moisture, and also are reusable for the reactions. When supported on other non-acidic micro- and macro-porous supports, these catalysts also show high benzylation activity.

#### 5.1.2 RESULTS AND DISCUSSION

The supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts were characterized for their surface area and strong acid sites (measured in terms of the pyridine chemisorbed on them at 400°C). The catalysts characterization data are presented in Table 5.1.1.

Results of the benzylation of benzene over the different Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts are presented in Table 5.1.2.

From the results in Tables 5.1.1 and 5.1.2, following important observations could be made:

- Both the Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts supported on mesoporous Si-MCM-41 have very high benzene benzylation activity, the supported In<sub>2</sub>O<sub>3</sub> is, however, more active.
- The activity of In<sub>2</sub>O<sub>3</sub> is increased markedly by supporting it on the different supports, most probably due to its dispersion on the supports, causing an increase in its surface area.

**Table 5.1.1** Physico-chemical properties of the supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts.

Catalysts	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore type (micro, meso or macro)	Pyridine chemisorbed at 400 <sup>0</sup> C (mmol.g <sup>-1</sup> )
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	3	macro	0.0
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (HS)	255	meso	0.10
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica (LS)	3.7	macro	0.0
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica gel	330	Micro/meso	0.0
Ga <sub>2</sub> O <sub>3</sub> (5 %)/Si-MCM-41	1125	meso	0.0
Ga <sub>2</sub> O <sub>3</sub> (10 %)/Si-MCM-41	1012	meso	0.0
Ga <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	994	meso	0.0
Ga <sub>2</sub> O <sub>3</sub> (5 %)/silicalite-I	291	micro	0.0
Ga <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	286	micro	0.18
Ga <sub>2</sub> O <sub>3</sub> (10 %)/γ-alumina	188	meso	0.03
Ga <sub>2</sub> O <sub>3</sub> (10 %)/ZrO <sub>2</sub> (LS)	5.3	macro	0.0
In <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	3.1	macro	0.0
In <sub>2</sub> O <sub>3</sub> (10 %)/ZrO <sub>2</sub> (LS)	3.9	macro	0.0
In <sub>2</sub> O <sub>3</sub> (10 %)/Si-MCM-41	861	meso	0.0
In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	846	meso	0.0
In <sub>2</sub> O <sub>3</sub> (20 %)/Al.Si-MCM-41	723	meso	0.05
In <sub>2</sub> O <sub>3</sub> (without support)	6.1	-	0.0

**Table 5.1.2** Results of the benzylation of benzene over supported micro-, meso- and macroporous Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts at 80°C (reaction conditions: reaction mixture = 13 ml benzene and 1 ml benzyl chloride, amount of catalyst = 0.1 g).

Catalysts	Reaction induction period <sup>a</sup> (min)	Time for 50 % and 90 % conversion of benzyl chloride		Apparent reaction rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )
		50 %	90 %	
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	0.4	4.7	15.2	165.7
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS) <sup>b</sup>	10.7	14.6	22.0	207.0
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (HS)	8.0	81.0	230.0	107.1
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica (LS)	0.5	16.0	48.0	49.5
Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica gel	0.8	11.0	33.8	72.9
Ga <sub>2</sub> O <sub>3</sub> (5 %)/Si-MCM-41	1.4	12.0	34.0	74.9
Ga <sub>2</sub> O <sub>3</sub> (10 %)/Si-MCM-41	0.9	5.3	16.0	155.6
Ga <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	0.2	2.5	7.8	311.2
Ga <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41 <sup>b</sup>	5.1	7.4	12.5	324.4
Ga <sub>2</sub> O <sub>3</sub> (5 %)/silicalite-I	0.5	6.0	18.5	135.6
Ga <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	0.6	6.2	18.8	133.5
Ga <sub>2</sub> O <sub>3</sub> (10 %)/ $\gamma$ -alumina	75.0	306	-	-
Ga <sub>2</sub> O <sub>3</sub> (10 %)/ZrO <sub>2</sub> (LS)	0.5	5.4	18.0	142.4
In <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	0.3	4.1	12.1	198.5
In <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS) <sup>b</sup>	5.4	8.6	15.5	229.5
In <sub>2</sub> O <sub>3</sub> (10 %)/ZrO <sub>2</sub> (LS)	0.9	7.3	22.8	108.1
In <sub>2</sub> O <sub>3</sub> (10 %)/Si-MCM-41	0.8	4.9	13.1	193.5
In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	0.2	2.4	7.5	329.0
In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41 <sup>b</sup>	4.3	6.4	11.3	338.5
In <sub>2</sub> O <sub>3</sub> (20 %)/Al.Si-MCM-41	0.6	3.3	8.9	287.8
In <sub>2</sub> O <sub>3</sub> (without support)	3.5	12.8	29.0	92.1

<sup>a</sup> Obtained from the intercept on the time axis of the benzyl chloride conversion vs. time plot extrapolated to zero conversion.

<sup>b</sup> Moist catalyst and benzene saturated with water (at room temperature) used for the reaction.

- The benzylation activity of the  $\text{Ga}_2\text{O}_3$  (which is amphoteric in nature) and  $\text{In}_2\text{O}_3$  (which is basic in nature) [7] supported on non-acidic supports, such as Si-MCM-41, silica-alumina (LS), silicalite-I and silica gel is comparable or even much higher in some cases than that of the  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  supported on acidic supports, such as H-AlSi-MCM-41, silica-alumina (HS), H-ZSM-5 and  $\gamma$ -alumina, respectively. This indicates that acidity does not play significant role in the reaction over these catalysts. However, supported  $\text{Al}_2\text{O}_3$  (which is amphoteric) and  $\text{B}_2\text{O}_3$  (which is acidic) catalysts showed little activity (< 5 % conversion of benzyl chloride in 2h) in the benzylation reaction.
- The  $\text{Ga}_2\text{O}_3$  (or  $\text{In}_2\text{O}_3$ ) (20 %) / Si-MCM-41 and  $\text{Ga}_2\text{O}_3$  (or  $\text{In}_2\text{O}_3$ ) (10 %) / silica-alumina (LS) catalysts show high benzylation activity even in the presence of moisture in the reaction mixture (i.e. when the catalyst was saturated with water vapors at room temperature and the substrate, benzene, was also saturated with water). However, because of the presence of moisture, the reaction induction period is increased very markedly.

Among the supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts, the  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  shows best performance in the benzylation reaction. This catalyst could also be reused repeatedly for the reaction. When the  $\text{In}_2\text{O}_3$  (20 %)/Si-MCM-41 was reused five times for the benzylation of benzene, in the fifth reuse of the catalyst, the time required for the 50 % conversion of benzyl chloride was 2.8 min, which is very close to that (2.5 min) observed for the fresh catalyst. The  $\text{Ga}_2\text{O}_3$  catalyst supported on silica-alumina (HS) and  $\gamma$ -alumina shows poor activity, indicating strong metal oxide – support interactions causing catalyst deactivation.

The  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts supported on macroporous low surface area silica-alumina, and mesoporous Si-MCM-41 also show high activity in the benzylation of other aromatic compounds (Table 5.1.3). However, unlike the acidic catalysts, the benzene benzylation activity of these catalysts is comparable to that or even higher than that observed for the benzylation of substituted benzenes having electron donating methyl groups (Tables 5.1.2 and 5.1.3).

The benzylation activity of the present Si-MCM-41 supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts are compared with that of the highly acidic catalysts, reported earlier [2,4-6], in Table 5.1.4. The  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  is basic in nature. The  $\text{Ga}_2\text{O}_3/\text{Si-MCM-41}$  is poorly acidic in nature, unlike zeolites, it does not contain strong acid sites that can chemisorb

pyridine at 400°C or even at 300°C. The comparison shows that the present catalysts are much more active than the highly acidic catalysts reported earlier. Moreover, since the Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts are supported on meso- and macro-porous supports, these can be used for the reaction with large size aromatic compounds. Also, because of their poorly acidic or basic nature, these catalysts can be used for the reactions with acid sensitive organic compounds.

**Table 5.1.3** Results of the benzylation of different aromatic compounds over supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts at 80°C (reaction conditions: reaction mixture = 13 ml aromatic compound and 1 ml benzyl chloride, amount of catalyst = 0.1 g).

Aromatic compound	Catalyst	Reaction induction period (min)	Time (min) required for benzyl chloride conversion		Apparent reaction rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )
			50 %	90 %	
Toluene	Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	0.5	4.3	12.7	193.5
p-Xylene	Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	1.8	5.9	15.0	184.2
Mesitylene	Ga <sub>2</sub> O <sub>3</sub> (10 %)/silica-alumina (LS)	1.0	6.4	18.0	143.0
Toluene	Ga <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	0.2	3.2	8.9	284.3
p-Xylene	Ga <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	1.0	3.7	10.0	264.7
Mesitylene	In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	0.9	3.8	9.8	270.9
Durene <sup>a</sup>	In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	0.7	4.6	13.0	201.2
2-methyl naphthalene <sup>a</sup>	In <sub>2</sub> O <sub>3</sub> (20 %)/Si-MCM-41	1.0	5.0	14.2	178.5

<sup>a</sup> Reaction mixture = 1.5 g durene or 2-methyl naphthalene + 13 cm<sup>3</sup> dichloroethane + 1 cm<sup>3</sup> benzyl chloride.

In case of the benzylation reaction over the supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts, the presence of moisture causes only an increase in the reaction induction period but, after the induction period, the reaction proceeds with almost a same rate ( or even with a faster rate) (Table 5.1.2). The observed high activity of the supported Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> catalysts, even in the presence of moisture in the reaction mixture, and moreover the

beneficial rate enhancement effect of moisture on the benzylation reaction is of great practical importance.

**Table 5.1.4** Comparison of the earlier highly acidic solid catalysts with the present ones for their benzylation activity.

Aromatic substrate	Catalyst	Catalyst/ C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl wt. ratio	Tempe- rature ( <sup>o</sup> C)	Conversion of benzyl chloride and reaction time		Ref.
				Conversion (%)	Time (min)	
Benzene	Sulfated ZrO <sub>2</sub>	0.1	80	50	135	4
Benzene	Sulfated ZrO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub>	0.1	80	50	33	4
Benzene	Heteropolyacids	0.05	80	100	120	2
Benzene	Nafion-H	0.1	80	24	120	2
Benzene	H-AlMFI	0.1	80	No reaction for 2h		5
Benzene	H-FeMFI	0.1	80	90	25	5
Benzene	H-GaMFI	0.1	80	90	82.5	5
Benzene	H-GaAlMFI	0.1	80	90	56.2	5
Benzene	Ga <sub>2</sub> O <sub>3</sub> (20%)/Si-MCM-41	0.1	80	90	7.8	Present
Benzene	In <sub>2</sub> O <sub>3</sub> (20%)/Si-MCM-41	0.1	80	90	7.5	Present
Toluene	HY (ultrastable)	0.1	110	50	42	6
Toluene	H-Beta	0.1	110	50	370	6
Toluene	H-ZSM-5	0.1	110	50	1200	6
Toluene	Ga <sub>2</sub> O <sub>3</sub> (20%)/Si-MCM-41	0.1	80	50	3.2	Present

When the [Ga<sub>2</sub>O<sub>3</sub> (or In<sub>2</sub>O<sub>3</sub>) (20 %) / Si-MCM-41 or Ga<sub>2</sub>O<sub>3</sub> (or In<sub>2</sub>O<sub>3</sub>) (10 %) / silica-alumina (LS)] was refluxed with benzene for 4h in the absence of any benzylating agent, the reaction induction period for the benzylation of benzene (at 80<sup>o</sup>C) was found to be negligibly small (< 0.1 min). This and the results in Tables 5.1.2 show that the induction period for the benzylation reaction is due to the presence of adsorbed moisture on the



catalyst and it is the period required for replacing the adsorbed moisture by the reactant(s) to start the catalytic reaction.

All the above observations indicate that, the acidic properties of the supported metal oxide catalysts do not play significant role for deciding their high benzylation activity,. The metal oxide species present in the catalysts have redox properties, which are expected to play important role in the benzylation over the present catalyst. The benzylation reaction proceeds through redox mechanism similar to that described earlier (Reaction scheme 4.1.2 - 4.1.7).

In summary, the Si-MCM-41 supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  is highly active and reusable solid catalysts for the benzylation of benzene and other aromatic compounds and these catalysts do not demand stringent moisture-free conditions for them to be highly active in the benzylation process. Among the supported metal oxide catalysts,  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  shows best performance in regard to both the catalytic activity and moisture insensitivity in the benzylation reaction.

### 5.1.3 REFERENCES

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## 5.2 BENZOYLATION OF BENZENE AND SUBSTITUTED BENZENES BY BENZOYL CHLORIDE OVER $\text{In}_2\text{O}_3$ (OR $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 CATALYST

### 5.2.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

A number of solid acid catalysts, such as: heteropoly acids [1-5], modified  $\text{ZrO}_2$  [6-7], H-beta and Ga-, Fe- or In substituted H-beta [8-9], H-ZSM-5, H-mordenite, HY and H-RE-Y [10-12], Montmorillonite-K10 or KSF clay [13] and EPZG [14] for the benzylation of benzene [8, 14] and other aromatic compounds [1-7, 9-12, 13] are reported earlier. However, these solid acid catalysts showed quite poor acylation activity.

In the present studies, we have found that  $\text{In}_2\text{O}_3$  (which is basic in nature) and  $\text{Ga}_2\text{O}_3$  (which is amphoteric in nature) supported on the mesoporous Si-MCM-41 showed high activity in the benzylation of aromatic compounds even in the presence of moisture, indicating the important of their redox properties rather than their Lewis acidity in the acylation. A detailed investigation on the benzylation of benzene and other aromatic compounds over supported metal oxide catalysts having redox function, such as  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and ZnO supported on Si-MCM-41 has carried out. Influence of the presence of moisture in the reaction mixture on the benzene benzylation activity of  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 catalyst has also been investigated.

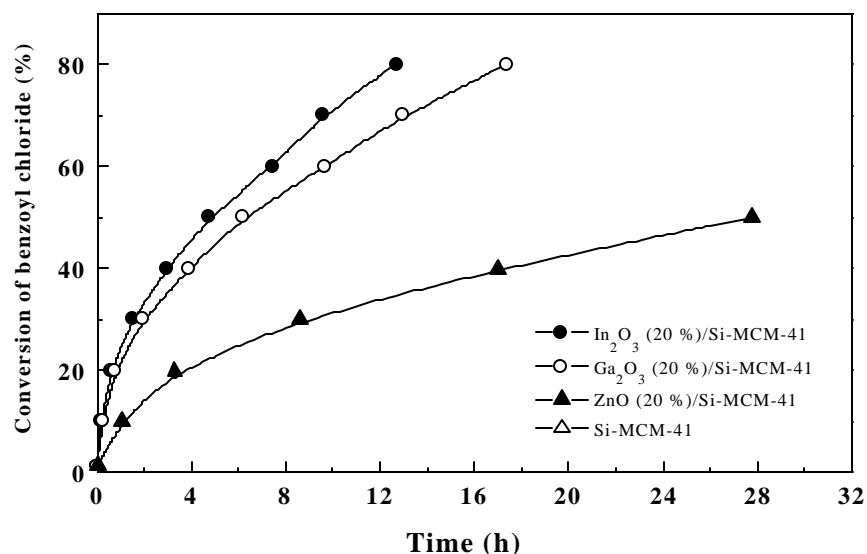
### 5.2.2 RESULTS AND DISCUSSION

#### 5.2.2.1 Comparison of the Supported Metal Oxide Catalysts for Benzene Benzylation

The  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and ZnO catalysts supported on the mesoporous Si-MCM-41 are compared for their performance in the benzene benzylation (at  $80^\circ\text{C}$ ) in Figure 5.2.1.

From the comparison of results in Figure 5.2.1, following important observations can be made:

- The catalyst support (Si-MCM-41) shows no catalytic activity in the benzylation of benzene. However, the Si-MCM-41 supported  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and ZnO catalysts are active in the benzene benzylation.
- Among the different metal oxide supported catalysts, the  $\text{In}_2\text{O}_3$ /Si-MCM-41 showed highest activity and the ZnO/Si-MCM-41 showed the lowest activity in the benzene benzylation.



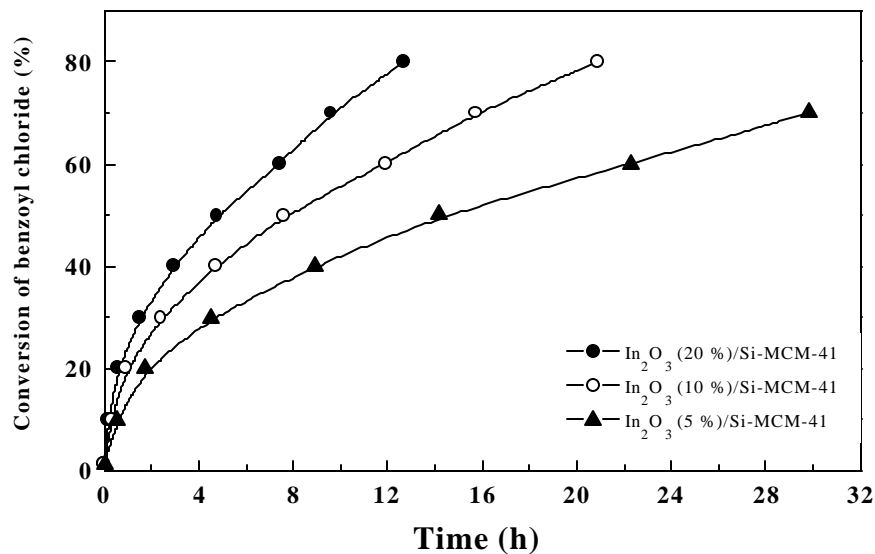
**Figure 5.2.1** Conversion vs. reaction time plots for the benzylation of benzene by benzoyl chloride (at 80<sup>0</sup>C) over supported In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and ZnO catalysts.

It is interesting to note that the benzene benzylation activity of both the In<sub>2</sub>O<sub>3</sub>/Si-MCM-41 and Ga<sub>2</sub>O<sub>3</sub>/Si-MCM-41 is much higher than that reported for the H $\beta$  zeolite catalyst [8]. The time required for half the reaction under similar conditions is 12 h for the H $\beta$  zeolite [8] but 6.2 and 4.8 h for Ga<sub>2</sub>O<sub>3</sub>/Si-MCM-41 and In<sub>2</sub>O<sub>3</sub>/Si-MCM-41, respectively.

In<sub>2</sub>O<sub>3</sub> and ZnO are basic oxides and Ga<sub>2</sub>O<sub>3</sub> is amphoteric in nature and the benzylation activity of the supported metal oxide catalysts is in the following order: In<sub>2</sub>O<sub>3</sub>/Si-MCM-41 > Ga<sub>2</sub>O<sub>3</sub>/Si-MCM-41 > ZnO/Si-MCM-41. This shows that the acidic or basic nature of these catalysts does not play significant role for deciding their benzylation activity. However, the redox properties of these catalysts are important in deciding their catalytic activity, as discussed later.

#### 5.2.2.2 Effect of Metal Oxide Loading

The influence of metal oxide loading on the conversion of benzoyl chloride in the benzylation of benzene over the In<sub>2</sub>O<sub>3</sub>/Si-MCM-41 catalyst is shown in Figure 5.2.2. The time required for half the benzylation reaction ( $t_{1/2}$ ) is decreased markedly with increasing the metal oxide loading on the Si-MCM-41 support, for the In<sub>2</sub>O<sub>3</sub> loading of 5, 10 and 20%, the observed value of  $t_{1/2}$  is 14.2, 7.6 and 4.8 h, respectively. The increase in the catalytic activity with increasing the In<sub>2</sub>O<sub>3</sub> loading is almost linear.

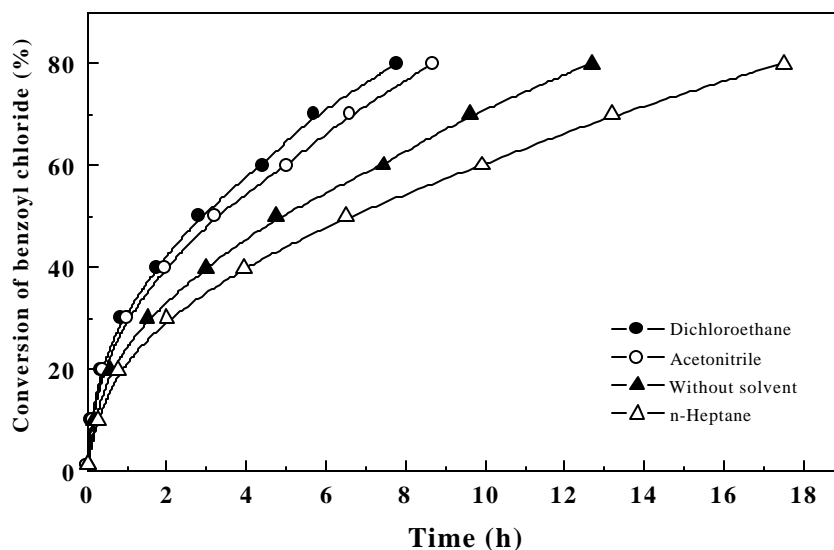


**Figure 5.2.2** Effect of metal oxide loading in the  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  catalyst on its activity in the conversion of benzoyl chloride in the benzylation of benzene (at  $80^\circ\text{C}$ ).

### 5.2.2.3 Effect of Solvent

Results showing the effect of solvent on the rate of benzylation of benzene over  $\text{In}_2\text{O}_3/\text{Si-MCM-41}$  are presented in Figure 5.2.3. The time required for half the benzene benzylation reaction with the different solvents is in the following order: dichloroethane (2.8 h) < acetonitrile (3.2 h) < n-heptane (6.5 h). Results indicate that the benzylation activity of the catalyst is higher when polar solvent (e.g. acetonitrile or dichloroethane) is used but it is relatively lower when non-polar solvent (e.g. n-heptane) is used. Among the polar solvents, dichloroethane is a better solvent for the benzylation reaction.

It is interesting to note that the half reaction period when the polar solvents (dichloroethane and acetonitrile) are used in the benzene benzylation is appreciably lower than that ( $t_{1/2} = 4.8$  h) when no solvent is used. Thus the catalyst is more active in the reaction in presence of the polar solvent. This is consistent with that observed earlier. It is believed that the benzoyl carbo-cations (formed from benzoyl chloride) are stabilized in the presence of polar solvent.

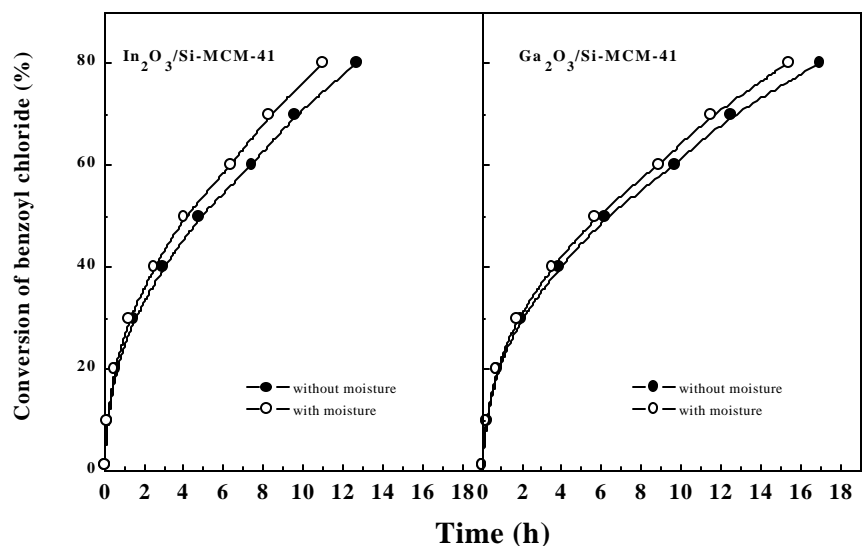


**Figure 5.2.3** Effect of solvent on the conversion of benzoyl chloride in the benzylation of benzene over  $\text{In}_2\text{O}_3$  (20 %)/Si-MCM-41 catalyst (at  $80^\circ\text{C}$ ).

#### 5.2.2.4 Effect of Moisture on the Catalytic Activity

Results showing the effect of moisture present in the reaction mixture (i.e. using the benzene saturated with water, 0.37 mol % water in benzene) on the benzylation of benzene over the  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 catalyst are presented in Figure 5.2.4.

The benzylation activity of both the supported  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  catalysts is increased significantly due to the presence of moisture in the reaction mixture. The observed high benzylation activity of the supported  $\text{In}_2\text{O}_3$  or  $\text{Ga}_2\text{O}_3$  catalyst even in the presence of moisture in the reaction mixture is of great practical importance. The results reveal that these catalysts do not demand stringent moisture-free conditions for them to be highly active in the benzylation process. The results also indicate that the Lewis acid sites (which are deactivated by water) of the catalysts do not play a significant role in the benzylation reaction.



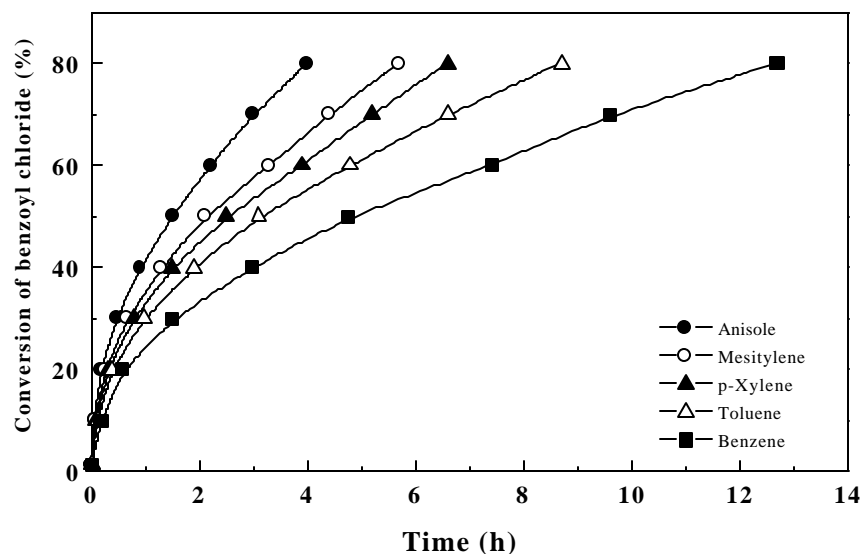
**Figure 5.2.4** Effect of moisture in the reaction mixture on the conversion of benzoyl chloride in the benzylation of benzene over In<sub>2</sub>O<sub>3</sub> or Ga<sub>2</sub>O<sub>3</sub> (20 %)/Si-MCM-41 catalyst (at 80<sup>0</sup>C).

#### 5.2.2.5 Effect of Electron Donating Substituent Group(s)

Results showing high activity of the In<sub>2</sub>O<sub>3</sub>/Si-MCM-41 catalyst in the benzylation of benzene and substituted benzenes by benzoyl chloride at 80<sup>0</sup>C are presented in Figure 5.2.5. The yields of the isolated products of the benzylation of the different aromatic compounds are as follows:

- Benzophenone (from benzene in 13.1 h) : 74.2 %
- 4-Methyl benzophenone (from toluene in 10.2 h) : 79.6 %
- 2,5-di-Methyl benzophenone (from p-xylene in 7.3 h) : 74.3 %
- 2,4,6-tri-Methyl benzophenone (from mesitylene in 7.1 h) : 81.4 %
- 4-Methoxy benzophenone (from anisole in 6.1 h) : 89.7 %

The above products have been characterized by NMR. The time required for half the benzoyl chloride conversion for the benzylation of benzene and substituted benzenes is in the following order: benzene (4.8 h) > toluene (3.1 h) > p-xylene (2.5 h) > mesitylene (2.1 h) > anisole (1.5 h). The results indicate that the benzylation activity of the catalyst is increased due to the presence of electron donating groups, such as methyl and methoxy groups, in the aromatic substrate. This is consistent with that observed in the earlier studies.



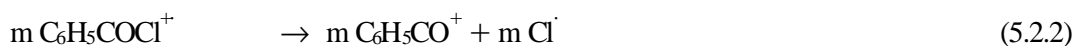
**Figure 5.2.5** Conversion vs. reaction time plots for the benzylation of benzene and substituted benzenes by benzoyl chloride (at 80°C) over In<sub>2</sub>O<sub>3</sub> (20 %)/Si-MCM-41 catalyst.

### 5.2.2.6 Reaction Mechanism

As discussed earlier, the acidic or basic properties of the supported metal oxides do not play significant role for deciding their benzylation activity. However, the metal oxide species present in the catalysts have redox properties, which are expected to play important role in the benzylation reaction over the present catalysts. It is also interesting to note that the order for the benzylation activity of the supported metal oxide catalysts is quite similar to that for the redox potential of the metal in the catalysts [ $E_{\text{In}^{3+}/\text{In}^{1+}}^0$  (- 0.44 V) =  $E_{\text{Ga}^{3+}/\text{Ga}^{1+}}^0$  (- 0.44 V) >  $E_{\text{Zn}^{2+}/\text{Zn}}^0$  (- 0.74 V) and  $E_{\text{In}^{3+}/\text{In}}^0$  (- 0.34 V) >  $E_{\text{Ga}^{3+}/\text{Ga}}^0$  (- 0.53 V)]. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal oxides. A following probable redox mechanism for the benzylation reaction over the catalyst is proposed.



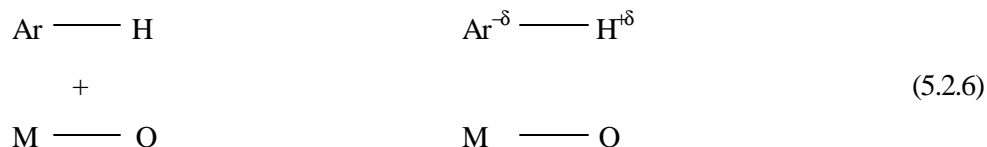
[where M = In, Ga or Zn, n = 3 (for In and Ga) or 2 (for Zn) and m = 2 (for In and Ga) and 1 (for Zn)]





The above mechanism is similar to that proposed earlier for the acylation reactions over cation exchanged clays [15].

The observed high benzylation activity of the  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 catalyst also suggests the possibility of the activation of the aromatic substrate by the catalyst. The activation may result from a strong interaction of the aromatic substrate with the metal oxide, as follows:



In case of the highly acidic catalysts, such as HY, HRE-Y, H-ZSM-5, H- $\beta$ , H-mordenite and heteropolyacids, reported earlier [1-5,8-12], though the formation of benzoyl carbo-cation is accomplished with ease, the benzylation activity of these acidic catalysts as compared to that of the  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 is very poor. This indicates that just the formation of benzoyl carbo-cation is not enough for achieving the high rates of benzylation. Thus apart from the activation of benzoyl chloride leading to the formation of benzoyl carbo-cations, the activation of aromatic substrate as above is essential for the catalyst to be highly active in the benzylation process.

### 5.2.3. CONCLUSIONS

Following important conclusions have been drawn from this investigation:

1.  $\text{In}_2\text{O}_3$  /Si-MCM-41 is a highly active catalyst for the benzylation of aromatic compounds, even in the presence of moisture in the reaction mixture.  $\text{Ga}_2\text{O}_3$ /Si-MCM-41 is also a moisture insensitive catalyst, useful for the benzylation. However,  $\text{ZnO}$ /Si-MCM-41 shows much lower activity than the two in the benzene benzylation. The order for the benzene benzylation activity of the supported  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{ZnO}$  catalysts is found to be same as that for the redox potential of the metal present in the supported metal oxide catalysts, indicating the importance of their redox properties in the benzylation process.
2. The benzene benzylation over  $\text{In}_2\text{O}_3$ /Si-MCM-41 is strongly influenced by the solvent used in the process. The order of its catalytic activity for the different



solvents is as follows: dichloroethane > acetonitrile > without solvent > n-heptane.

3. The presence of moisture in the reaction mixture has no detrimental effect on the catalytic activity when  $\text{In}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )/Si-MCM-41 catalyst is used in the benzene benzylation; on the contrary it has a small beneficial effect.

#### 5.2.4 REFERENCES

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## ***CHAPTER-6***

***HIGHLY ACTIVE AND LOW  
MOISTURE SENSITIVE SUPPORTED  
THALLIUM OXIDE CATALYSTS FOR  
FRIEDEL-CRAFTS TYPE  
BENZYLATION AND ACYLATION  
REACTIONS: STRONG THALLIUM  
OXIDE-SUPPORT INTERACTIONS***

## CHAPTER-6

# HIGHLY ACTIVE AND LOW MOISTURE SENSITIVE SUPPORTED THALLIUM OXIDE CATALYSTS FOR FRIEDEL-CRAFTS TYPE BENZYLATION AND ACYLATION REACTIONS: STRONG THALLIUM OXIDE-SUPPORT INTERACTIONS.

### 6.1 EARLIER LITERATURE AND OBJECTIVE OF THE PRESENT WORK

Liquid phase Friedel-Crafts type reactions, using solid acid catalysts, such as heteropolyacids salts [1,2], sulfated  $ZrO_2$  or  $Fe_2O_3$  [3-5], sulfated  $Al_2O_3-ZrO_2$  (or  $TiO_2$ ) [6], acid treated clays [7], Fe/MCM-41 [8], cation-exchanged clays [9,10],  $ZnCl_2$ ,  $CuCl_2$ ,  $MgCl_2$  or  $FeCl_3$  supported on Montmorillonite K-10 [11,12], HY, H-beta and H-ZSM-5 zeolites [13-16] and Ga or Fe substituted H-ZSM-5 [17,18], for benzylation [1-3, 8-11,17,18] and benzoylation [1,2,4,7,12,14-16] of aromatic compounds.

Acidic catalysts are in general moisture sensitive and hence demand moisture-free reaction mixture for these reactions. It is, therefore, of great practical interest to have a solid catalyst having high activity but little or no moisture sensitivity for the Friedel-Crafts type reactions. In our earlier study, we have observed clay or Si-MCM-41 supported  $GaCl_3$  and  $InCl_3$  catalysts, showing high activity and only a little moisture sensitivity in the benzylation of benzene, which is otherwise relatively difficult to accomplish because of the absence of any electron donating group in the aromatic substrate [19,20]; these catalysts also show high activity in the acylation of benzene and other aromatic compounds [21,22]. We have also observed that Si-MCM-41 supported  $Ga_2O_3$  and  $In_2O_3$  catalysts show very high activity in the benzylation of benzene with benzyl chloride [23]; these catalysts also found to be highly active in the benzoylation of benzene and other aromatic compounds [24,25]. The supported  $In_2O_3$  and  $InCl_3$  catalysts showed higher benzene benzylation and benzoylation activity than that showed by supported  $Ga_2O_3$  and  $GaCl_3$  catalysts. Since, Tl is the next group IIIA element, it is interesting to study the activity of the supported  $TlO_x$  and  $TlCl$  catalysts in the Friedel-Crafts type reactions.

Our present investigation indicated that  $TlCl$  deposited on Si-MCM-41 or Montmorillonite K-10 is almost inactive for the benzene benzylation with benzyl chloride and the benzylation activity of supported  $TlO_x$  (which is basic in nature) varies drastically

depending upon nature and/or surface area of the support used. The present investigation was, therefore, undertaken to study  $\text{TiO}_x$  (catalyst) - support interactions, which strongly influence the catalytic activity of supported  $\text{TiO}_x$  (viz.  $\text{TiO}_x$  deposited on different supports with or without containing surface hydroxyls) in the Friedel-Crafts type benzylation and acylation reactions.

## **6.2 RESULTS**

### **6.2.1 Catalyst Characterization**

#### **6.2.1.1 Color and Surface Area of Catalysts**

Data on the color and surface area of the  $\text{TiO}_x$  catalysts with and without catalyst support are given in Table 6.1.

The color of catalysts varies from off white/light grey to dark grey depending upon the catalyst support, more particularly its surface area. In general, the color of catalyst supported on high surface area support was lighter than that on the low surface area support. The catalyst color is changed from grey to dark grey with increasing the loading of  $\text{TiO}_x$  from 20 to 40 wt.% on zirconia (HS).

It is interesting to note that, the surface area of supported  $\text{TiO}_x$  is lower than that of the support itself for the high surface area supports, but it is higher for the low surface area supports (Table 6.1). There is a reduction in the surface area after deposition of  $\text{TiO}_x$  on the high surface area supports. The reduction is, however, drastic for the silica gel and it is more drastic for the Si-MCM-41.

#### **6.2.1.2 XRD**

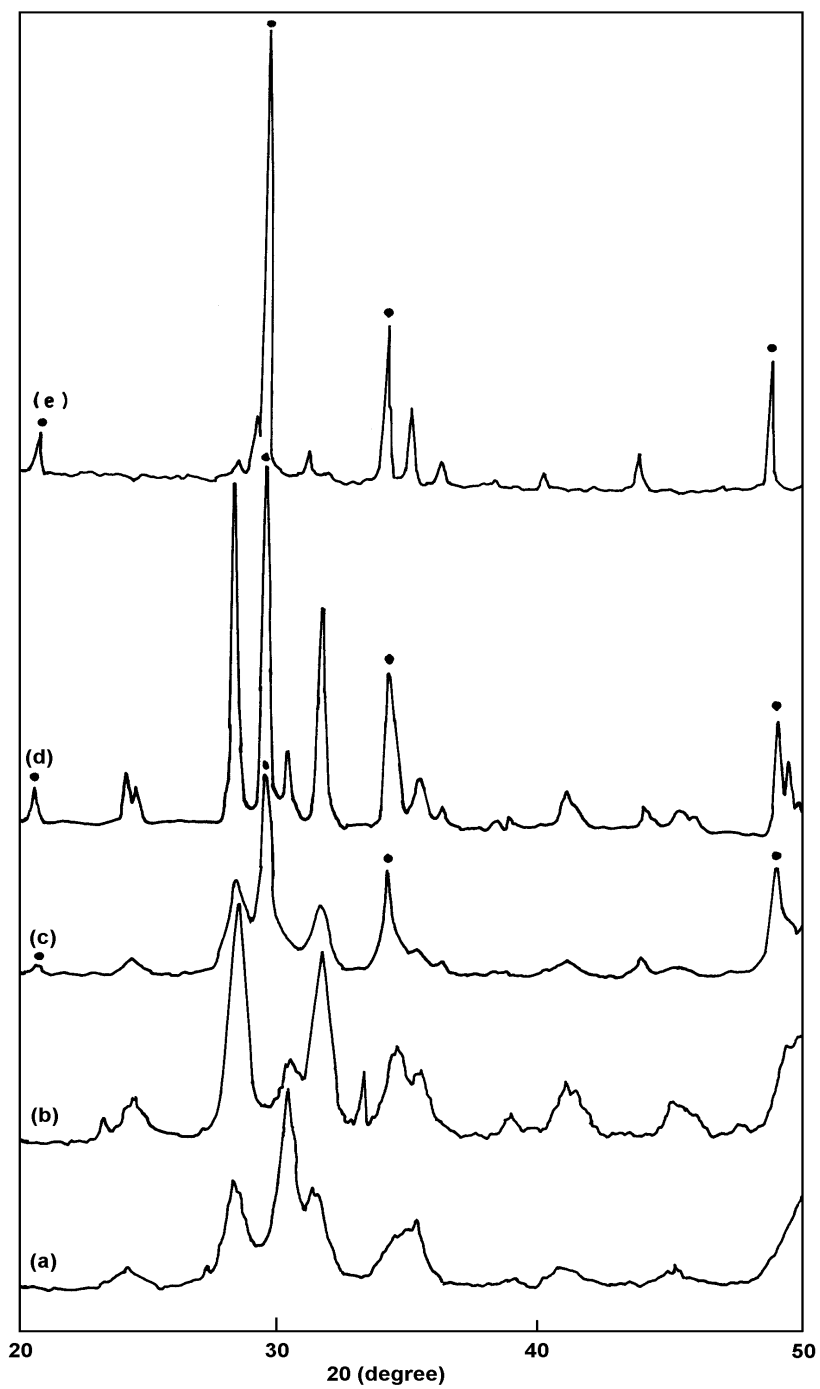
XRD spectra of the  $\text{TiO}_x$  catalysts with and without the different supports are presented in Figures 6.1 and 6.2.

The XRD spectra (Figure 6.1) show that there is no presence of  $\text{Ti}_2\text{O}_3$  phase in the  $\text{TiO}_x$  (20 wt.%) / zirconia (HS) but the  $\text{Ti}_2\text{O}_3$  phase appears when the  $\text{TiO}_x$  loading on the support is increased from 20 to 40 wt.% (Figure 6.1b,c). However, even at 20 wt.% loading of  $\text{TiO}_x$ , presence of  $\text{Ti}_2\text{O}_3$  phase at a larger concentration is observed for the  $\text{TiO}_x$  (20 wt.%) / zirconia (LS) catalyst (Figure 6.1d).

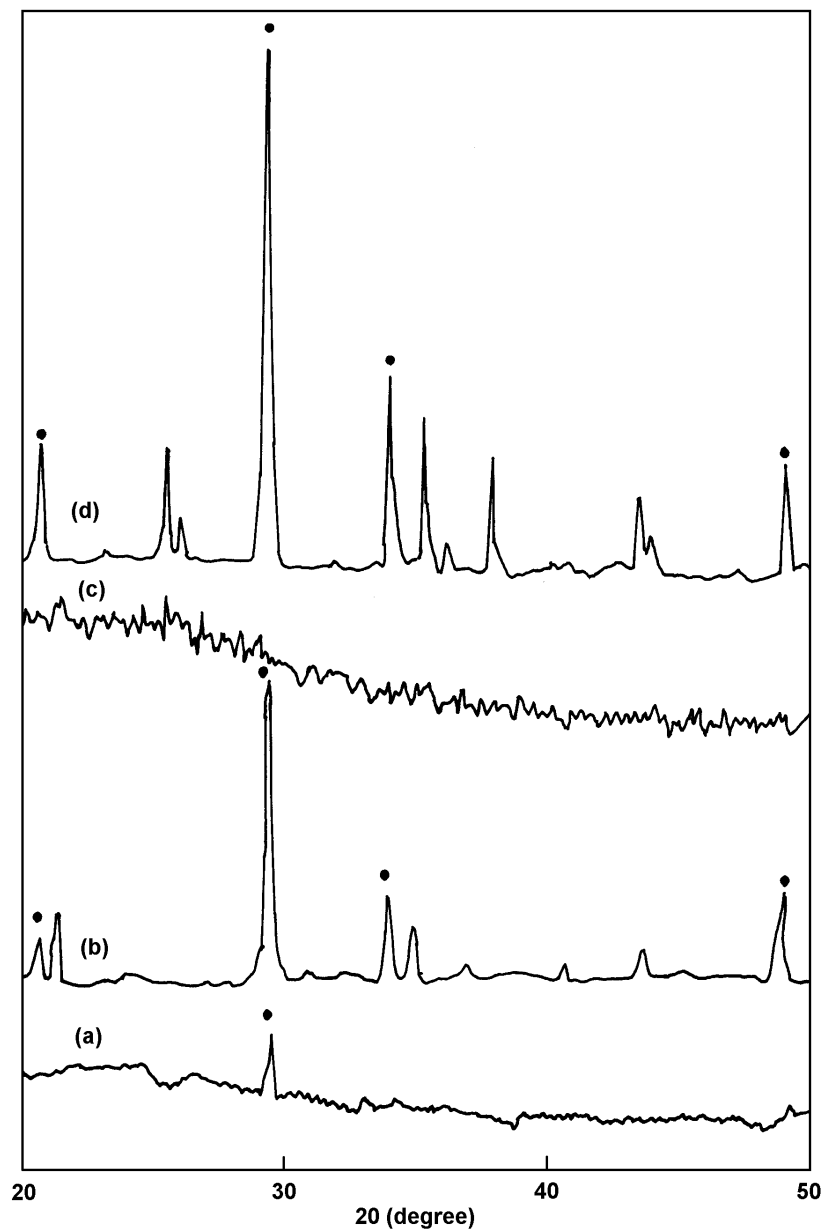
Table 6.1 Results of the benzylation of benzene with benzyl chloride over  $\text{TiO}_x$  and supported  $\text{TiO}_x$  (loading of  $\text{TiO}_x = 20$  wt %) catalysts at  $80^\circ\text{C}$  [reaction conditions: reaction mixture = 13 ml of moisture-free substrate and 1.0 ml of benzyl chloride, amount of catalyst = 0.1 g supported  $\text{TiO}_x$  and 0.02 g  $\text{TiO}_x$ ]

Catalyst	Colour of the catalyst	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )		Substrate	Time for 50 % and 90 % conversion of benzyl chloride (min)		Induction period (min)	TON for half reaction ( $\text{min}^{-1}$ )	Apparent reaction rate constant, $k_a \times 10^3$ ( $\text{min}^{-1}$ )
		Support	$\text{TiO}_x$ or supported $\text{TiO}_x$		50 %	90 %			
$\text{TiO}_x$ (without support)	Dark grey	-	0.5	Dry benzene	29.3	40.7	24.8	3.2	153.6
$\text{TiO}_x$ / silica-alumina (HS)	Light grey	255	207	Dry benzene	No reaction for 2.5h		-	-	-
$\text{TiO}_x$ / silica-alumina (LS)	Dark grey	< 0.05	0.2	Dry benzene	3.3	10.0	0.3	28.0	248.0
$\text{TiO}_x$ / silica-gel (HS)	Light grey	280	51	Dry benzene	No reaction for 2.5h		-	-	-
$\text{TiO}_x$ / Si-MCM-41 (HS)	Very light grey	1180	49	Dry benzene	No reaction for 2.5h		-	-	-
$\text{TiO}_x$ / silica (LS)	Grey	0.2	0.3	Dry benzene	9.0	19.0	4.0	10.3	163.3
$\text{TiO}_x$ / alumina (HS)	Off white	151	116	Dry benzene	No reaction for 2.5h		-	-	-
$\text{TiO}_x$ / zirconia (HS)	Grey	51	29	Dry benzene	No reaction for 2.5h		-	-	-
$\text{TiO}_x$ / zirconia (LS)	Dark grey	0.1	0.3	Dry benzene	2.4	8.2	0.1	38.5	291.5
$\text{TiO}_x$ / zirconia (LS)	Dark grey	0.1	0.3	Moist benzene <sup>b</sup>	3.5	9.8	0.4	26.4	267.8
$\text{TiO}_x$ / zirconia (LS)	Dark grey	0.1	0.3	Moist benzene <sup>b</sup>	3.8	10.0	0.6	24.3	274.2
(moist) <sup>a</sup>									
$\text{TiO}_x$ / zirconia (LS) <sup>c</sup>	Very light grey	0.1	0.2	Dry benzene	No reaction for 1.5h		-	-	-

<sup>a</sup> Catalyst was stored over water in desiccator at  $30^\circ\text{C}$  for 12h. <sup>b</sup> Benzene saturated with water at  $30^\circ\text{C}$  (0.37 mol % water in benzene). <sup>c</sup> Catalyst was prepared by decomposing thallos nitrate deposited on zirconia (LS) under  $\text{N}_2$  atmosphere at  $450^\circ\text{C}$  for 4.5h.



**Figure 6.1** XRD spectra of (a) zirconia (HS), (b)  $\text{TiO}_x$  (20 %) / zirconia (HS), (c)  $\text{TiO}_x$  (40 %) / zirconia (HS), (d)  $\text{TiO}_x$  (20 %) / zirconia (LS) and (e)  $\text{TiO}_x$  obtained from Tl (I) acetate by decomposition in air [ $\text{Ti}_2\text{O}_3$  phase (●)].



**Figure 6.2** XRD spectra of (a)  $\text{TiO}_x$  (20 %) / Si-MCM-41, (b)  $\text{TiO}_x$  (20 %) / silica (LS), (c)  $\text{TiO}_x$  (20 %) / silica-alumina (HS) and (d)  $\text{TiO}_x$  (20 %) / silica-alumina (LS) [ $\text{TiO}_3$  phase (•)].

The XRD spectra in Figure 6.2 show that for the same loading of  $\text{TlO}_x$ , there is little or no presence of the  $\text{Tl}_2\text{O}_3$  phase in  $\text{TlO}_x$  (20 wt.%) / Si-MCM-41 (Figure 6.2a) and  $\text{TlO}_x$  (20 wt.%) / silica-alumina (HS) (Figure 6.2c). However, for the catalyst supported on the low surface area supports [ $\text{TlO}_x$  (20 wt.%) / silica (LS) (Figure 6.2b) or silica-alumina (LS) (Figure 6.2d)], the  $\text{Tl}_2\text{O}_3$  phase is observed distinctly.

For the  $\text{TlO}_x$  (20 wt.%) / Si-MCM-41, no characteristic XRD peak (at  $2\theta = 1^{0-20}$ ) is observed, indicating a structural collapse of the Si-MCM-41.

### 6.2.1.3 FTIR

FTIR spectra of the Si-MCM-41, silica gel (HS) and silica-alumina (HS) with or without  $\text{TlO}_x$  deposited on them are shown in Figure 6.3.

Because of the deposition of  $\text{TlO}_x$  on the above supports, the IR spectra are influenced as follows:

- There is a significant decrease in the intensity of IR peak at around  $960\text{ cm}^{-1}$ , which is assigned for terminal Si-OH [26].
- There is a shift in the IR peaks (assigned for Si-O-Si) at around  $450\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  and also a change in the IR band at  $700 - 900\text{ cm}^{-1}$ , which is also assigned for Si-O-Si [26].

### 6.2.1.4 XPS

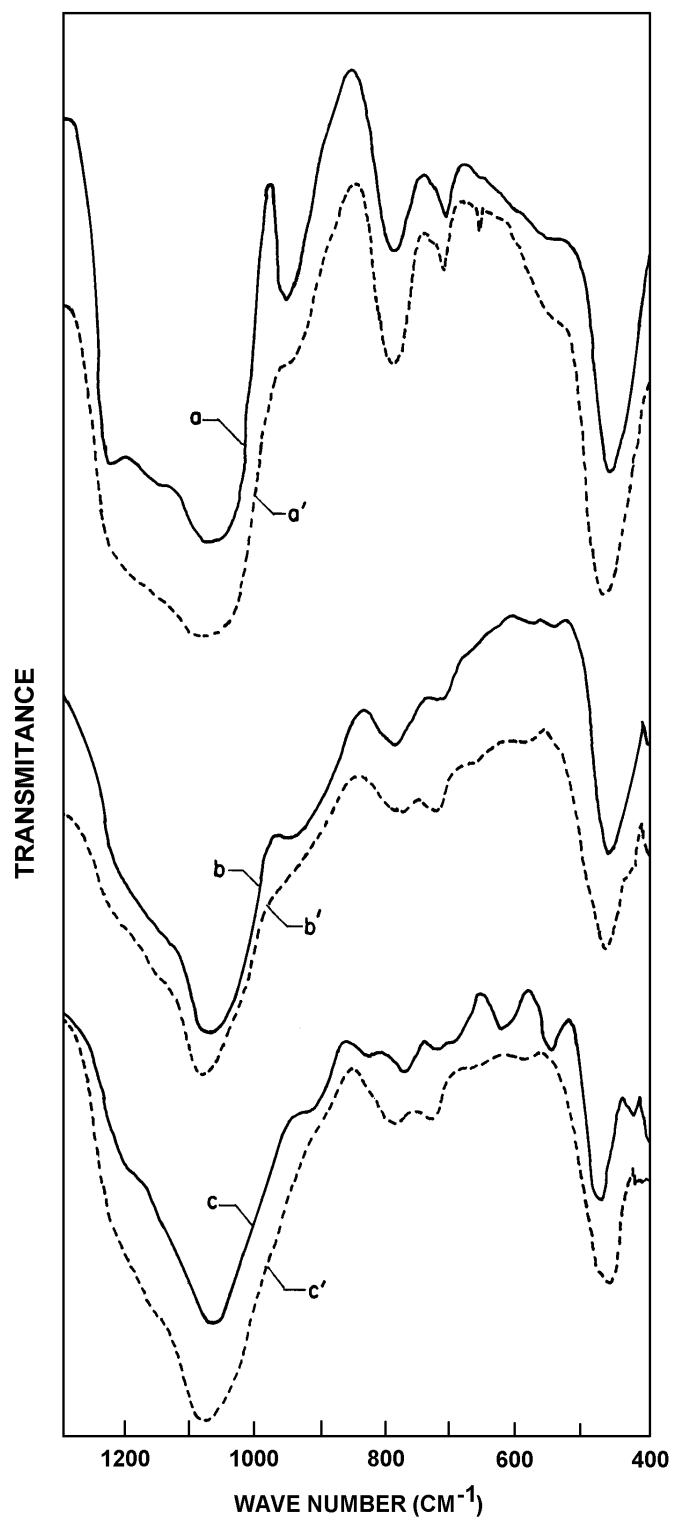
XPS data for the zirconia supported  $\text{TlO}_x$  catalysts are presented in Table 6.2.

The surface Tl/Zr ratio is increased by 5 to 6 fold with increasing the  $\text{TlO}_x$  loading on the high surface zirconia from 20 to 40 wt.%. However, even for the lower loading, the Tl/Zr ratio is much higher when  $\text{TlO}_x$  is deposited on the low surface area zirconia (Table 6.2).

## 6.2.2 Benzylation Reactions

The  $\text{TlO}_x$  catalysts with and without different commonly used high and low surface area supports are compared in Table 6.1 for their performance in the benzylation of benzene (at  $80^\circ\text{C}$ ). The catalysts which showed little or no benzene benzylation activity also did not show any activity for the benzylation of benzene (at  $80^\circ\text{C}$ ) or toluene (at  $110^\circ\text{C}$ ) for a long period (3 h). Turn over number (TON) for half the benzene benzylation reaction (i.e. at 50 % conversion of benzyl chloride) was estimated as the moles of benzyl chloride converted per mole of  $\text{TlO}_x$  per unit time. The apparent reaction rate constant ( $k_a$ ) for the benzylation of benzene by benzyl chloride (with excess of





**Figure 6.3** IR spectra of Si-MCM-41 (a), TiO<sub>x</sub> / Si-MCM-41 (a'), silica gel (b), TiO<sub>x</sub> / silica gel (b'), silica-alumina (HS) (c) and TiO<sub>x</sub> / silica-alumina (c').

benzene) was estimated from the linear plots (Figure 6.4) according to the first order rate expression:

**Table 6.2** XPS data for zirconia supported TiO<sub>x</sub> catalysts.

Catalyst	Binding energy (BE) (ev)					Surface Ti/Zr ratio
	Ti (4f <sub>7/2</sub> )	BE [Ti (4f <sub>7/2</sub> )]- BE [Ti (4f <sub>5/2</sub> )]	Zr (3d <sub>5/2</sub> )	BE [Zr (3d <sub>5/2</sub> )]- BE [Zr (3d <sub>3/2</sub> )]	O (1s)	
TiO <sub>x</sub> (20)/ zirconia (HS)	119.1	4.4	182.8	2.0	531.1	0.04
TiO <sub>x</sub> (40)/ zirconia (HS)	119.1	4.5	182.2	2.0	530.9	0.22
TiO <sub>x</sub> (20)/ zirconia (LS)	119.4	4.1	183.0	2.5	531.8	0.43

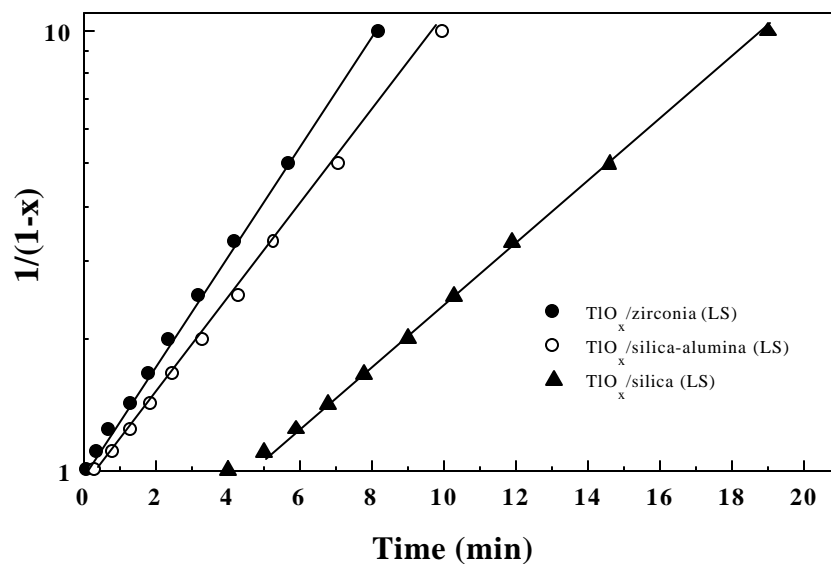
$$\log [1/(1-x)] = (k_d/2.303) \cdot (t-t_0) \quad (6.1)$$

where, x is the fractional conversion of benzyl chloride and t and t<sub>0</sub> are the time and induction period, respectively, of the reaction.

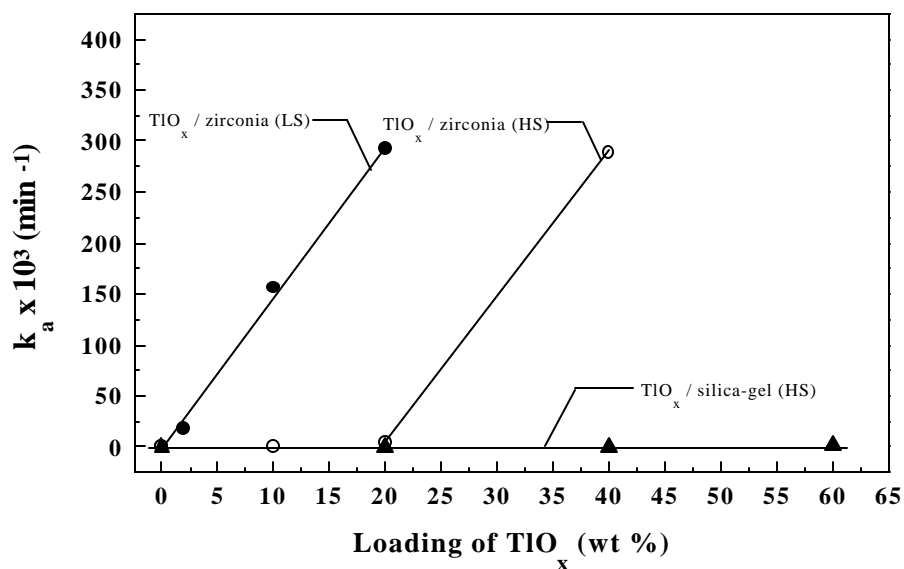
From the comparison in Table 6.1, following important observations can be made:

- For the chemically similar supports, that with low surface area provided a much more active supported TiO<sub>x</sub> catalyst for the benzene benzylation reaction. TiO<sub>x</sub> when supported on the high surface area catalyst carriers showed almost no catalytic activity in the reaction.
- The TiO<sub>x</sub> without support also shows high catalytic activity but the reaction induction period for this catalyst is much larger.
- Among the TiO<sub>x</sub> catalysts supported on the low surface area catalyst carriers, the TiO<sub>x</sub> / zirconia (LS) showed the best performance (lowest induction period and highest catalytic activity, TON).
- The TiO<sub>x</sub> / zirconia (LS) shows high benzene benzylation activity even when moisture at the level of its saturation is present in the substrate and/or in the catalyst. However, because of the presence of moisture in the reaction mixture, the reaction induction period is increased from 0.1 to 0.6 min.
- When the TiO<sub>x</sub> / zirconia (LS) catalyst was prepared by the calcination under N<sub>2</sub> instead of air, it showed no activity for the benzene benzylation.

Results showing the influence of TiO<sub>x</sub> loading on the reaction rate constant (k<sub>a</sub>) for the zirconia (LS), zirconia (HS) and silica gel (HS) supported TiO<sub>x</sub> catalysts are presented in Figure 6.5.



**Figure 6.4** First order reaction plots (according to Equation 6.1 for the benzylation of benzene at 80°C) over different supported  $\text{TiO}_x$  catalysts.

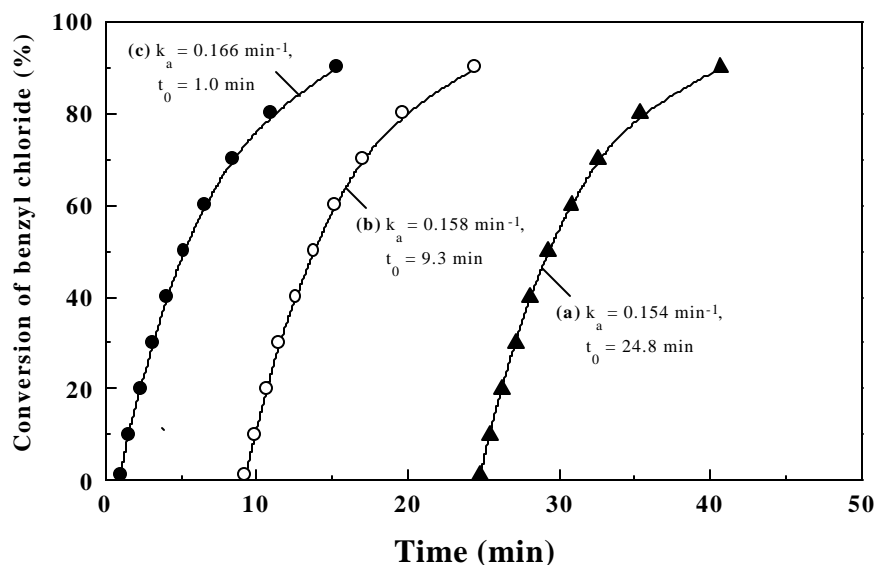


**Figure 6.5** Variation of apparent reaction rate constant ( $k_a$ ) for the benzylation of benzene (at 80°C) over  $\text{TiO}_x/\text{zirconia (LS)}$ ,  $\text{TiO}_x/\text{zirconia (HS)}$  and  $\text{TiO}_x/\text{silica gel (HS)}$  with the loading of  $\text{TiO}_x$  on the different supports.

For the zirconia (LS) supported  $\text{TiO}_x$  catalyst, the reaction rate constant is increased almost linearly with the  $\text{TiO}_x$  loading. However, the zirconia (HS) supported  $\text{TiO}_x$  catalyst shows catalytic activity only above the  $\text{TiO}_x$  loading of 20 wt.% but the silica gel (HS) supported  $\text{TiO}_x$  does not show any catalytic activity even at the  $\text{TiO}_x$  loading as high as 60 wt.%.

Figure 6.6 shows effect of the time of reflux of the unsupported  $\text{TiO}_x$  catalyst (with dry benzene) and also of the HCl (gas) pretreatment to the catalyst, before starting the benzylation reaction, on the induction period in the benzene benzylation reaction.

The induction period is decreased markedly (from 24.8 to 9.3 min) with increasing the reflux time (from 0.5 to 4h) (Figure 6.6a,b). It is also decreased drastically due to the pretreatment by HCl gas of the catalyst (Figure 6.6a,c). It is interesting to note here that, although the induction period is strongly influenced by the reflux period and the HCl pretreatment of the catalyst, there is only a very small change in the reaction rate constant. Thus in all the cases, after the induction period, the reaction proceeds with almost the same rate.

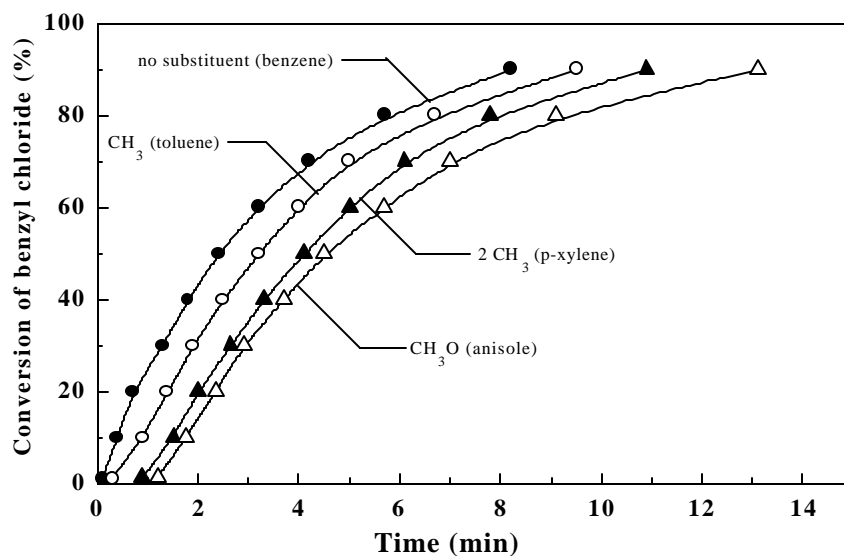


**Figure 6.6** Effect of time of reflux with benzene and HCl pretreatment of the catalyst, before starting the reaction, on the induction period ( $t_0$ ) and conversion of benzyl chloride in the benzylation of benzene (at  $80^\circ\text{C}$ ) over  $\text{TiO}_x$  obtained from  $\text{Ti}(\text{I})$  acetate [reflux time: (a) 0.5h and (b) 4h; (c) HCl pretreated catalyst].

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 TiO<sub>x</sub> (20 wt.%) / zirconia (LS) catalyst are presented in Figure 6.7. The first order rate constants ( $k_a$ ) and induction period for the benzylation reactions are as follows:

Substrate	:	Benzene	Toluene	p-Xylene	Anisole
$k_a \times 10^3 \text{ (min}^{-1}\text{)}$	:	291.5	267.8	253.0	203.8
Induction period (min)	:	0.1	0.3	0.9	1.2

The results indicate that unlike the conventional acid catalyst [27], the benzylation activity of the catalyst is decreased due to the presence of electron donating groups, such as methyl and methoxy groups, in the aromatic compound.



**Figure 6.7** Effect of the presence of different substituent groups in the aromatic (benzene) nucleus on its benzylation with benzyl chloride over the TiO<sub>x</sub> (20 %) / zirconia (LS) at 80°C (reaction mixture = 13 ml of benzene or substituted benzene + 1 ml of benzyl chloride + 0.1g catalyst).

### 6.2.3 Acylation Reactions

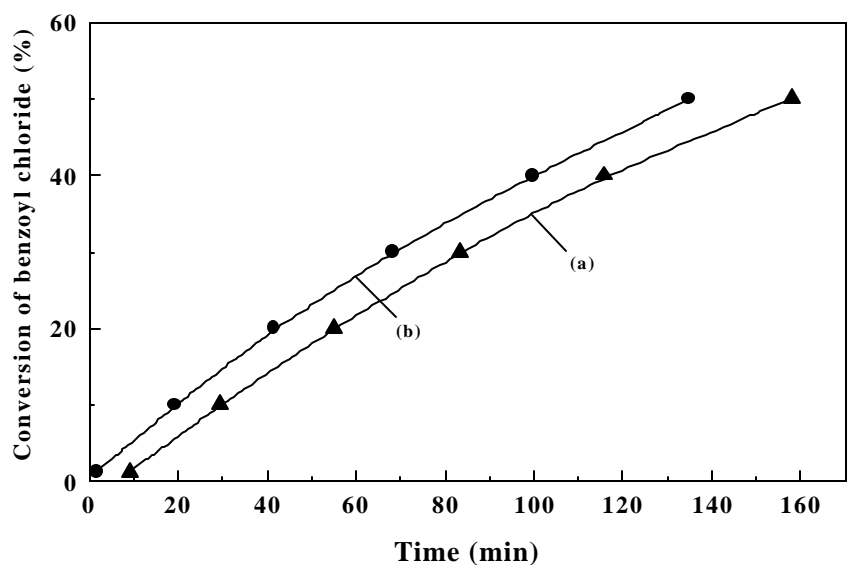
The high and low surface area zirconia supported  $\text{TlO}_x$  catalysts are compared for their performance in benzene benzoylation (at  $80^\circ\text{C}$ ) and toluene benzoylation (at  $110^\circ\text{C}$ ) reactions in Table 6.3.

Like the benzoylation reaction, the  $\text{TlO}_x$  (20 wt.%) / zirconia (LS) showed much higher benzene or toluene benzoylation activity than that of the  $\text{TlO}_x$  (40 wt.%) / zirconia (HS). The reaction induction period for the former is also smaller. The  $\text{TlO}_x$  (20 wt.%) / zirconia (HS) showed no activity in both the benzene and toluene benzoylation reactions.

Like the benzene benzoylation, the induction period in the benzene benzoylation reaction over  $\text{TlO}_x$  / zirconia (LS) catalyst is decreased very markedly due to the HCl pretreatment of the catalyst before the reaction (Figure 6.8). The rate of benzoylation after the induction period for both the cases (i.e. with and without the HCl pretreatment) remained almost the same.

**Table 6.3** Results of the benzoylation with benzoyl chloride of benzene and toluene over supported  $\text{TlO}_x$  catalysts [reaction mixture = 13 ml of benzene or toluene and 1.0 ml of benzoyl chloride, amount of catalyst = 0.4 g].

Catalyst	Induction period (min)	Time (min) required for 50 % and 80 % conversion of acylating agent		TON for half reaction ( $\text{min}^{-1}$ )
		50 %	80 %	
<u>Benzoylation of benzene at <math>80^\circ\text{C}</math>:</u>				
$\text{TlO}_x$ (20)/ zirconia (LS)	9.2	158.0	-	0.15
$\text{TlO}_x$ (20)/ zirconia (HS)	-	No reaction for 2.5h		-
$\text{TlO}_x$ (40)/ zirconia (HS)	11.5	196.0	-	0.06
<u>Benzoylation of toluene at <math>110^\circ\text{C}</math>:</u>				
$\text{TlO}_x$ (20)/ zirconia (LS)	2.3	17.4	96.5	1.32
$\text{TlO}_x$ (20)/ zirconia (HS)	-	No reaction for 2.5h		-
$\text{TlO}_x$ (40)/ zirconia (HS)	4.5	32.0	165.0	0.36



**Figure 6.8** Effect of HCl pretreatment of the catalyst, before starting the reaction, on the induction period ( $t_0$ ) and conversion of benzoyl chloride in the benzylation of benzene (at 80°C) over  $\text{TiO}_x$  / zirconia (LS) catalyst [(a) without HCl pretreatment and (b) with HCl pretreatment].

The  $\text{TiO}_x$  (20 wt.%) / zirconia (LS) and  $\text{TiO}_x$  (20 wt.%) / Si-MCM-41 catalysts are compared with the earlier reported catalysts for their performance in the benzene benzylation, benzene benzylation and toluene benzylation reactions under similar conditions in Table 6.4.

## 6.3 DISCUSSION

### 6.3.1 Influence of Catalyst Support: Strong $\text{TiO}_x$ - Support Interactions

A comparison of the supported  $\text{TiO}_x$  catalysts for their performance in the benzene benzylation (Table 6.1) shows that  $\text{TiO}_x$  deposited on the low surface area supports has high catalytic activity in the reaction but that deposited on the high surface area supports has almost no activity for the reaction. On the contrary, the  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts deposited on high surface area supports, such as Si-MCM-41 and silica gel (Table 6.4), showed very high benzene benzylation activity [23]. The observed strong influence of the catalyst support on the activity of the supported  $\text{TiO}_x$  catalysts clearly

**Table 6.4** Comparison of the present catalysts with the earlier ones for their activity in the benzylation of benzene (at 80<sup>0</sup>C) and benzylation of benzene and toluene.

Catalyst	Catalyst/(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl /or C <sub>6</sub> H <sub>5</sub> COCl) wt. ratio	Conversion of benzyl or benzoyl chloride and reaction time required		Ref.
		Conversion (%)	Time (min)	
<u>Benzene benzylation by benzyl chloride (at 80<sup>0</sup>C)</u>				
TiO <sub>x</sub> / zirconia (LS)	0.1	50	2.4	Present work
TiO <sub>x</sub> / Si-MCM-41	0.1	No reaction for 2.5h		Present work
Ga <sub>2</sub> O <sub>3</sub> / zirconia (LS)	0.1	50	5.4	23
In <sub>2</sub> O <sub>3</sub> / zirconia (LS)	0.1	50	7.3	23
Ga <sub>2</sub> O <sub>3</sub> / Si-MCM-41	0.1	50	2.5	23
Ga <sub>2</sub> O <sub>3</sub> / silica gel	0.1	50	11	23
In <sub>2</sub> O <sub>3</sub> / Si-MCM-41	0.1	50	2.4	23
GaCl <sub>3</sub> /Mont. K-10	0.1	50	4.7	19
InCl <sub>3</sub> /Mont. K-10	0.1	50	2	19
H-FeMFI	0.1	50	6.7	17
H-GaAlMFI	0.1	50	22.8	17
Nafion-H	0.1	24	120	3
Sulfated ZrO <sub>2</sub>	0.1	50	135	4
Sulfated Fe <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	0.1	50	33	4
<u>Benzene benzylation by benzoyl chloride (at 80<sup>0</sup>C)</u>				
TiO <sub>x</sub> / zirconia (LS)	0.33	50	165	Present work
TiO <sub>x</sub> / Si-MCM-41	0.33	No reaction for 2.5h		Present work
In <sub>2</sub> O <sub>3</sub> / Si-MCM-41	0.33	50	286	23
H-Beta	0.33	54	1080	11
<u>Toluene benzylation by benzoyl chloride (at 110<sup>0</sup>C)</u>				
TiO <sub>x</sub> / zirconia (LS)	0.33	83	103	Present work
TiO <sub>x</sub> / Si-MCM-41	0.33	No reaction for 2.5h		Present work
In <sub>2</sub> O <sub>3</sub> / Si-MCM-41	0.33	83	148	23
Ga <sub>2</sub> O <sub>3</sub> / Si-MCM-41	0.33	83	205	23
H-Beta	0.33	83	1083	12
Sulfated ZrO <sub>2</sub>	0.5	50	192	5



shows strong  $\text{TlO}_x$  - support interactions. Strong metal - support interactions are well known and are observed for many supported metals [28,29]. However, the information on the strong metal oxide - support interactions which are mainly chemical in nature is scarce, these have been observed for a few supported metal oxide (Li-MgO, La-MgO and La-CaO) catalysts [30-32]. In the present case, since  $\text{TlO}_x$  is basic, it can interact chemically with the weakly or strongly acidic surface hydroxyls of the high surface area supports.

The low surface area supports (Table 6.1) are highly sintered macroporous materials and hence have no surface hydroxyl groups. Whereas, the high surface area supports (Table 6.1) are known to have appreciable amounts of surface hydroxyl groups. Even a highly crystalline material like mesoporous Si-MCM-41 has different types of surface hydroxyls, as terminal Si-OH groups [27,28]. The Si-MCM-41 sample used in the present study has also appreciable amounts of surface hydroxyl groups [29]. The silica gel support has also large amounts of surface hydroxyl. The strong  $\text{TlO}_x$  - support interactions in the present case are mostly due to the presence of surface hydroxyl groups in the high surface area supports. This hypothesis is supported by the following observations:

- For the high surface area supports, the surface area of the supported  $\text{TlO}_x$  catalysts is much lower than that of the corresponding support (Table 6.1). In the case of Si-MCM-41 support, its structure is collapsed with a drastic reduction in the surface area (from 1180 to 49  $\text{m}^2.\text{g}^{-1}$ ) because of the deposition of  $\text{TlO}_x$ .
- The intensity of IR peak at 960  $\text{cm}^{-1}$  (assigned to terminal Si-OH) is reduced markedly due to the deposition of  $\text{TlO}_x$  on the Si-MCM-41, silica gel and high surface area silica-alumina (Fig. 6.3). This indicates the consumption of the surface hydroxyl groups in the chemical interactions with the deposited  $\text{TlO}_x$ .
- The XRD spectra of the  $\text{TlO}_x$  (20 wt.%) supported on Si-MCM-41, silica-alumina (HS) and zirconia (HS) show little or no presence of the  $\text{Tl}_2\text{O}_3$  phase (Figs. 6.1b and 6.2a,c). A small  $\text{Tl}_2\text{O}_3$  phase for the  $\text{TlO}_x$  / zirconia (HS) is seen only when the  $\text{TlO}_x$  loading is increased from 20 to 40 wt.% (Fig. 6.1b,c). On the contrary, for the  $\text{TlO}_x$  / zirconia (LS), even for the  $\text{TlO}_x$  loading of 20 wt.%, a distinct  $\text{Tl}_2\text{O}_3$  phase is observed (Fig. 6.1d). It may be noted that only those supported  $\text{TlO}_x$  catalysts are active in the reaction for which distinct XRD peaks showing the presence of  $\text{Tl}_2\text{O}_3$  phase are observed.

- The surface Ti/Zr ratio is an order of magnitude (10 times) larger when  $\text{TiO}_x$  is deposited on the low surface area zirconia as compared to on the high surface area zirconia (Table 6.2). Also there is a large increase in the surface Ti/Zr ratio (from 0.04 to 0.22) with doubling the  $\text{TiO}_x$  loading on the high surface area zirconia.

The observations on the  $\text{Tl}_2\text{O}_3$  phase and surface Ti/Zr ratio for the high surface area zirconia for the two  $\text{TiO}_x$  loadings (20 and 40 wt.%) shows that an appreciable fraction of the  $\text{TiO}_x$  loaded on the support is consumed in the  $\text{TiO}_x$  - support interactions.

The drastic reduction in the surface area of the Si-MCM-41 and silica gel after the deposition of  $\text{TiO}_x$  on them is due to their structural collapse resulting from the reaction between their surface hydroxyls and  $\text{TiO}_x$ . The reduction in the surface area for the silica-alumina (HS) is relatively smaller and this may be due to its smaller number of surface hydroxyls.

Thus, unlike  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ ,  $\text{TiO}_x$  interacts strongly with the high surface area supports, mostly through their surface hydroxyl groups. Further studies are necessary for understanding the nature of chemical interactions. Nevertheless, when compare for the low surface area supports, the supported  $\text{TiO}_x$  is more active than the supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts for the benzene benzylation (Table 6.4). Also, like the supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  catalysts [20], the activity of the  $\text{TiO}_x$  / zirconia (LS) catalyst is only little affected by the presence of moisture in the catalyst or in the reaction mixture (Table 6.1). However, because of its toxicity the  $\text{TiO}_x$  catalyst should be handled much more carefully.

### **6.3.2 Effect of Moisture and HCl Pretreatment on Reaction Induction Period**

The induction period for the benzene benzylation is reduced markedly because of increasing the reflux period and consequently removing the adsorbed moisture from the unsupported  $\text{TiO}_x$  catalysts (Fig. 6a,b). It is also interesting to note that, the  $\text{TiO}_x$  catalysts supported on the low surface area support (which are sintered macroporous materials and hence do not contain significant amounts of adsorbed moisture) have much lower induction period (Table 6.1). These observations indicate that the adsorbed moisture present in the catalyst is responsible for the high induction period for the unsupported  $\text{TiO}_x$ ; the removal of adsorbed water from the catalyst results in a decrease in the induction period.

The induction period of the unsupported  $\text{TiO}_x$  catalyst is reduced drastically because of the HCl pretreatment to the catalyst before the benzene benzylation reaction

(Fig. 6a,c). A similar observation is also made for the benzylation of benzene over the  $\text{TlO}_x$  / zirconia (LS) (Fig. 6.8). These observations reveal that, during the induction period the catalyst is activated by the HCl (which is a by-product) produced in both the benzylation and benzoylation reactions. The influence of moisture on the induction period is, therefore, attributed to a reduction due to the presence of moisture in the rate of catalyst activation by the HCl produced in the initial reaction.

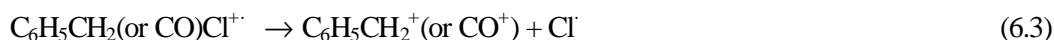
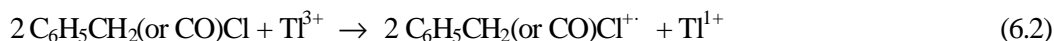
The catalyst activation by HCl during the induction period may result from the removal of adsorbed water from the catalyst ( $\text{TlO}_x$  is basic in nature and hence adsorption of HCl on it is stronger than that of water) or from the chemisorption of HCl on the catalyst modifying its surface active sites or from the both. After the use in the reaction, the catalyst showed a presence of significant amount of chlorine. A further detailed investigation is necessary for understanding the catalyst activation during the induction period.

### 6.3.3 Effect of Electron Donating Substituent Groups

According to the classical mechanism of the Friedel-Crafts type acid catalyzed benzylation or acylation reaction, the benzylation or acylation of an aromatic compound is easier if one or more electron donating groups are present in the aromatic ring. Surprisingly, in the present case the activity of the  $\text{TlO}_x$  / zirconia (LS) catalyst for benzylation (under the same conditions) of the aromatic compounds with or without containing electron donating groups ( $\text{CH}_3$  and  $\text{CH}_3\text{O}$ ) is opposite to that expected from the classical mechanism (Figure 6.7). The first order rate constant for the benzylation of benzene and substituted benzenes is in the following order: benzene > methyl benzene > p-dimethyl benzene > methoxy benzene. This shows that for this catalyst, the reaction mechanism is different from that for the classical acid catalyzed benzylation reactions.

### 6.3.4 Reaction Mechanism

The active supported  $\text{TlO}_x$  catalysts were found to contain  $\text{Tl}_2\text{O}_3$ , which is basic in nature. The standard reduction potential for  $\text{Tl}^{3+} \rightarrow \text{Tl}^{1+}$  ( $E_{\text{Tl}^{3+}/\text{Tl}^{1+}}^0$ ) is positive (+ 2.06 V), and hence the reduction of  $\text{Tl}^{3+}$  to  $\text{Tl}^{1+}$  is relatively easy. The benzylation and acylation reactions over these catalysts are, therefore, expected to follow redox mechanism similar to that proposed earlier for the alkylation [9] and acylation reactions [30], as follows:





The  $\text{TiO}_x$  / zirconia (LS) obtained by the calcination in  $\text{N}_2$  atmosphere contained  $\text{Ti}_2\text{O}$  and no  $\text{Ti}_2\text{O}_3$ . This catalyst showed no activity for the benzene benzylation (Table 6.1), which is consistent with the above mechanism.

## 6.4 CONCLUSIONS

Following important conclusions have been drawn from this investigation:

1. Because of its basic nature,  $\text{TiO}_x$  interacts strongly (chemically) with the surface hydroxyls (both weakly and strongly acidic ones) of high surface area catalyst supports such as Si-MCM-41, silica gel, alumina, silica-alumina and zirconia, causing a large reduction in the surface area of the support; structure of Si-MCM-41 is collapsed after the deposition of  $\text{TiO}_x$  on it. The supported  $\text{TiO}_x$  prepared using the high surface area supports are inactive in the benzylation of benzene. On the contrary, the  $\text{TiO}_x$  supported on low surface area sintered macroporous zirconia, silica or silica-alumina catalyst carriers shows high benzene benzylation activity.  $\text{TiO}_x$  / zirconia (LS) is a highly promising catalyst for both the benzylation and acylation of benzene and other aromatic hydrocarbons. It shows high benzene benzylation activity even in the presence of moisture in the catalyst or in the reaction mixture. Only the catalyst which contains  $\text{Ti}_2\text{O}_3$  shows activity for the benzylation and acylation reactions.
2.  $\text{TiO}_x$  / zirconia (LS) catalyst shows a following trend for its activity in the benzylation of benzene and substituted benzenes containing electron donating groups (viz.  $\text{CH}_3$  and  $\text{CH}_3\text{O}$ ): benzene > methyl benzene > p-dimethyl benzene > methoxy benzene, which is totally opposite to that observed for the acid catalyzed Friedel-Crafts type benzylation reactions. This trend and the basic nature of the catalyst indicate that the benzylation and acylation reactions follow redox mechanism in the present case.
3. The induction period for the benzylation and acylation reactions depends strongly on the presence of moisture in the catalyst and/or in the reaction mixture; it is decreased with decreasing the amount of moisture. During the induction period, the catalyst is activated most probably by the modification of its surface by interaction with the HCl (a by-product) produced in the initial benzylation or acylation reaction. The

pretreatment by HCl gas of the catalyst causes a drastic reduction in the induction period for both the benzylation and acylation reactions.

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## **CHAPTER-7**

**HIGHLY ACTIVE, REUSABLE AND  
MOISTURE INSENSITIVE  
CATALYST OBTAINED FROM BASIC  
Ga-Mg-HYDROTALCITE ANIONIC  
CLAY FOR FRIEDEL-CRAFTS TYPE  
BENZYLATION AND ACYLATION  
REACTIONS**

# **HIGHLY ACTIVE, REUSABLE AND MOISTURE INSENSITIVE CATALYST OBTAINED FROM BASIC Ga-Mg-HYDROTALCITE ANIONIC CLAY FOR FRIEDEL-CRAFTS TYPE BENZYLATION AND ACYLATION REACTIONS.**

## **7.1. EARLIER LITERATURE AND OBJECTIVE OF THE PRESENT WORK**

A number of highly acidic solid catalysts, such as heteropolyacids [1], sulfated  $ZrO_2$  or  $Fe_2O_3$  [2], Nafion-H [1] and Fe- or Ga-substituted H-ZSM-5 [3] for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene [4], and heteropolyacids [1], H-beta [5], H-ZSM-5 [6] and sulfated  $ZrO_2$  [7] for benzoylation of aromatic compounds are reported in the literature. However, the reports on the use of basic catalysts for the benzylation and acylation reactions are scarce [8]. Very recently, we [9] have observed high activity of supported basic  $In_2O_3$  in these reactions. Hydrotalcite anionic clays are known to be highly basic solids [10]. The use of these anionic clays after their thermal decomposition to mixed metal oxides has been reported for a number of catalytic reactions [10]. However, their direct use as catalyst is scarce [11,12]. No information is available on the use of hydrotalcites or also the basic catalysts derived from them for the benzylation and acylation reactions.

In the present investigation, we have shown that Ga-Mg hydrotalcite anionic clay, after its first use in the reaction or HCl gas pretreatment, shows very high activity both in the benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of toluene and even of benzene, which is otherwise relatively difficult by the known acidic catalysts. It is also shown that, the active catalyst, obtained from the hydrotalcite after its first use or HCl gas pretreatment, has little or no moisture sensitivity and also has excellent reusability, which is of great practical importance.

## **7.2. RESULTS AND DISCUSSION**



### 7.2.1 Composition and Properties of the Ga-Mg-Hydrotalcite Catalysts

Results of the characterization of the fresh, HCl treated and used (in the toluene benzylation) Ga-Mg-HT catalysts are presented in Tables 7.1-7.3. After the HCl treatment and/or use in the reaction of the hydrotalcite catalysts,

- its color and crystalline phases are changed (Table 7.1),
- its surface area and basicity are reduced (Table 7.1),
- its surface composition is changed drastically, the surface Cl/(Ga+Mg) ratio is increased markedly, while the surface  $\text{CO}_3^{2-}/(\text{Ga}+\text{Mg})$  ratio is decreased (Table 7.2), and
- its IR frequency in the different regions (except  $1377.1 \text{ cm}^{-1}$ ) is shifted towards lower side (Table 7.3).

All the above reveal that the catalyst undergoes an appreciable change in its surface properties by the HCl treatment and a structural collapse after its use in the reaction. The catalyst in its most active form seems to consist of chlorides of Ga and Mg dispersed on MgO.

**Table 7.1** Physico-chemical properties of the fresh, HCl treated and used Ga-Mg-HT catalysts.

Catalyst	Color	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )	pH of catalyst (0.1 g) - water (20 ml) mixture	XRD phases
Fresh Ga-Mg-HT-80	White	-	-	Pure HT
Fresh Ga-Mg-HT-200	White	9.7	9.4	Pure HT
HCl treated Ga-Mg-HT-200	Off-white	6.1	7.8	HT (major), $\text{MgCl}_2$ (minor) and $\text{GaCl}_3$ (minor)
Used Ga-Mg-HT-200	Yellowish	2.3	7.3	$\text{GaCl}_3$ , $\text{MgCl}_2$ and $\text{MgO}$ , $\text{MgCO}_3$ (trace)

**Table 7.2** XPS data for the fresh, HCl treated and used Ga-Mg-HT catalysts.

Catalyst	Binding energy (ev)					Relative surface composition (mol ratio)		
	C <sub>1s</sub>	O <sub>1s</sub>	Mg <sub>2p</sub>	Ga <sub>2p</sub>	Cl <sub>2p</sub>	Ga/Mg	Cl/(Ga+Mg)	CO <sub>3</sub> <sup>2-</sup> /(Ga+Mg)
Fresh Ga-Mg-HT-200	285.0 288.3	531.8	50.1	1119.1	-	0.014	0.0	0.18
HCl treated Ga-Mg-HT-200	285.0 288.2	532.0	50.2	1118.8	198.8	0.014	0.21	0.16
Used Ga-Mg-HT-200	285.0 288.4	532.4	51.6	1119.0	195.5	0.021	0.98	0.03

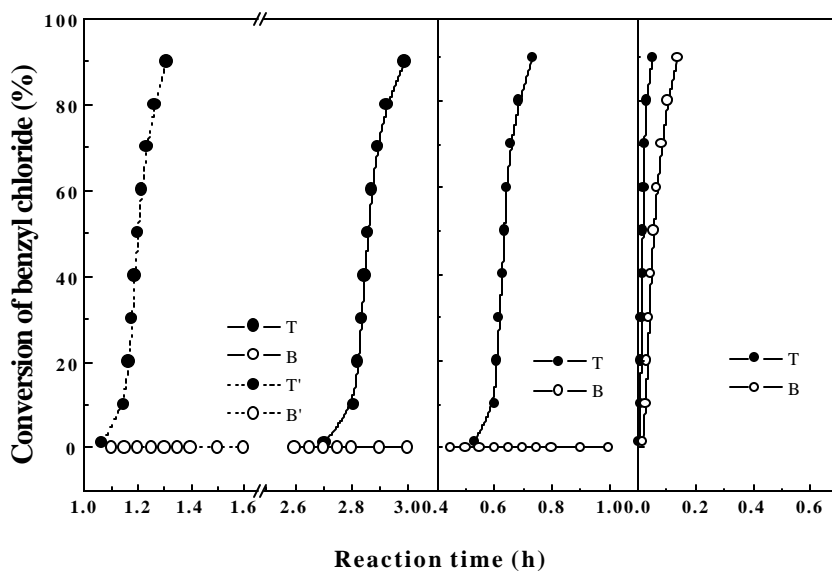
**Table 7.3** IR data for the fresh, HCl treated and used Ga-Mg-HT catalysts.

Catalyst	IR frequency in different regions (cm <sup>-1</sup> )			
	>3000 cm <sup>-1</sup>	1600-1700 cm <sup>-1</sup>	1300-1400 cm <sup>-1</sup>	500-600 cm <sup>-1</sup>
Fresh Ga-Mg-HT-200	3525	1643	1377.1	577
HCl treated Ga-Mg-HT-200	3400	1639	1377.1	575
Used Ga-Mg-HT-200	3360	1614	1377.1	540

### 7.2.2 Benzylation and Acylation Reactions

Results of the benzylation of toluene in Figure 7.1a,b show a very strong influence of the calcination temperature and pre-reflux period of the Ga-Mg-hydrotalcite catalyst on the reaction induction period. The induction period is decreased very markedly with increasing the calcination temperature (from 80<sup>o</sup>C to 200<sup>o</sup>C) or the pre-reflux period (from 0.25 h to 7.0 h), mostly due to removal of water molecules occluded between the interlamellar layers of the hydrotalcite [13]. However, the Ga-Mg-HT-80 (or 200) does not show any benzene benzylation activity for the reaction period of 3 h. Interestingly, the hydrotalcite after its use in the toluene benzylation shows very high activity with almost zero induction period not only for the toluene benzylation but also for the benzene benzylation, which is relatively more difficult to accomplish [14] because of the absence of any electron donating group (Figure 7.1c). Moreover, the used catalyst

also shows high activity for the acylation (by benzoyl chloride) of both toluene and benzene (Figure 7.2b,c). The used Ga-Mg-HT catalyst shows much higher activity in the benzylation or acylation reaction than the highly acidic catalysts, such as H-ZSM-5, HY, H-beta, sulfated  $ZrO_2$  (or  $ZrO_2-Fe_2O_3$ ), heteropolyacids, H-Ga(or Fe)MFI and H-GaAlMFI, reported earlier[1-7]. This catalyst also shows higher benzene or toluene benzylation activity when compared to the  $GaCl_3$ /Mont. K-10 [15] and  $Ga_2O_3$ /Si-MCM-41 [9] catalysts. Moreover, the hydrotalcite based catalyst showed excellent reusability in both the benzylation and acylation reactions. After its third reuse, the half reaction time for the toluene benzylation and toluene benzoylation was 1.1 min and 77 min, respectively (Table 7.4).



**Figure 7.1** Benzylation of benzene at  $80^{\circ}C$  (- -) and toluene at  $110^{\circ}C$  (- -) with benzyl chloride over a) Ga-Mg-HT-80, b) Ga-Mg-HT-200 and c) Ga-Mg-HT-80 (or 200) used before in the toluene benzylation (solid line and dotted line correspond to the catalyst refluxed in pure aromatic substrate for a period of 0.25 h and 7.0 h, respectively, before the reaction).

**Table 7.4** Reusability of Ga-Mg HT (200, used) catalyst for the toluene benzylation and benzoylation reactions (at 110<sup>0</sup>C).

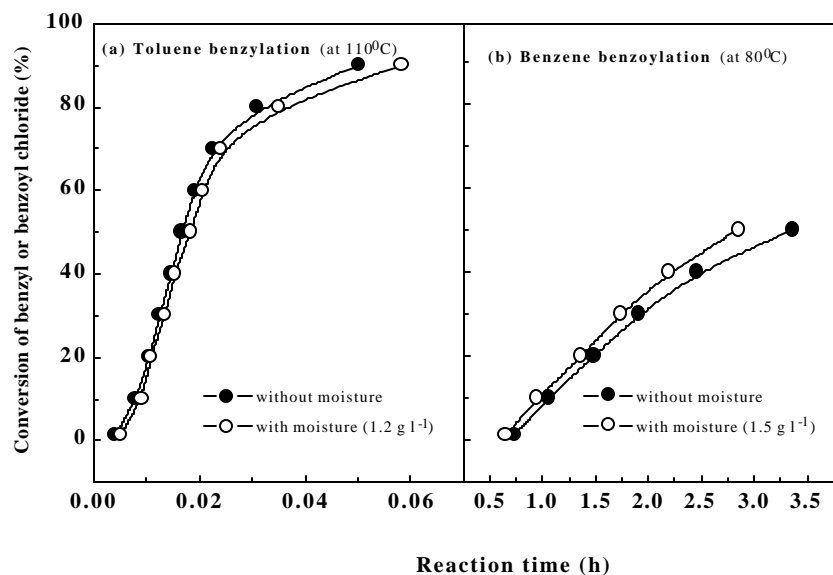
Expt. No.	Catalyst	Time (min) for conversion of benzoyl chloride		Reaction induction period (min)
		50 %	80 %	
<b>I ] <u>Benzylation of Toluene</u></b>				
1	Ga-Mg HT (200) used in the toluene benzylation reaction	1.0	1.8	0.0
2	The catalyst used in the first experiment	1.1	1.9	0.0
3	The catalyst used in the second experiment	1.1	1.9	0.0
4	The catalyst used in the third experiment	1.1	1.9	0.0
<b>II ] <u>Benzoylation of Toluene</u></b>				
1	Ga-Mg HT (200) used in the toluene benzoylation reaction	73.5	164.5	16.0
2	The catalyst used in the first experiment	74.6	167.8	14.5
3	The catalyst used in the second experiment	75.0	170.0	14.8
4	The catalyst used in the third experiment	77.0	175.0	15.0

### 7.2.3 Effect of Moisture and HCl Pretreatment on the Catalytic Activity/Reaction Induction Period

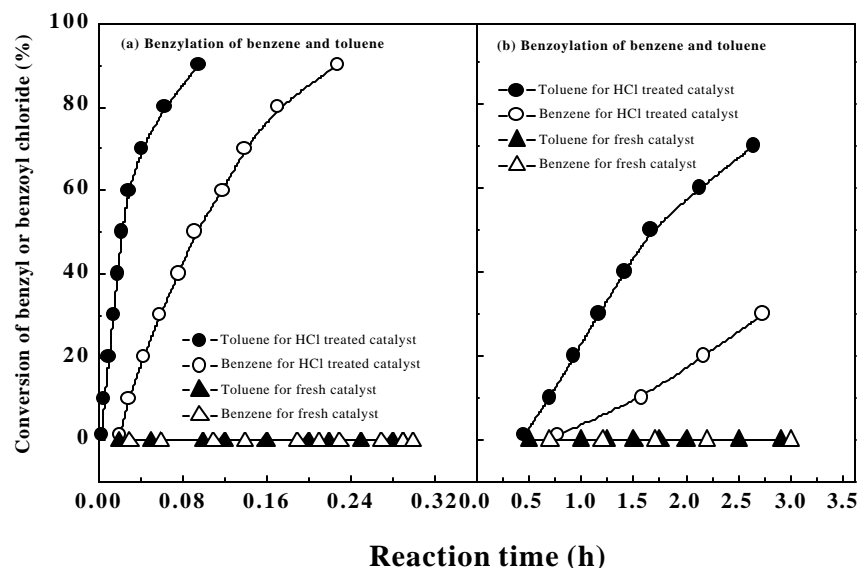
The used hydrotalcite catalyst shows a very small effect of the presence of moisture in the reaction mixture on its performance in both the benzylation and acylation reactions (Figure 7.2). Thus, unlike the commonly used acidic catalysts, the used hydrotalcite catalyst shows almost no moisture sensitivity. In the benzylation reaction, the presence of moisture causes a small increase in the induction period depending upon the concentration of water in the reaction mixture. However, after the induction period, the benzylation reaction proceeds with almost the same rate (Figure 7.2a). On the contrary, in the case of the acylation, the presence of moisture causes a small decrease in the induction period and an appreciable increase in the reaction rate, thus showing a beneficial effect (Figure 7.2b,c).

It is interesting to note that the induction period for the fresh hydrotalcite catalyst is quite large but after its use, it is drastically reduced (Figure 7.1). Also, after the induction period the toluene benzylation proceeds rapidly almost at the same rate in all

these cases. This clearly shows that the catalyst is modified during the induction period creating new active sites on the catalyst, probably by the HCl formed in the reaction, and this process of the catalyst activation is enhanced after the removal of strongly held water molecules between the interlamellar space. For confirming this hypothesis, the fresh hydrotalcite catalyst was first treated with HCl vapors and then used for the reactions; the results on both the fresh and HCl treated hydrotalcite catalysts are compared in Figure 7.3. The results are consistent with the hypothesis. After the HCl treatment, the benzylation and acylation activity of the catalyst is increased drastically. The HCl treated catalyst shows performance in both the reactions comparable to that showed by the used catalyst (Figures 7.1c, 7.2b,c and 7.3).



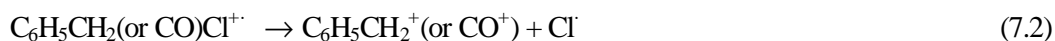
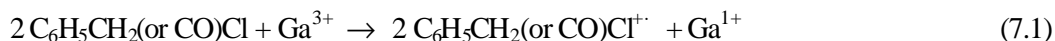
**Figure 7.2** Influence of moisture in the reaction mixture on a) benzylation of toluene, b) acylation of toluene and c) acylation of benzene over the Ga-Mg-HT-200 used before in the toluene benzylation [reaction mixture: without moisture (- -), with 1.5 g.l<sup>-1</sup> water (- -) or with 2.5 g.l<sup>-1</sup> water (- -)].



**Figure 7.3** Influence of HCl treatment to Ga-Mg-HT-200 on its activity in a) benzylation and b) acylation reactions [benzylation or acylation of toluene (-) and benzene (-) over the HCl treated catalyst, benzylation or acylation of toluene (-) and benzene (-Δ) over the untreated catalyst].

#### 7.2.4 Reaction Mechanism

The observed high benzylation and acylation activity of the HCl gas pretreated and used (in toluene benzylation) Ga-Mg-HT catalysts were found to contain  $\text{GaCl}_3$  and the fresh Ga-Mg-HT was also contain  $\text{Ga}^{3+}$  species. The standard reduction potential for  $\text{Ga}^{3+}$  to  $\text{Ga}^{1+}$  ( $E_{\text{Ga}^{3+}/\text{Ga}^{1+}}^0$ ) is - 0.44 V, and hence the reduction of  $\text{Ga}^{3+}$  to  $\text{Ga}^{1+}$  is relatively easy. The benzylation and acylation reactions over these catalysts are, therefore, expected to follow the redox mechanism similar to that proposed earlier for the alkylation and acylation reactions [16-18], as follows.



### 7.3 CONCLUSIONS

Ga-Mg-hydrotalcite, a basic anionic clay, shows very large induction period in the benzylation of toluene. But after its use in the reaction or HCl pretreatment, the hydrotalcite derived catalyst shows very high activity in the benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of toluene and also high activity in the benzene benzylation or acylation reaction, with a drastic reduction in the induction period, even in the presence of appreciable moisture in the reaction mixture. The structure and basic nature of the hydrotalcite are changed but not very significantly by the HCl pretreatment. However, after the use in the reaction, there is a structural collapse of the hydrotalcite, forming different crystalline phases, viz. GaCl<sub>3</sub>, MgCl<sub>2</sub> and MgO as major phases and also the surface composition [Ga/Mg, Cl/(Ga+Mg) and CO<sub>3</sub><sup>2-</sup>/(Ga+Mg) mole ratios] is changed markedly. The hydrotalcite-derived catalyst in its most active form consists of highly dispersed gallium and magnesium chlorides on MgO. The presence of moisture has beneficial effects on the acylation reactions; because of the moisture the induction period is decreased and the reaction rate is enhanced.

### 7.4 REFERENCES

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## ***CHAPTER-8***

### ***POLYCONDENSATION OF BENZYL CHLORIDE OVER Fe-, Ga- AND In- CONTAINING SOLID CATALYSTS***

## Chapter-8

### 8.1 POLYCONDENSATION OF BENZYL CHLORIDE OVER Fe-CONTAINING MICRO-, MESO- AND MACROPOROUS SOLID CATALYSTS.

#### 8.1.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

At the time of undertaking this work, a very few studies on the polycondensation of benzyl chloride over homogeneous stannic chloride catalyst [1,2] and heterogeneous catalysts, such as ferrous sulfate [3] and iron oxide [4] were reported in the literature.

Since there is a high possibility of polycondensation of benzyl chloride during the benzylation reaction, it is practically important to have the knowledge of the polycondensation over the solid catalysts used in the benzylation reactions. A number of Fe-containing solid catalysts such as: H-FeMFI, H-FeAlMFI, Fe<sub>2</sub>O<sub>3</sub>/H-ZSM-5 [5,6], Fe-MCM-41 [7,8], Fe/Si-MCM-41 [9], FeCl<sub>3</sub>/Mont.-K10 [10,11], FeCl<sub>3</sub>/Kaolin [12], Fe (III) exchanged Kaolinites [13], Fe-pillared clays [14] and sulfated Fe<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> [15] have been reported earlier for their high activity in the benzylation of benzene and other aromatic compounds by benzyl chloride. The present investigation was, therefore, undertaken to examine the activity of different Fe-containing micro-, meso- and macroporous solid catalysts such as FeCl<sub>3</sub> deposited on Montmorillonite K10 clay and mesoporous MCM-41 zeolite, Fe<sub>2</sub>O<sub>3</sub> supported on macroporous commercial silica-alumina catalyst carrier or mesoporous MCM-41, and Fe-modified ZSM-5 type zeolites (viz. Fe/H-ZSM-5, H-FeMFI and H-FeAlMFI) for the polycondensation reaction. In addition, the effect of temperature and solvent on the polycondensation reaction over a selected catalyst has also been studied. All these Fe-containing catalysts show high activity in the polycondensation reaction at the reaction temperature normally employed in the benzylation of aromatic compounds by benzyl chloride.

#### 8.1.2 RESULTS AND DISCUSSION

##### 8.1.2.1 Comparison of Catalysts for Polycondensation of Benzyl Chloride

Results on the polycondensation of benzyl chloride over the different Fe-containing micro-, meso- and macroporous solid catalysts are presented in Table 8.1.1.

The kinetic curves of the polycondensation reactions with different catalysts are shown in Figure 8.1.1.

H-ZSM-5 zeolite (which is highly acidic) shows no activity in the polycondensation reaction, but its catalytic activity is increased drastically because of a partial or complete substitution of its framework Al by Fe or because of the impregnation of the H-ZSM-5 zeolite with  $\text{Fe}_2\text{O}_3$ . All the above observations are quite consistent with that observed earlier in the case of benzylation of benzene over these catalysts [5,6]. The high polycondensation activity of the Fe-modified ZSM-5 type zeolite catalysts is attributed to the presence of non-framework Fe-oxide species (which are added externally by impregnation or formed due to deferiation of the framework Fe during their calcination/pretreatment) [5,6] in their channels and also on their external surface, in combination with the zeolitic protons. It is interesting to note that the polycondensation reaction over the Fe-modified ZSM-5 zeolite catalysts undergoes to completion (upto 100 % conversion of benzyl chloride). This is not possible if the polycondensation would have occurred in the zeolite channels (which are small in diameter, 0.5-0.7 nm) because of the blockage of the channel by the polymer molecules formed in the initial reaction. At this reaction temperature ( $80^\circ\text{C}$ ), there is no possibility of the desorption of polymer molecules from the zeolite channel. Hence, the polycondensation reaction over the Fe-modified H-ZSM-5 occurs essentially on the Fe-oxide present on external surface of the zeolite crystals.

The high silica mesoporous MCM-41 (having no acidity) or sintered low surface area macroporous commercial silica alumina catalyst carrier, SA-5205 (having low acidity) shows no polycondensation activity but the  $\text{Fe}_2\text{O}_3$  supported on Si-MCM-41 or SA-5205 shows very high polycondensation activity.

Similarly, Mont.-K10 (having low acidity) shows no polycondensation activity but the Mont.-K10 or Si-MCM-41 supported  $\text{FeCl}_3$  catalyst show very high polycondensation activity, however,  $\text{FeCl}_3/\text{Mont.-K10}$  shows higher activity.

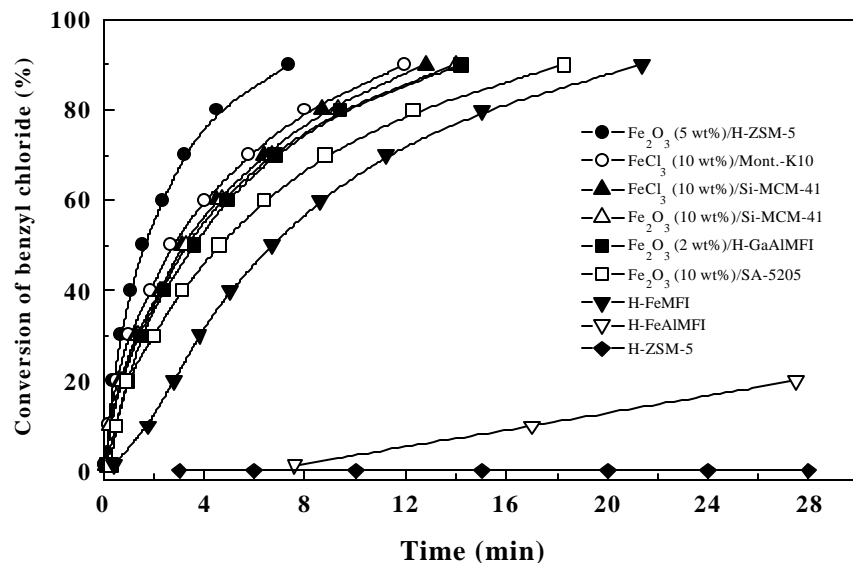
The above results reveal that the acidity alone is not enough for a catalyst to be active in the polycondensation reaction. The observed high polycondensation activity of the Fe-containing catalysts seems to be attributed to the redox properties of the iron species present in the catalyst.



**Table 8.1.1** Results of the polycondensation of benzyl chloride over different Fe-containing catalysts (reaction mixture=1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst) at different reaction temperature.

Catalyst	Types of pores	Solvent	Temperature (°C)	Time (min) required for BnCl conversion of		Induction period, $t_0$ (min)	Apparent rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )
				50 %	90 %		
H-ZSM-5	Microporous	EDC	80	No conversion upto 90 min.			
H-FeMFI	Microporous	EDC	80	6.7	23.4	0.4	112.9
H-FeAlMFI	Microporous	EDC	80	80.5	-	7.6	10.3
Fe <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	Microporous	EDC	80	1.4	7.6	≈ 0.0	348.9
Fe <sub>2</sub> O <sub>3</sub> (2 %)/H-GaAlMFI	Microporous	EDC	80	3.1	14.2	0.2	164.5
FeCl <sub>3</sub> (10 %)/Mont. K10	microporous	EDC	80	2.7	11.3	≈ 0.0	180
FeCl <sub>3</sub> (10 %)/MCM-41	mesoporous	EDC	80	2.9	12.7	≈ 0.0	170.1
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41	mesoporous	EDC	70	8.3	24	1.8	109.6
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41	mesoporous	EDC	60	15.6	36.5	6.6	82.3
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41	mesoporous	n-hexane	70	126.9	-	1.4	5.4
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41	mesoporous	n-octane	80	2.5 % conversion in 55 min.			
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41	mesoporous	ethanol	80	No conversion upto 90 min.			
Fe <sub>2</sub> O <sub>3</sub> (10 %)/MCM-41 <sup>a</sup>	mesoporous	Nil	80	Instantaneous reaction forming foamy solid product.			
Fe <sub>2</sub> O <sub>3</sub> (10 %)/SA5205	macroporous	EDC	80	4.5	18.3	0.9	125.2

<sup>a</sup> Reaction mixture = 5 ml benzyl chloride + 0.5 g catalyst.



**Figure 8.1.1** Conversion vs. reaction time plots for the polycondensation of benzyl chloride at 80°C over different Fe-containing catalysts.

### 8.1.2.2 Effect of Solvent on Polycondensation

In order to study the effect of solvent on the rate of polycondensation of benzyl chloride over Fe<sub>2</sub>O<sub>3</sub> (10 %)/Si-MCM-41 catalyst, the reaction was carried out using different solvent (viz. dichloroethane, n-heptane and ethanol) under reflux. Among the different solvents used, the reaction rate in dichloroethane is much higher whereas, in case of n-heptane and ethanol as a solvent, it is very slow and almost zero, respectively (Table 8.1.1). This is expected mostly because of the high solubility of the polymer in dichloroethane and little or no solubility of the polymer in the other solvents. When the solubility of the polymer in a particular solvent is low, the polybenzyl formed on the catalyst surface is not removed from the surface and this is expected to deactivate the catalyst due to occupation of its active sites by the product formed during the initial reaction.

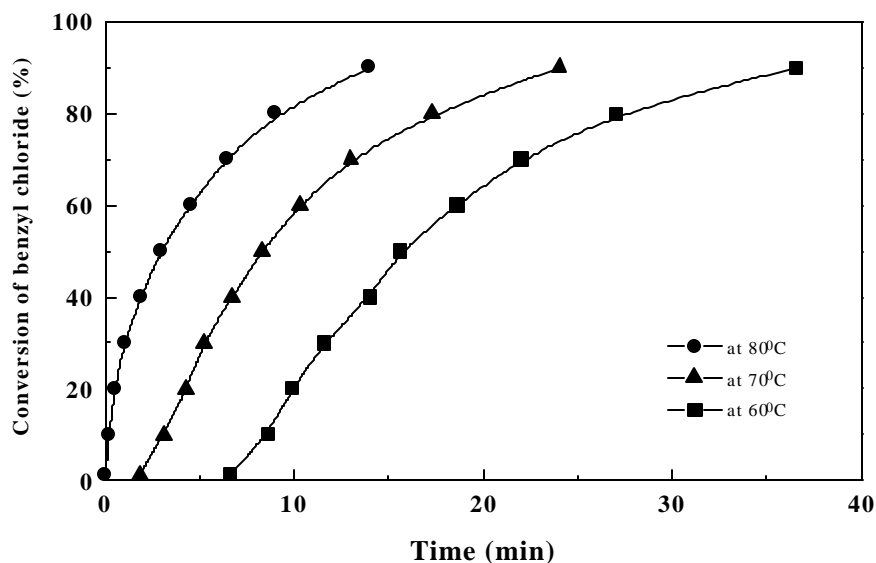
### 8.1.2.3 Kinetics and Mechanism of Polycondensation Reaction

Analysis of the results of the evolution of hydrogen chloride indicates that the polycondensation of benzyl chloride over these solid catalysts follows first order rate law (with respect to benzyl chloride conversion),

$$\log [1/(1-x)] = (k_a/2.303).(t-t_0) \quad (8.1.1)$$

where 'x' is the fractional conversion of benzyl chloride, measured in terms of the HCl evolved in the reaction, 'k<sub>a</sub>' is the apparent first order rate constant, 't' is the reaction time and 't<sub>0</sub>' is the reaction induction period. A plot of log [1/(1-x)] against (t-t<sub>0</sub>) is linear over a wide range of benzyl chloride conversion (10 % to 90 %). It was also observed in most of the earlier studies that the initial portion (upto 10 %) of the kinetic plot is not linear and the plot does not pass through the origin [1,2].

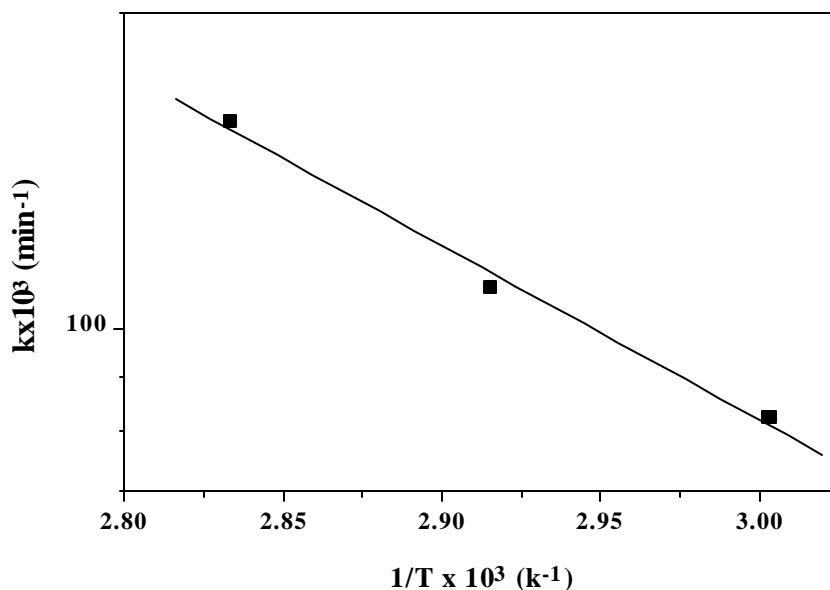
The effect of temperature on the rate of polycondensation reaction over Fe<sub>2</sub>O<sub>3</sub> (10 %)/Si-MCM-41 catalyst was studied by conducting the reaction at 60<sup>o</sup>, 70<sup>o</sup> and 80<sup>o</sup>C under similar conditions. The kinetic curves at different temperatures are shown in Figure 8.1.2. The apparent first order rate constants (k<sub>a</sub>) at the different temperatures are given in Table 8.1.2. A linear temperature dependence, according to the Arrhenius equation, for the polycondensation reaction is shown in Figure 8.1.3. The Arrhenius parameters [activation energy and frequency factor] for the polycondensation reaction, estimated from the linear Arrhenius plot for the reaction are included in Table 8.1.2.



**Figure 8.1.2** Effect of reaction temperature on the conversion of benzyl chloride in the polycondensation reaction over Fe<sub>2</sub>O<sub>3</sub> (10 wt %)/MCM-41 catalyst.

**Table 8.1.2** Kinetic parameters for the polycondensation reaction over Fe<sub>2</sub>O<sub>3</sub> (10 wt %)/MCM-41 catalyst (reaction conditions: ethylene dichloride/benzyl chloride mole ratio =18.5, catalyst/benzyl chloride wt. ratio = 0.1, volume of reaction mixture = 14 cm<sup>3</sup> and N<sub>2</sub> flow rate = 30 cm<sup>3</sup>.min<sup>-1</sup>).

Apparent rate constant, k x 10 <sup>3</sup> (min <sup>-1</sup> )			Activation energy, E (kcal.mol <sup>-1</sup> )	Frequency factor, A (min <sup>-1</sup> )
60 <sup>o</sup> C	70 <sup>o</sup> C	80 <sup>o</sup> C		
82.3	109.6	157.8	7.79	9.77 x 10 <sup>3</sup>



**Figure 8.1.3** Arrhenius plot of log k against 1/T for the polycondensation of benzyl chloride over Fe<sub>2</sub>O<sub>3</sub> (10 wt %)/MCM-41.

The polycondensation of benzyl chloride is a typical Friedel-Crafts reaction. The primary step in the polycondensation reaction seems to be the generation of stable benzyl carbonium ion, which attacks another molecule of benzyl chloride to form a dimer, as follows:







(where M = Fe and X = O or Cl and n is the no. of atoms of X needed to fulfil the valence requirement of M)

Once the dimer is formed, there is a competition between the dimer and the benzyl chloride to be attacked by the benzyl carbocation. Earlier studies [16] showed that the presence of chlorine atom in benzyl chloride reduces its reactivity, but its effect on dimer, trimer or higher polymer is small and because of this, the reactivity of polymer is assumed to be much greater than benzyl chloride. Hence the reaction proceeds to form polymer rather than leading to simple dimerisation. The conversion vs. time curves (Figure 8.1.1), showing an exponential increase in the conversion at lower reaction period (an auto-catalytic type nature) is consistent with the above.

#### **8.1.2.4 Reaction Induction Period**

Induction period for the polycondensation (Table 8.1.1) has been estimated from the intercept on the time axis of the benzyl chloride conversion vs. time curve extrapolated to the zero conversion. The kinetic curve (Figure 8.1.2) shows that the induction period increases with decreasing the reaction temperature. The observed induction period may be attributed to the formation of the active complex between the catalyst and reactants; the time required for its formation at higher temperature is shorter than that at lower temperature. It may also be due to a lower reactivity of benzyl chloride as compared to its dimer or higher polymer. It may be noted that, even in the homogeneously catalyzed polycondensation reaction of benzyl chloride [1], an induction period was observed. Our earlier studies of the benzene benzylation by benzyl chloride over these catalysts [6,17] revealed that the reaction induction period depends strongly on the moisture-content of the reaction mixture; it is increasing with increasing the moisture content and vice-versa. Further work is necessary for a clear understanding of the exact cause of the induction period in the polycondensation.

#### **8.1.2.5 Characterization of Polymer**

The polymer is characterized by NMR spectroscopy, which shows two broad singlets [ $\delta$  7.0 (4H, phenylene H) and 3.8 (2H, CH<sub>2</sub>)], indicates the condensation reaction takes place in the 4-position of the benzene ring.

The TG-DTA analysis in air of the polymer sample showed that the polymer is thermally stable upto 420<sup>0</sup>C above which it starts decomposing. The polymer is decomposed completely at 705<sup>0</sup>C.

### 8.1.3 CONCLUSIONS

From these studies, following important conclusions could be drawn:

1. All the Fe-containing catalysts [ $\text{Fe}_2\text{O}_3/\text{H-ZSM-5}$ , H-FeMFI, H-FeAlMFI,  $\text{Fe}_2\text{O}_3/\text{MCM-41}$ ,  $\text{Fe}_2\text{O}_3/\text{SA5205}$ ,  $\text{FeCl}_3/\text{MCM-41}$  and  $\text{FeCl}_3/\text{Mont. K10}$ ] show high activity with small induction period in the polycondensation reaction at the reaction temperature normally employed in the benzylation reaction with benzyl chloride. Among all the Fe-containing catalysts,  $\text{Fe}_2\text{O}_3/\text{H-ZSM-5}$  showed highest activity.
2. The polycondensation reaction over all the Fe-containing catalysts follows pseudo-first order kinetics, valid for the benzyl chloride conversion of 10 % to 90 %.
3. For the polycondensation reaction over  $\text{Fe}_2\text{O}_3$  (10 wt %)/MCM-41, the activation energy and frequency factor are  $7.79 \text{ kcal mole}^{-1}$  and  $9.77 \times 10^3 \text{ min}^{-1}$  respectively.
4. In the polycondensation reaction, the solvent plays an important role. The rate of the reaction in the different solvents is in the following order: ethylene dichloride  $\gg$  n-hexane  $>$  n-octane  $\gg$  ethanol, which is same as the order for the solubility of the polymer in the solvents.

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## 8.2 POLYCONDENSATION OF BENZYL CHLORIDE OVER Ga- AND In-MODIFIED ZSM-5 TYPE ZEOLITES AND Si-MCM-41 OR MONTMORILLONITE-K10 SUPPORTED GaCl<sub>3</sub> AND InCl<sub>3</sub> CATALYSTS.

### 8.2.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

At the time of undertaking this work, a very few studies on the polycondensation of benzyl chloride over homogeneous stannic chloride catalyst [1,2] and heterogeneous catalysts, such as ferrous sulfate [3], iron oxide [4] and Fe-containing micro-, meso- and macroporous solid catalysts [5] was reported in the literature.

Since there is a high possibility of polycondensation of benzyl chloride during the benzylation reaction, it is practically important to have the knowledge of the polycondensation over the solid catalysts used in the benzylation reactions. In our earlier studies, we have reported very high activity of different Ga- and In-modified ZSM-5 type zeolite catalysts [6-7] and Si-MCM-41 or Mont.-K10 supported GaCl<sub>3</sub> and InCl<sub>3</sub> catalysts [8-9] in the benzylation of benzene by benzyl chloride. The present investigation was, therefore, undertaken to examine the activity of the Ga- and In-containing solid catalysts for the polycondensation reaction. In addition, the effect of temperature and solvent on the polycondensation reaction over a selected catalyst has also been studied.

### 8.2.2 RESULTS AND DISCUSSION

#### 8.2.2.1 Comparison of Catalysts for Polycondensation of Benzyl Chloride

Results on the polycondensation of benzyl chloride over the different Ga- and In-containing solid catalysts are presented in Table 8.2.1.

H-ZSM-5 zeolite (which is highly acidic) shows no activity in the polycondensation reaction, but its catalytic activity is increased drastically because of a partial or complete substitution of its framework Al by Ga or because of the impregnation of the H-ZSM-5 zeolite with Ga<sub>2</sub>O<sub>3</sub> or In<sub>2</sub>O<sub>3</sub>. Among the Ga<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and In<sub>2</sub>O<sub>3</sub>/H-ZSM-5 catalysts, the later showed higher catalytic activity in the polycondensation reaction. All the above observations are quite consistent with that observed earlier in the case of benzylation of benzene over these catalysts [6,7]. The high polycondensation activity of the Ga- and In-modified ZSM-5 type zeolite catalysts is attributed to the presence of non-framework Ga- or In-oxide species (which are added externally by

**Table 8.2.1** Results of the polycondensation of benzyl chloride over different Ga- and In-containing solid catalysts (reaction conditions: reaction mixture = 1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst) at different reaction temperature.

Catalysts	Acidity <sup>a</sup> (mmol. g <sup>-1</sup> )	Solvent used in the reaction	Time (min)		Reaction induction period, $t_0$ (min)	Apparent rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )
			required for benzyl chloride conversion of 50 %	for benzyl chloride conversion of 90 %		
H-ZSM-5	0.26	Dichloroethane	No conversion upto 1.5h			
Ga <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	0.18	Dichloroethane	18.0	32.0	1.6	112.4
In <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	0.23	Dichloroethane	12.5	25.0	1.0	135.4
H-GaMFI	0.29	Dichloroethane	37.0	88.0	7.3	33.9
H-GaAlMFI	0.44	Dichloroethane	26.0	66.0	5.5	42.6
Mont.-K10	-	Dichloroethane	5 % conversion upto 1.5h			
GaCl <sub>3</sub> (10 %)/Mont.-K10	-	Dichloroethane	11.0	26.0	0.9	112.5
InCl <sub>3</sub> (10 %)/Mont.-K10	-	Dichloroethane	9.2	19.5	0.5	156.1
Si-MCM-41	-	Dichloroethane	No conversion upto 1.5h			
GaCl <sub>3</sub> (10%)/Si-MCM-41	-	Dichloroethane	14.5	30.5	2.0	104.6
InCl <sub>3</sub> (10%)/Si-MCM-41	-	Dichloroethane (at 80 <sup>0</sup> C)	10.5	22.5	1.0	148.1
InCl <sub>3</sub> (10%)/Si-MCM-41	-	n-Heptane (at 98 <sup>0</sup> C)	181.0	-	2.5	4.1
InCl <sub>3</sub> (10%)/Si-MCM-41	-	Ethanol (at 78 <sup>0</sup> C)	No conversion upto 1.5h			

<sup>a</sup> Acidity measured in terms of the pyridine chemisorbed at 400<sup>0</sup>C.

impregnation or formed due to degallation of the framework Ga during their calcination/pretreatment) [10,11] in their channels and also on their external surface, in combination with the zeolitic protons. It is interesting to note that the polycondensation reaction over the Ga- or In-modified ZSM-5 zeolite catalysts undergoing to completion (upto 100 % conversion of benzyl chloride). This is not possible if the polycondensation would have occurred in the zeolite channels (which are small in diameter, 0.5-0.7 nm) because of the blockage of the channel by the polymer molecules formed in the initial reaction. At this reaction temperature (80<sup>0</sup>C), there is no possibility

of the desorption of polymer molecules from the zeolite channel. Hence, the polycondensation reaction over the Ga- or In-modified H-ZSM-5 occurs essentially on the Ga-oxide or In-oxide present on external surface of the zeolite crystals.

Similarly, Mont.-K10, which is acidic shows very poor activity in the polycondensation reaction but the GaCl<sub>3</sub> or InCl<sub>3</sub> supported on the Mont.-K10 shows very high polycondensation activity.

Among the high silica mesoporous MCM-41 type catalysts, Si-MCM-41 (having no acidity) shows no polycondensation activity but the Si-MCM-41 supported GaCl<sub>3</sub> and InCl<sub>3</sub> catalysts show very high polycondensation activity.

The above results reveal that the acidity alone is not enough for a catalyst to be active in the polycondensation reaction. The observed high polycondensation activity of the Ga- or In-containing catalysts seems to be attributed to the redox properties of the gallium or indium species present in the catalyst. The polycondensation activity of Ga-, In- and Fe-containing catalysts (Table 8.2.2) is in the order same as that for their redox potential [ $E_{\text{Ga}^{3+}/\text{Ga}}^0$  (- 0.53 V) <  $E_{\text{In}^{3+}/\text{In}}^0$  (- 0.34 V) <  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$  (+ 0.77 V)].

**Table 8.2.2** Comparison of Ga- and In-containing solid catalysts with the corresponding Fe-containing catalysts (ref. 5) for their polycondensation activity (at 80°C) under identical reaction conditions (reaction mixture = 1 ml benzyl chloride + 13 ml solvent + 0.1 g catalyst).

Catalyst	Apparent rate constant, $k_a \times 10^3$ (min <sup>-1</sup> )	Reference
H-GaMFI	33.9	Present
H-FeMFI	112.9	5
Ga <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	112.4	Present
In <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	135.4	Present
Fe <sub>2</sub> O <sub>3</sub> (5 %)/H-ZSM-5	348.9	5
GaCl <sub>3</sub> (10 %)/Mont.-K10	112.5	Present
InCl <sub>3</sub> (10 %)/Mont.-K10	156.1	Present
FeCl <sub>3</sub> (10 %)/Mont.-K10	180.0	5

The In-containing ZSM-5, Mont.-K10 and MCM-41 catalysts show higher polycondensation activity as compared to the Ga-containing solid catalysts. Further, a comparison of the Ga- and In-containing solid catalysts with the corresponding Fe-containing solid catalysts [5] for their polycondensation activity in Table 8.2.2 shows that the Fe-containing catalysts are more active than the corresponding Ga- or In-containing catalysts. This is consistent with the earlier observations that the selectivity in the benzylation of benzene to diphenylmethane over the Ga- and In-containing solid catalysts was higher than that of the Fe-containing solid catalysts [7,8].

### **8.2.2.2 Effect of Solvent on Polycondensation**

In order to study the effect of solvent on the rate of polycondensation of benzyl chloride over  $\text{InCl}_3$  (10 %)/Si-MCM-41 catalyst, the reaction was carried out using different solvents (viz. dichloroethane, n-heptane and ethanol) under reflux. Among the different solvents used, the reaction rate in dichloroethane is much higher whereas, in case of n-heptane and ethanol as a solvent, it is very slow and almost zero, respectively (Table 8.2.1). This is expected mostly because of the high solubility of the polymer in dichloroethane and little or no solubility of the polymer in the other solvents. When the solubility of the polymer in a particular solvent is low, the polybenzyl formed on the catalyst surface is not removed from the surface and this is expected to deactivate the catalyst due to occupation of its active sites by the product formed during the initial reaction.

### **8.2.2.3 Kinetics and Mechanism of Polycondensation Reaction**

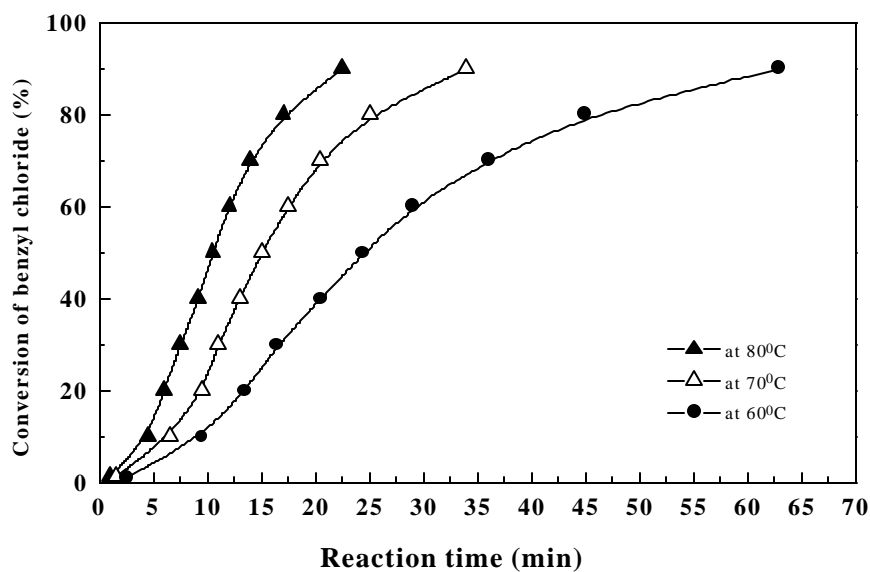
Analysis of the results of the evolution of hydrogen chloride indicates that the polycondensation of benzyl chloride over these solid catalysts follows first order rate law (with respect to benzyl chloride conversion),

$$\log [1/(1-x)] = (k_a/2.303).(t-t_0) \quad (8.2.1)$$

where 'x' is the fractional conversion of benzyl chloride, measured in terms of the HCl evolved in the reaction, 'k<sub>a</sub>' is the apparent first order rate constant, 't' is the reaction time and 't<sub>0</sub>' is the reaction induction period. A plot of  $\log [1/(1-x)]$  against (t-t<sub>0</sub>) is linear over a wide range of benzyl chloride conversion (10 % to 90 %). It was also observed in most of the earlier studies that the initial portion (upto 10 %) of the kinetic plot is not linear and the plot does not pass through the origin [1,2].

The effect of temperature on the rate of polycondensation reaction over  $\text{InCl}_3$  (10 %)/Si-MCM-41 catalyst (which showed highest polycondensation activity among the

catalysts) was studied by conducting the reaction at 60<sup>o</sup>, 70<sup>o</sup> and 80<sup>o</sup>C under similar conditions. The kinetic curves at different temperatures are shown in Figure 8.2.1. The apparent first order rate constants ( $k_a$ ) at the different temperatures are given in Table 8.2.3. A linear temperature dependence, according to the Arrhenius equation, for the polycondensation reaction is shown in Figure 8.2.2. The Arrhenius parameters [activation energy and frequency factor] for the polycondensation reaction, estimated from the linear Arrhenius plot for the reaction are included in Table 8.2.3.

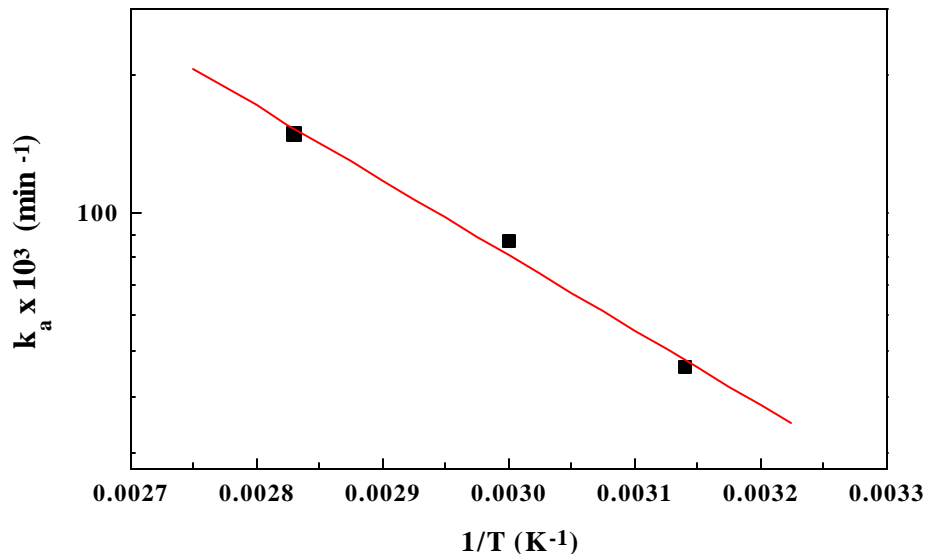


**Figure 8.2.1** Effect of reaction temperature on the conversion of benzyl chloride in the polycondensation reaction over  $\text{InCl}_3$  (10 %)/Si-MCM-41 catalyst.

**Table 8.2.3** Kinetic parameters for the polycondensation of benzyl chloride over  $\text{InCl}_3$  (10 %)/Si-MCM-41 catalyst (reaction conditions: dichloroethane/benzyl chloride mole ratio = 18.5, catalyst/benzyl chloride wt. ratio = 0.1, volume of the reaction mixture = 14 ml and  $\text{N}_2$  flow rate = 30  $\text{ml}\cdot\text{min}^{-1}$ ).

Apparent rate constant, $k_a \times 10^3$ ( $\text{min}^{-1}$ )			Activation energy, E ( $\text{kcal}\cdot\text{mol}^{-1}$ )	Frequency factor, A ( $\text{min}^{-1}$ )
60 <sup>o</sup> C	70 <sup>o</sup> C	80 <sup>o</sup> C		
46.2	87.0	148.1	7.45	$6.07 \times 10^3$





**Figure 8.2.2** Arrhenius plot of  $\log k_a$  against  $1/T$  for the polycondensation of benzyl chloride over  $\text{InCl}_3$  (10 %)/Si-MCM-41 catalyst.

The polycondensation of benzyl chloride is a typical Friedel-Crafts reaction. The primary step in the polycondensation reaction seems to be the generation of stable benzyl carbonium ion, which attacks another molecule of benzyl chloride to form a dimer, as follows:



(where  $M = \text{Ga}$  or  $\text{In}$  and  $X = \text{O}$  or  $\text{Cl}$  and  $n$  is the no. of atoms of  $X$  needed to fulfil the valence requirement of  $M$ )

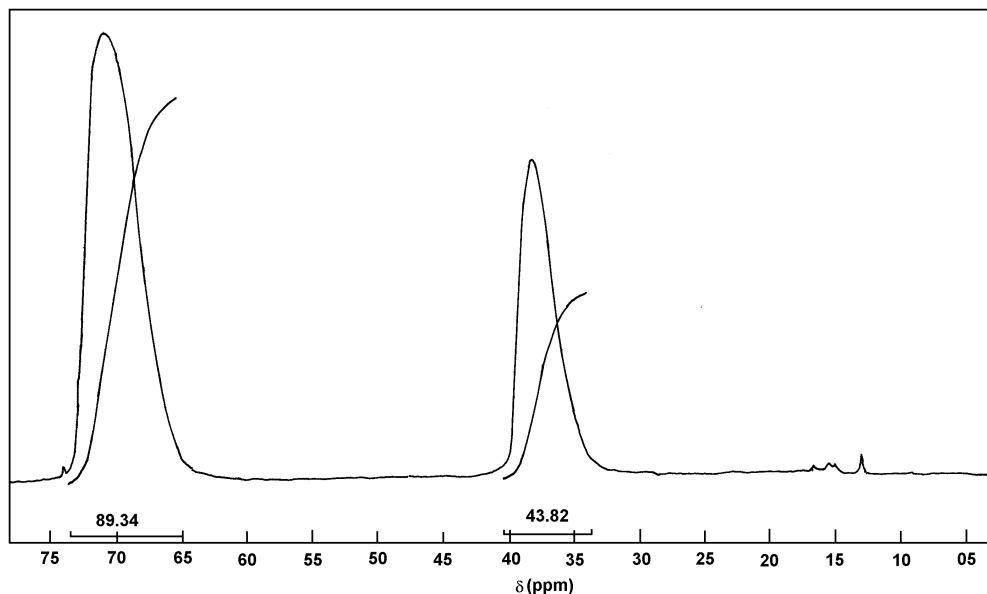
Once the dimer is formed, there is a competition between the dimer and the benzyl chloride to be attacked by the benzyl carbocation. Earlier studies [12] showed that the presence of chlorine atom in benzyl chloride reduces its reactivity, but its effect on dimer, trimer or higher polymer is small and because of this, the reactivity of polymer is assumed to be much greater than benzyl chloride. Hence the reaction proceeds to form polymer rather than leading to simple dimerisation. The conversion vs. time curves (Figure 8.2.1), showing an exponential increase in the conversion at lower reaction period (an auto-catalytic type nature) is consistent with the above.

#### **8.2.2.4 Reaction Induction Period**

Induction period for the polycondensation (Table 8.2.1) has been estimated from the intercept on the time axis of the benzyl chloride conversion vs. time curve extrapolated to the zero conversion. The kinetic curve (Figure 8.2.1) shows that the induction period increases with decreasing the reaction temperature. The observed induction period may be attributed to the formation of the active complex between the catalyst and reactants; the time required for its formation at higher temperature is shorter than that at lower temperature. It may also be due to a lower reactivity of benzyl chloride as compared to its dimer or higher polymer. It may be noted that, even in the homogeneously catalyzed polycondensation reaction of benzyl chloride [1], an induction period was observed. Our earlier studies of the benzene benzylation by benzyl chloride over these catalysts [7,13] revealed that the reaction induction period depends strongly on the moisture-content of the reaction mixture; it is increasing with increasing the moisture content and vice-versa. Further work is necessary for a clear understanding of the exact cause of the induction period in the polycondensation.

#### **8.2.2.5 Characterization of Polymer**

The polymer NMR (Figure 8.2.3) shows two broad singlets  $\delta$  7.0 (4H, phenylene H) and 3.8 (2H, CH<sub>2</sub>). The elemental analysis showed that the polymer contains 6.6-6.7 % hydrogen, 93.1-93.3 % carbon and only a trace amounts (below detectable levels) of chlorine. The elemental analysis and NMR spectra of the polymer clearly show that the polymer formed in the polycondensation is predominantly linear Para-substituted polybenzyl. The average molecular weight (measured by the vapour pressure asymmetry using benzene at 28<sup>o</sup>C) of the polymer was found to be 4400 $\pm$ 100. The polymer is also characterized by TG-DTA analysis in air, which shows that the polymer is thermally stable upto 420<sup>o</sup>C above which it starts decomposing. The polymer is decomposed completely at 705<sup>o</sup>C.



**Figure 8.2.3** NMR spectrum of the polycondensation product.

### 8.2.3 CONCLUSIONS

This work led to the following important conclusions:

1. The modification of H-ZSM-5 by completely or partially substituting its framework Al by Ga or by depositing on it  $\text{Ga}_2\text{O}_3$  or  $\text{In}_2\text{O}_3$  results in a drastic increase in its benzyl chloride polycondensation activity. Among the Ga- and In-containing solid catalysts, the  $\text{Ga}_2\text{O}_3$  (or  $\text{In}_2\text{O}_3$ )/H-ZSM-5,  $\text{GaCl}_3$ /Si-MCM-41 (or Mont.-K10) and  $\text{InCl}_3$ /Si-MCM-41 (or Mont.-K10) catalysts showed very high polycondensation activity; the  $\text{InCl}_3$ /Si-MCM-41 (or Mont.-K10) showed the highest activity. However, these catalysts are less active than the corresponding Fe-containing catalysts for the polycondensation and hence are more selective for the benzylation of aromatic compounds by benzyl chloride.
2. The polycondensation reaction over all the In- and Ga-containing catalysts follows first order kinetics, valid for the benzyl chloride conversion in the range of 10 % to 90 %.

3. For the polycondensation reaction over  $\text{InCl}_3$  (10 %)/Si-MCM-41, the activation energy and frequency factor are found to be  $7.45 \text{ kcal mole}^{-1}$  and  $6.07 \times 10^3 \text{ min}^{-1}$ , respectively.
4. The solvent used as a reaction medium plays an important role in the polycondensation. The reaction rate in the different solvents is in the following order: dichloroethane  $\gg$  n-heptane  $\gg\gg$  ethanol, which is same as the order for the solubility of the polymer in the solvents.

#### 8.2.4 REFERENCES

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## **CHAPTER-9**

***SELECTIVE ESTERIFICATION OF  
TERT-BUTANOL BY ACETIC ACID  
ANHYDRIDE OVER CLAY  
SUPPORTED  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  AND  
 $\text{ZnCl}_2$  CATALYSTS***

## Chapter-9

# SELECTIVE ESTERIFICATION OF TERT-BUTANOL BY ACETIC ACID ANHYDRIDE OVER CLAY SUPPORTED $\text{InCl}_3$ , $\text{GaCl}_3$ , $\text{FeCl}_3$ AND $\text{ZnCl}_2$ CATALYSTS

### 9.1 EARLIER LITERATURE AND OBJECTIVE OF PRESENT WORK

Recently, Nagasawa et. al. [1,2] reported the use activated basic alumina as a catalyst at mild conditions (at room temperature under argon) for the esterification of tert-butanol by acid chlorides or acid bromides. They got a good yield of tert-butyl ester but the amount of catalyst relative to the reactants used by them was very large (catalyst/reactants wt. ratio =  $2.1 \pm 0.4$  and the reaction period was also very long (9 - 15h). It is not of practical interest to use such a large amount of catalyst relative to the reactants, and moreover the removal of high molecular weight adsorbed products from the catalyst is quite difficult and expensive too. Other important drawback of their butyl ester synthetic method results from the use of an acid halide as esterification agent, because of which a highly toxic by-product, gaseous hydrogen halide, is produced in stoichiometric quantities. Hence, there is a need to develop an environmentally benign method for the esterification of tert-butanol using a highly active, selective and reusable solid catalyst having a little or no activity for the dehydration of tert-butanol.

In the present investigation, we have reported the use of clay supported  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$ , particularly Montmorillonite-K10 supported  $\text{InCl}_3$ , as a highly active and reusable catalyst for the selective esterification of tert-butanol by acetic anhydride, producing acetic acid as a by-product, at close to the room temperature.

### 9.2 RESULTS AND DISCUSSION

Results of the esterification of tert-butanol by acetic anhydride and also of the dehydration of tert-butanol to iso-butylene over the different clay supported metal chloride catalysts are presented in Tables 9.1 and 9.2, respectively. TOF (turn over frequency) of the catalysts is the number of molecules of tert-butanol converted per molecule of metal chloride present in the catalyst per second.

**Table 9.1** Results of esterification of tert-butanol with acetic anhydride to tert-butyl acetate over different clay supported  $\text{InCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  catalysts [reaction mixture = tert-butanol (t-B) + acetic anhydride (AA) + catalyst; volume of reaction mixture = 10  $\text{cm}^3$ ; t-B = tert-butanol; AA = acetic anhydride, t-BA = tert-butyl acetate; and i-B = iso-butylene].

Catalyst	Catalyst/ (t-B+AA) wt. Ratio	t-B/AA mole ratio	Reaction tempera- ture ( $^{\circ}\text{C}$ )	Reaction time (h)	Conversion (%)		Selectivity (%)		TOF ( $\text{s}^{-1}$ )
					t-B	AA	t-BA	i-B	
$\text{InCl}_3$ (without support) <sup>a</sup>	0.007	1.1	26	2	89.8	98.6	99.1	0.9	0.023
$\text{InCl}_3/\text{Mont.-K10}$	0.028	1.1	26	2	91.4	100	99.1	0.9	0.025
$\text{GaCl}_3/\text{Mont.-K10}$	0.028	1.1	26	2	87.2	95.3	99.1	0.9	0.023
$\text{FeCl}_3/\text{Mont.-K10}$	0.028	1.1	26	2	73.4	80.3	98.8	1.2	0.020
$\text{ZnCl}_2/\text{Mont.-K10}$	0.028	1.1	26	2	72.1	79.2	98.5	1.5	0.019
$\text{InCl}_3/\text{Mont.-KSF}$	0.028	1.1	26	2	77.8	85.8	98.8	1.2	0.021
$\text{FeCl}_3/\text{Mont.-KSF}$	0.028	1.1	26	2	52.2	57.3	99.6	0.4	0.014
$\text{ZnCl}_2/\text{Mont.-KSF}$	0.028	1.1	26	2	56.7	62.1	99.4	0.6	0.015
$\text{InCl}_3/\text{Kaolin}$	0.028	1.1	26	2	52.0	57.3	99.6	0.4	0.014
$\text{GaCl}_3/\text{Kaolin}$	0.028	1.1	26	2	54.0	59.3	99.6	0.4	0.014
$\text{FeCl}_3/\text{Kaolin}$	0.028	1.1	26	2	53.0	58.0	99.7	0.3	0.014
$\text{ZnCl}_2/\text{Kaolin}$	0.028	1.1	26	2	57.5	63.0	99.2	0.8	0.015
$\text{InCl}_3/\text{Mont.-K10}$	0.027	0.5	26	2	100	50.6	98.3	1.7	0.017
$\text{InCl}_3/\text{Mont.-K10}$	0.03	2.0	26	2	52.3	100	99.0	1.0	0.018
$\text{InCl}_3/\text{Mont.-K10}$	0.14	1.1	9	5	86.7	95.1	98.2	1.8	0.002
$\text{InCl}_3/\text{Mont.-K10}$	0.028	1.1	80	0.5	92.1	100	22.8	77.2	0.098
Mont-K10	0.028	1.1	80	0.5	96.5	100	≈0.0	100	-

<sup>a</sup> Homogeneous catalyst.

A comparison of the activity (TOF) of each catalyst for the esterification and dehydration reactions at the same temperature (Tables 9.1 and 9.2) shows that all the clay supported metal chloride catalysts have much lower activity for the dehydration of tert-butanol to iso-butylene. The dehydration activity of all the catalysts is very low at the room temperature ( $26^{\circ}\text{C}$ ). It is, however, increased very markedly with increasing the temperature.

**Table 9.2** tert-Butanol dehydration activity of different clay supported metal chloride catalysts at different temperatures (reaction mixture = 10 ml t-butanol + 0.2 g catalyst; reaction time = 0.5 h).

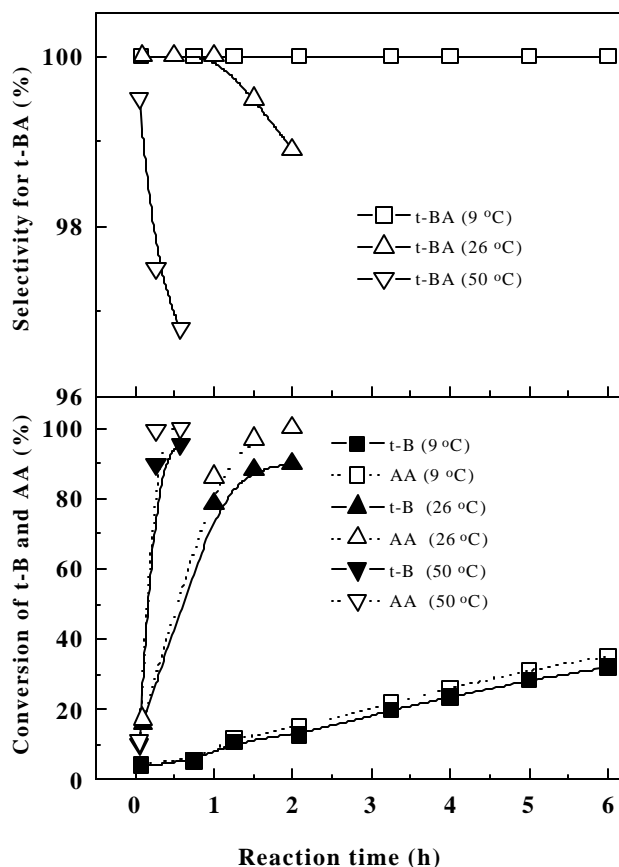
Catalyst	TOF $\bar{O}$ $10^3$ (s <sup>-1</sup> )		
	26°C	50°C	80°C
InCl <sub>3</sub> /Mont.-K10	0.23	1.35	11.10
GaCl <sub>3</sub> /Mont.-K10	0.23	0.98	10.94
FeCl <sub>3</sub> /Mont.-K10	0.23	1.92	9.86
ZnCl <sub>2</sub> /Mont.-K10	0.11	1.80	8.12
InCl <sub>3</sub> /Mont.-KSF	0.17	1.47	6.76
FeCl <sub>3</sub> /Mont.-KSF	0.11	1.41	6.20
ZnCl <sub>2</sub> /Mont.-KSF	0.11	1.38	6.11
InCl <sub>3</sub> /Kaolin	0.17	1.78	6.20
GaCl <sub>3</sub> /Kaolin	0.23	0.96	5.75
FeCl <sub>3</sub> /Kaolin	0.11	1.69	4.85
ZnCl <sub>2</sub> /Kaolin	0.17	1.67	4.96

For their esterification activity and selectivity at 26°C, the catalysts are compared in Table 9.1. The important observations made from the comparison are as follows:

- All the clay supported metal chloride catalysts show high selectivity (>98%) but they (except the Kaolin supported metal chloride catalysts) differ significantly in their esterification activity. Among the catalysts, the InCl<sub>3</sub>/Mont.-K10 shows the best performance, giving 99% selectivity for tert-butyl acetate at 100% and 91.4% (close to stoichiometric) conversion of acetic anhydride and tert-butanol, respectively.
- Among the different clays used for supporting the metal chloride catalysts, the Mont.-K10 is the best support for each of the metal chloride catalysts and the order for the choice of the clay support is Mont.-K10 > Mont.-KSF > Kaolin. The Mont.-K10 supported metal chloride catalysts have the esterification activity in the following order: InCl<sub>3</sub> > GaCl<sub>3</sub> > FeCl<sub>3</sub> ≥ ZnCl<sub>2</sub>.
- There is no decrease but a small increase in the catalytic activity of InCl<sub>3</sub> after supporting it on Mont.-K10.



Dependence of both the conversion and selectivity on the reaction time in the esterification over the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst at different temperatures ( $9^\circ - 50^\circ\text{C}$ ) is shown in Figure 9.1. The esterification reaction is very slow at  $9^\circ\text{C}$  but at higher temperatures ( $\geq 26^\circ\text{C}$ ), it is quite fast. However, the observed decrease in the selectivity with increasing the reaction time is sharper at the higher temperatures.

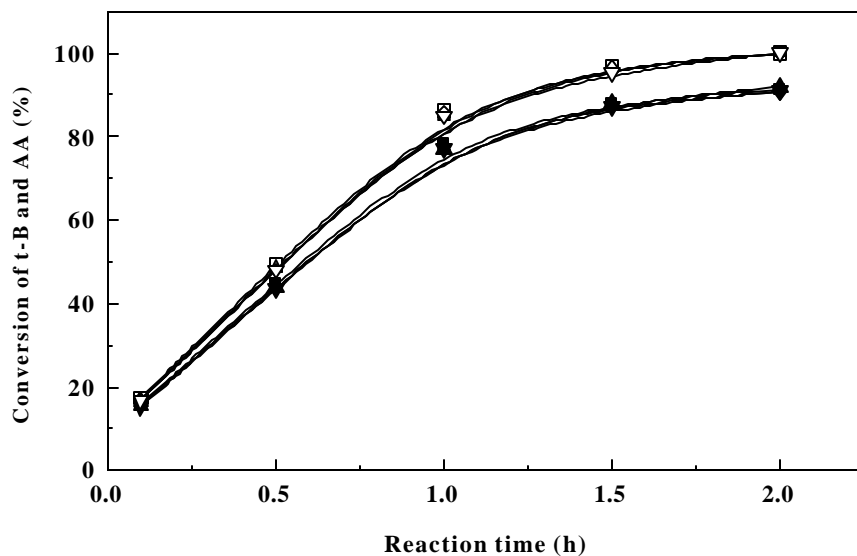


**Figure 9.1** Reaction time dependent conversion and selectivity in the esterification of tert-butanol (t-B) by acetic anhydride (AA) over the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst at different temperatures [t-B/AA mole ratio = 1.1 and catalyst/(t-B+AA) wt. ratio = 0.028].

The observed selectivity for tert-butyl acetate (t-BA) at  $50^\circ\text{C}$  (96.7%) (Figure 9.1) and particularly at  $80^\circ\text{C}$  (22.8%) at the 100 % conversion of acetic anhydride (Table 9.1)

is significantly lower than that expected from the dehydration activity of the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst at the corresponding temperatures (Table 9.2). This is due to the presence of acetic anhydride in the esterification. The acid anhydride promotes or enhances the rate of tert-butanol dehydration in the esterification process by removing the water formed in the dehydration. However, in the absence of catalyst, the conversion of tert-butanol to iso-butylene at 50°C and 80°C for the reaction period of 0.5 h was 0.5% and 3.2%, respectively. The clay support (Mont.-K10) itself shows high activity but no selectivity in the esterification at 80°C (Table 9.1). This is consistent with the earlier observation in the case of Mont.-KSF [3].

Results in Figure 9.2 show that the  $\text{InCl}_3$  (1.1mmol.  $\text{g}^{-1}$ )/Mont.-K10 catalyst is reusable in the reaction for several times. Even in its 5<sup>th</sup> reuse, the  $\text{InCl}_3/\text{Mont.-K10}$  catalyst shows very high activity and selectivity, indicating an excellent reusability of the catalyst.



**Figure 9.2** Reusability of  $\text{InCl}_3/\text{Mont.-K10}$  catalyst in the esterification reaction (reaction conditions: t-B/AA mole ratio = 1.1; catalyst/(t-B+AA) wt. ratio = 0.028 and reaction temperature = 26 °C). [Conversion of acetic anhydride: □, Δ, and ◊ for the fresh catalyst and its 1<sup>st</sup>, 3<sup>rd</sup> and 5<sup>th</sup> reuse, respectively; conversion of tert-butanol: ■, ●, ◆ and ◊ for the fresh catalyst and its 1<sup>st</sup>, 3<sup>rd</sup> and 5<sup>th</sup> reuse, respectively in the esterification].

The reactions involved in the overall esterification process are as follows:

Main Reaction:



Side Reactions:



Acetic acid in stoichiometric amounts is formed as a by-product in the process. However, it has a commercial value and it can be converted back to acetic anhydride and recycled in the process. Thus, this process does not pose any serious problem of handling and/or treating highly corrosive and toxic by-product, such as hydrogen halide produced in the process based on the use of an acid halide as an esterification agent [1,2]. Apart from its cleaner nature, the present process requires much less amount of catalyst (about 75 times less) and also less reaction period (over 10 times less) for obtaining the complete conversion of the limiting reactant than that required for the tert-butanol esterification in the earlier studies [1,2].

Other acid anhydride may also be used for the synthesis of different tert-butyl esters from tert-butanol, using the clay supported metal chloride catalysts.

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