# VALUE ADDITION OF SPENT CATALYST

By

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**Department of Chemical Engineering**

**(Environmental Process Design)**

**Institute of Technology, Nirma University**

**Ahmedabad-382481**

**May, 2011**

# VALUE ADDITION OF SPENT CATALYST

## Major Project

Submitted in partial fulfillment of the requirements

For the degree of

Master of Technology in Chemical Engineering (Environmental Process Design)

By

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**May, 2011**

# Declaration

This is to certify that

i) The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Nirma University and has not been submitted elsewhere for a degree.

ii) Due acknowledgement has been made in the text to all other material used.

**Madeti Madhavi Priyadarshini**

# Certificate

This is to certify that the Major Project entitled ”Value Addition of Spent Catalyst” submitted by Madeti Madhavi Priyadarshini (09MCH004), towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering(Environmental Process Design) of Nirma University of Science and Technology, Ahmedabad is the record of work carried out by her under our supervision and guidance. In our opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of our knowledge, haven’t been submitted to any other university or institution for award of any degree or diploma.

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# Abstract

Catalysis is one of the 12 principles of the green chemistry in which catalyst is used to change the rate of chemical reaction and affect the reaction environment favorably. But the catalyst activity may decrease to very low levels and further regeneration may not be economically feasible. Hence the spent catalysts are eventually discarded as solid wastes.

Present study is aimed at exploring an effective method to utilize exhausted petroleum catalyst discarded in large volume from petroleum refining industries. Silica and alumina are the major components of selected spent catalyst. Considering the quality and quantity of the available exhausted catalyst, an attempt to use this as raw material for synthesis of zeolite is explored. Also, its probable application as support for making heterogeneous catalyst is explored.

Conversion of spent catalyst into NaA(4A) zeolite was carried out by hydrothermal synthesis comprising of two primary steps: i) Extraction of silica followed by gel formation and ii) Hydrothermal synthesis at elevated temperature and time. Extraction of silica was studied under different conditions like use of spent catalyst i) with and without grinding and ii) varying parameters like gel conditions like ageing and stirring and iii)parameters like time and temperature of hydrothermal synthesis. Synthesized samples were characterized using various techniques like ICP-OES, X-ray diffraction, FTIR for composition of material, identification of crystalline phases and crystallinity, formation of zeolites, respectively. Water adsorption property of selected samples showed lower adsorption compared to reference samples. This was due to the impurity phases present in the sample confirmed from XRD data. Ion exchange properties of synthesized 4A were also evaluated for the removal of heavy metals like cadmium (Cd), copper (Cu) and lead (Pb) from water under static conditions.

Suitability of spent catalyst as a support for making zincoxide and indiumoxide catalyst was studied and their catalytic performance for liquid phase benzylation was evaluated.

Around 93% crystallinity is obtained for 4A synthesized with ground spent catalyst and the lowering in crystallinity is attributed to the unconverted spent catalyst. Substantial calcium exchange capacity was observed (5.14 meq$CaCO_3$/g)indicating its possible use in detergent applications. Ion exchange capacity of synthesized 4A for the removal of heavy metals like cadmium (Cd), copper (Cu) and lead (Pb) from water was found to be quite efficient.The binding property of the spent catalyst to use it as support in heterogeneous catalyst was found to be poor which needs to be improved.

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# Chapter 1

# Introduction

**Green chemistry**, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances [1] . In the last decade, it has been recognized as a new approach to scientifically based environmental protection, and catalysis has manifested its role as a fundamental tool in pollution prevention [2] . Large variety and volume of heterogeneous catalysts are used in the petroleum refining industry for the up-gradation and purification of various petroleum streams and residues. The catalysts deactivate with time and when the activity of the catalyst declines below the acceptable level, it is usually regenerated and reused. But, regeneration is not always possible and after a few cycles of regeneration and reuse, the catalyst activity may decrease to very low levels and further regeneration may not be economically feasible. Hence the spent catalysts are eventually discarded as solid wastes.

The quantity of spent catalysts discharged from different processing units depends largely on the amount of fresh catalysts used, their life as well as effect of reaction conditions like temperature and pressure, amount and type of the deposits formed during use. In most refineries, a major portion of the spent catalyst waste comes from hydrotreating, fluid catalytic cracking and hydroprocessing units. This is because the catalysts used in these processes deactivate rapidly by coke and metal (V and Ni) deposits, and have a short life [3]. Furthermore, technology for regeneration and reactivation of the catalysts deactivated by metal fouling is not available to the refiners [4].

Major refineries worldwide along with their capacity are listed in figure 1.1 [3] which need huge amount of catalyst for the processing of crude oil. One of the largest refinery of India, Reliance Industries Limited, Jamnagar, uses various catalytic processes for hydrocarbon refining. Hence spent catalyst generated is also very high figure 1.2 [4] . The total spent catalyst waste, however, is highest in North America as number of refineries in USA is more followed by Asia Pacific.

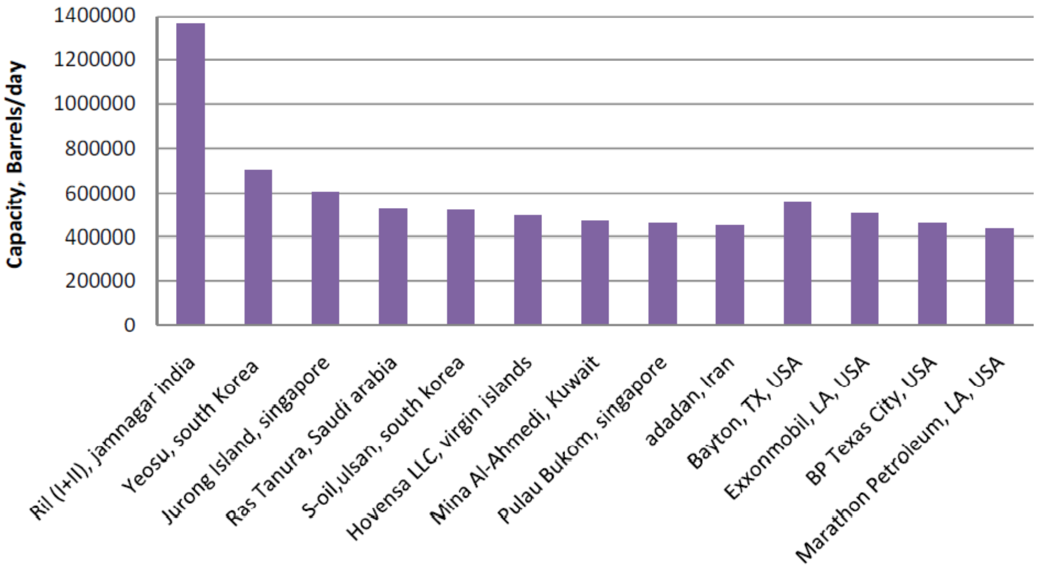


Figure 1.1: Major Refineries worldwide

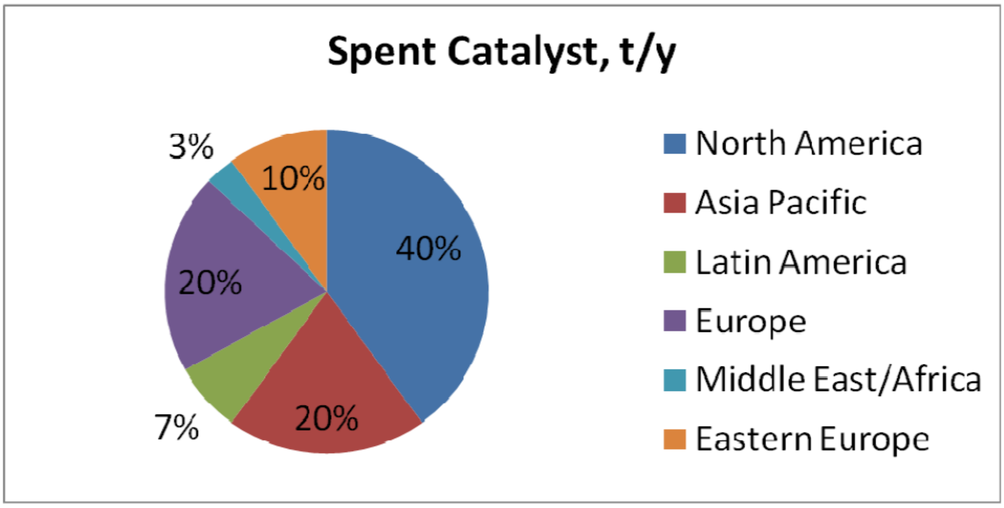


Figure 1.2: Approximate generation rate of Spent Catalyst worldwide (2006)

## 1.1 The Hazardous Wastes (Management and Handling) Amendment Rules

The Ministry of Environment and Forests (MoEF), Government of India [5], notified the Hazardous Waste (Management and Handling) Rules, in July 1989 under the Environment (Protection) Act, 1986. On 6th of January 2000, major amendments in these rules were done with regard to redefined categories of hazardous wastes and harmonizing them with the international environmental laws. Again, these rules have been amended as the Hazardous Wastes (Management and Handling) Third Amendment Rules, 2010. In this act, hazardous waste listing had also been done in which spent catalyst from petroleum refining is also considered [6].

## 1.2 Environmental Impact

Environmental laws concerning disposal of spent heterogeneous catalyst have become increasingly more severe in recent years. The most important hazardous characteristic of spent refinery catalysts is their toxic nature. Chemicals such as V, Ni, Mo and

Co present in the catalyst can be leached out by ground water after their disposal and pollute the environment. Besides the formation of leachates, spent catalysts, when in contact with water, can liberate toxic gases. The formation of the dangerous HCN gas from the coke deposited on spent catalyst that contains a substantial amount of nitrogen has been reported [2].

The hazardous nature of the spent catalysts is attracting the attention of environmental authorities in many countries and the refiners are experiencing pressures from environmental authorities for safe handling of spent catalysts. Several alternative methods such as disposal by landfills, reclamation of metals, regeneration or rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problem. The choice between these options depends on technical feasibility and economic considerations [2].

## 1.3 Spent Catalyst Handling

### 1.3.1 Disposal as Landfill

Historically, spent catalysts have been disposed off as landfill in approved dump-sites. Catalyst or any other waste could be disposed off into a secured landfill only if it could be proven with certainty that the landfill met non-hazardous criteria. In the USA, the disposal and treatment of spent refinery catalysts is governed by the Resource Conservation and Recovery Act (RCRA), which holds not only the approved dump-site owner liable, but the owner of the buried waste as well. This environmental responsibility continues for the life of the dump-site. The current RCRA regulations require landfills to be built with double liners as well as with leachate collection and groundwater monitoring facilities. Thus, the landfill option is becoming expensive today. In addition, it carries with it a continuing environmental liability. However, when the other alternatives such as regeneration and reclamation are not viable economically, disposal as landfill is the only option available. But there are various alternatives available to handle spent catalyst [2].

### 1.3.2 Reclamation of Metals

Recovery of metals and other components from the spent catalysts is possible, and the technology for the metal reclamation is well established. For catalysts containing precious metals such as platinum, palladium, metals recovery processes are highly profitable. For spent petrorefining catalysts which contain Mo, Ni, Co and V, process economics for the recovery of the metals are influenced by metal prices, metals content, transportation costs and purity of recovered metals.

Metal reclaimer use one of the two methods: hydrometallurgy or pyrometallurgy. Hydrometallurgy dissolves the metals by leaching the catalyst with an acid or base. The metals are then recovered as marketable metal compounds or metals. Pyrometallurgy uses a heat treatment such as roasting or smelting to separate the metals. It melts the spent catalyst at high temperatures, often with the aid of a flux to lower the melting temperature and viscosity of the slag. The metals sink to the bottom of the melt and are recovered and sold. The catalyst base/ substrate floats to the surface as a slag that can be recovered and sold as a commercial commodity. In case spent refining catalysts, all components can be recovered without leaving any residue by these processes. The recovered metals such as Mo, V, Ni and Co could be used in steel manufacture. [2]

## 1.4 Various alternatives to handle Spent Catalyst

Safe disposal of spent catalysts is a significant environmental problem as landfill disposal is no longer accepted as the best practice. In many cases, the spent catalysts have been classified as hazardous waste material and are subject to stringent disposal guidelines. Most major refinery companies have set up special disposal practices and only allow authorized waste collectors and processors to dispose the catalyst waste. Some of the alternate uses of spent catalysts are given below:

### 1.4.1 Processing waste over spent FCC catalyst

Distress feeds, such as refinery sludge and slop oils are removed from an FCC regenerator. Hot spent catalyst demetallizes and / or demulsifies slop and sludge streams in an auxiliary reactor without contaminating the FCC catalyst inventory. Waste streams are upgraded with a 'Waste' Catalyst stream. The auxiliary reactor and FCC reactor may share a product fractionator [7].

### 1.4.2 Spent refinery catalyst as a synergistic agent in intumescent formulations

Spent FCC catalyst and its individual components were incorporated into ammonium polyphosphate and pentaerythritol intumescent systems. The influence of spent catalyst particle size on flame retardancy performance was clearly demonstrated. By using finer catalyst fractions, the materials produced exhibited a greater amount of high temperature residue and lower rates of heat release, CO, $CO_2$ and smoke emission. From the major catalyst components only the zeolite and kaolin enhanced fire performance of the intumescent systems. Experimental results indicated that aluminosilicates are efficient flame retardancy enhancers than silica or alumina alone [8].

### 1.4.3 Application in construction industry

Spent FCC catalyst has been successfully used as a very reactive pozzolanic material. The presence of spent FCC catalyst in Portland cement systems with low water/binder ratio enhanced the mechanical properties of mortars due to the important portlandite fixation degree. Selected interesting data on FCC reactivity and compressive strength ($R_c$) behavior for FCC-concrete are described and analyzed. It has been shown by Monzo et. al. that by replacing cement with spent FCC catalyst, compressive strength is substantially increased by 20% than that of concrete alone (Rc¿100MPa for 28 days curing time) [9].

### 1.4.4 Encapsulation of heavy metals on Spent FCC Catalyst

Vanadium and Nickel were found as major contaminants on spent FCC catalyst in oxide form at levels of 3518 and 3225 ppm respectively. The catalysts tested had lower levels than projected levels of 5000 ppm for both vanadium and nickel. Spent FCC with such a high content of toxic metals cannot be securely landfilled. Hence to meet the environmental regulations, encapsulation treatment with up to 60 wt % spent FCC catalyst in Portland cement, is an effective means of stabilization [10].

### 1.4.5 Conversion to new catalyst

Utilization of spent residue hydroprocessing catalysts, which contained high levels of vanadium, in the preparation of active new hydrodemetallization catalyst compositions. The metal fouled spent catalyst with very low surface area and pore volume was subjected to metal-leaching or hydrothermal treatment to reduce the fouling effect of vanadium and then mixed and extruded with boehmite to prepare new catalysts extrudates. The recycling of spent residue hydroprocessing catalysts containing high levels of vanadium was used successfully in the preparation of active new hydrotreating catalyst. Spent catalyst was subjected to different treatments such as decoking, acid-leaching and hydrothermal treatment for its use [11].

### 1.4.6 New Material from Spent Catalyst

Heterogeneous spent catalysts are generally aluminosilicate compounds containing active and promoter metals. Many refining catalysts are having high concentration of silica and alumina hence they can be used as silica source in making new inorganic materials. Table 2.1 shows the composition of a spent catalyst and other waste materials. Looking at the chemical composition, the spent catalyst can be a good source of silica to make a zeolite.

### 1.4.7 Using the spent catalyst for catalysis applications

Much information or literature was not available for using the spent catalyst in catalysis application for synthesizing fine chemicals. But an approach has been taken to utilize it in heterogeneous catalysis with and without modification of the decoked spent catalyst with metal loading for the Freidel Crafts liquid phase benzylation of *o*-xylene and benzyl chloride.

## 1.5 Scope and outline of the thesis

Present study is aimed at exploring an effective method to utilize spent petroleum catalyst for an alternate use.. Spent catalyst was collected from the Refining unit of Reliance Industries Limited. Considering the quality and quantity, attempt has been made to convert this exhausted catalyst into 4A zeolite having suitable characteristics for detergent application. For achieving required quality of 4A zeolite, synthesis was carried out with varied parameters, viz. particle size of spent catalyst, method of silica extraction, aging period of gel, hydrothermal synthesis temperature, and time. Synthesized 4A material was evaluated for their application in removal of heavy metals from water.. An adsorption uptake of the metal ions with time has been calculated for synthesized 4A and reference 4A zeolite and compared.

Application of spent catalyst in preparation of new catalyst is also explored. Spent catalyst under study contains small amount of mixed zeolites. It is well known that zeolites are considered as environmentally friendly catalysts. Deposition of active components like zinc and indium chloride by wet incipient technique is attempted and the material was characterized for its acidic characteristics. Catalytic application of new material in Friedal Crafts liquid phase benzylation of o-xylene and benzyl chloride is also tested.

# Chapter 2

# Literature Review

## 2.1 Zeolite 4A

From 1949 through the early 1950s, the commercially significant zeolites A, X and Y were discovered by Milton and Breck at the Tonawanda, New York, laboratories of the Linde Air Products Division of Union Carbide Corporation [12]. In 1953, Linde Type A zeolite, also called zeolite A, NaA and 4A zeolite, figure 2.1 became the first synthetic zeolite to be commercialized as an adsorbent to remove oxygen impurity from argon at a Union Carbide plant [13]. New zeolites and new uses appeared steadily through the 1960s. An explosion of new molecular sieve structures and compositions occurred in the 1980s and 1990s from the aluminosilicate zeolites to the microporous silica polymorphs to the microporous aluminophosphate based polymorphs and metallo-silicate compositions [14]. Molecular sieves now serve the petroleum refining, petrochemical, and chemical process industries as selective catalysts, adsorbents and ion exchangers.

Zeolite A has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units 4, 6, 8, and 4-4. The pore diameter is defined by an eight member oxygen ring and is small

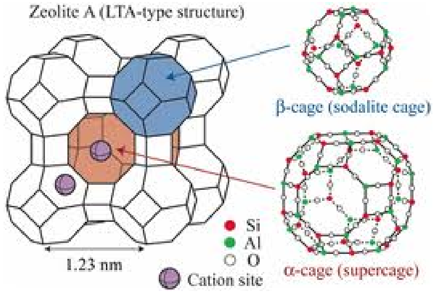


Figure 2.1: Zeolite A

at 4.2Å. This leads into a larger cavity of minimum free diameter 11.4Å. The cavity is surrounded by eight sodalite cages (truncated octahedra) connected by their square faces in a cubic structure. Zeolite A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700℃[15], [16], [17].

## 2.2 Synthesis of 4A Zeolite

Silica and alumina are the two major components of selected spent catalyst. Enormous literature is available in the area of zeolite synthesis using cheaper silica source from the spent catalyst [18], coal fly ash [19],[20],[21],[22],[23],[24] as well as rice husk ash [25],[26],[27]. The constituents of Coal Fly Ash (CFA) [23] and Rice Husk Ash (RHA) [29] are shown in table 2.1. Various alternate silica sources and different synthesis approaches like synthesis using ultrasound and microwave technology are used. By sonocrystallization there is a possibility of increasing the nucleation and crystallization rates of zeolites, improving the yield and particle size distribution of the product crystals [28]. When synthesis is carried out using microwave technology, Crystallization rate increases by 45% more than the conventional hydrothermal synthesis.

The common hydrothermal synthesis procedure for zeolite A is shown in figure 2.2.

Table 2.1: Elemental Analysis of Spent Catalyst, CFA and RHA

| **Element mass %** | **Spent Catalyst** | **Coal Fly Ash (CFA)** | **Rice Hush Ash (RHA)** |
|---|---|---|---|
| $SiO_2$ | 58.8 | 50.09 | 88.86 |
| $Al_2O_3$ | 26.8 | 24.91 | 6.4 |
| $Na_2O$ | 0.16 | 0.14 | 1.16 |
| $Fe_2O_3$ | 0.48 | 7.6 | 0.35 |
| $La_2O_3$ | 1.97 | - | - |
| $P_2O_5$ | 2.98 | - | - |
| **Other** | 8.81 | 16.45 | 3.23 |

## 2.3 Environmental Applications of Zeolite 4A

Due to high cation exchange capacity (CEC), as well as small size particles, type A zeolite is widely used in water treatment, in particular for incorporation into the composition of detergents for the sequestration of calcium from wash water [30], [31].However, for this application, the cost of the zeolite must be low, demanding the utilization of cheap raw materials for the production process. However, the main environmental application of zeolite A is particularly concerned in wastewater treatment(Figure 2.3). Many industrial processing and wastewater streams, such as waters from leaching, mining, rinsing, etc., contain rare and/or toxic heavy metals mixed with other pollutants, frequently organic substances and ammonium ions. They are known excellent adsorbents that can readily adsorb and exchange several toxic substances in their framework. The presence of heavy metals in the environment is an issue of great concern because of growing discharge, toxicity and other adverse effects of heavy metals on the receiving waters.

## 2.4 Removal of Heavy Metals

Heavy metal pollution is a global issue, although severity and levels of pollution differs from place to place. At least 20 metals are classified as toxic with half of them emitted

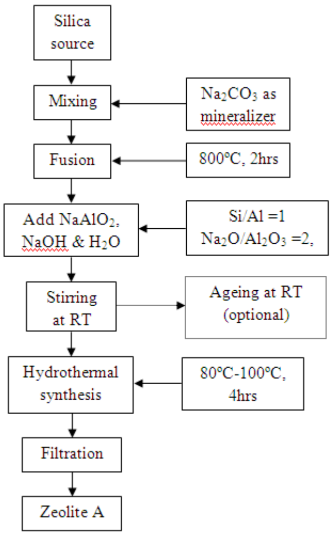


Figure 2.2: Hydrothermal Synthesis of Zeolite A

into environment in concentrations that pose great risks to human health. The common heavy metals that have been identified in polluted water include arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc. The release of these metals without proper treatment poses a significant threat to public health because of their persistence, biomagnification and accumulation in food chain. Severe effects include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system [32].

Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption and reverse osmosis. Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ionexchange is feasible when an exchanger has a high selectively for the metal to

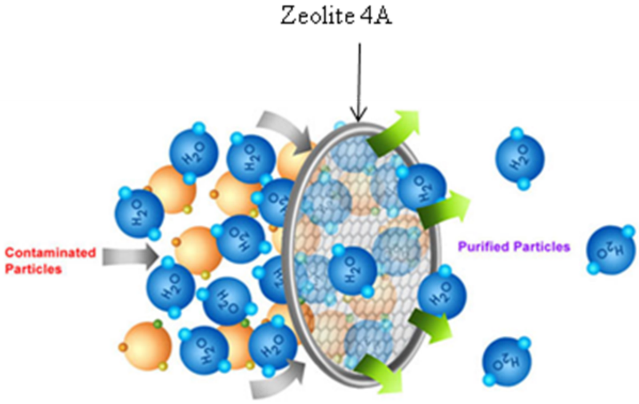


Figure 2.3: Wastewater treatment using Zeolite 4A

be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals [31], [33].

Adsorption of these heavy metals on conventional adsorbents such as activated carbon have frequently been employed, but just like the other conventional adsorbents, the use of expensive materials and the necessity to control the discharge of these loaded material makes the processes non-cost effective [34]. Zeolite A appears to be one of the most promising to perform metal purification function. The advantage of zeolite A over resins, apart from their much lower cost, is their ion selectivities. Owing to zeolite A structural characteristics and their adsorbent properties, they have been applied as chemical sieve, water softener and adsorbents [19].

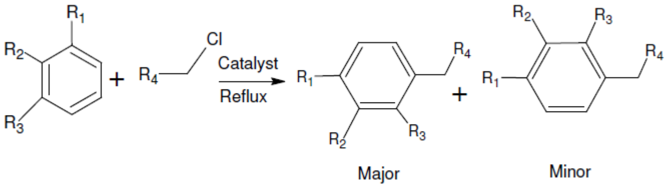
## 2.5 Friedal-Crafts Alkylation

Friedel-Crafts alkylations are a very important class of reactions commonly used in organic chemistry [35], [36]. Among these reactions, the liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride or benzyl alcohol is important for the production of diphenylmethane and substituted diphenylmethane which are industrially important compounds used as pharmaceutical intermediates [37] or fine chemicals [38], [39]. These reactions are generally known to proceed over homogeneous lewis acid catalyst using $AlCl_3$, $FeCl_3$, $BF_3$, $ZnCl_2$ and $H_2SO_4$ [40]. However, these acid catalysts are toxic and corrosive. Moreover, the isolation of the product is very difficult and causes severe pollution. The new environmental legislations urge for the replacement of all liquid acids by solid acid catalysts which are environmentally friendlier and allow to minimize pollution and waste [41]. Indeed, several solid acid catalysts having a good efficiency, which can be easily separated from the reaction mixture and also have high activity has been proposed for the benzylation of benzene and other aromatic compounds.

Zeolite catalysts due to their shape selectivity, thermostability, the easy separation from the products and the possibility of regeneration of the deactivated catalysts are used extensively in the petroleum refining and petrochemical industries for various cracking, hydrocracking, isomerization, alkylation, dehydrogenation and rearrangement reactions of hydrocarbons and their derivatives. The use of zeolite catalysts in the synthesis of fine chemicals is an increasing area of application of growing importance in recent years [42], [43].

The general Friedal crafts alkylation takes the route below:

- Compound I is benzene if $R_1$, $R_2$ and $R_3$ = H or Toluene if $R_1$, $R_2$ = H and $R_3$ = $CH_3$ or xylene if $R_1$ = H , $R_2$ and $R_3$ = $CH_3$.
- Compound II is benzyl chloride if $R_4$ = $C_6H_5$ or 4-methylbenzyl chloride if



$R_4 = p - CH_3C_6H_4$

- Compound III is diphenylmethane if $R_1$, $R_2$, $R_3$ = H, $R_4 = C_6H_5$ or 1-benzyl-4-methylbenzene if $R_1 = CH_3$, $R_2$ ,$R_3$ = H, $R_4 = C_6H_5$ or if $R_1$, $R_2$, $R_3$ = H, $R_4 = p - CH_3C_6H_4$ or diethylmethane if $R_1 = CH_3$, $R_2$, $R_3$ = H, $R_4 = p - CH_3C_6H_4$ or 4-benzyl-1,2-dimethylbenzene if $R_1$, $R_2 = CH_3$, $R_3$ = H, $R_4 = C_6H_5$ or 3,4-dimethyldiphenylmethane if $R_1$, $R_2 = CH_3$, $R_3$ = H, $R_4 = p - CH_3C_6H_4$

The present work focused on the benzylation of benzene, toluene and *o*-xylene with benzylchloride (BC) using the modified spent heterogeneous catalyst. The catalysts were prepared by incorporating $Zn^{+2}$ and $In^{+3}$ ions into the pores of the spent catalyst by wet incipient technique. Zeolite shows less activity in such type of reaction in spite of very strong acidity. In order to enhance the Lewis acidity and activity it was modified by transition metals [36], [43], [44], [45] [46].

# Chapter 3

# Materials and Experimental Methods

## 3.1 Raw materials

Commercially available chemical reagents (AR Grade, Sigma Aldrich and Labort Fine Chem Pvt. Ltd.) are of high purity and were used directly without further purification. The spent catalyst was received from Reliance Industries Limited, Jamnagar from its one of the processing unit was used in this study. It mainly contains Y zeolite, ZSM-5, additives and clay binders. The analysis of the spent catalyst was performed in duplicate using microwave digestion followed by estimation using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the data are presented in Table 3.1. Sample obtained was also ground at a speed of 5.0 for 20 min which was conducted in attrition "ball mill" (Fritts Pulverisers Analysands Laboratory).

Table 3.1: Chemical composition of Spent Catalyst (Mass %)

| | $SiO_2$ | $Al_2O_3$ | $Na_2O$ | $Fe_2O_3$ | $La_2O_3$ | $P_2O_5$ | Other |
|---|---|---|---|---|---|---|---|
| **Lot1** | 54.2 | 34.9 | 0.5 | 0.37 | 2.26 | 0.93 | 6.84 |
| **Lot2** | 58.8 | 26.8 | 0.16 | 0.48 | 2.98 | 1.97 | 8.81 |

## 3.2 Extraction of Si and Al

Extraction of silica and alumina was carried out by varying alkali concentration, temperature and time of extraction. Samples without grinding were subjected for extraction study. 5g of the sample was taken in 150ml of alkali (concentration, 2 to 5M) and digested at two different temperatures (80℃and 100℃) for various extraction times (30min - 240min). % silica extraction was computed by estimating silica.

## 3.3 Zeolite 4A Synthesis

Zeolite synthesis was carried out by hydrothermal method. Two approaches were used:
I) Synthesis without fusion
II) Synthesis after alkali fusion
For each method spent catalyst was used as such and after ball milling. The Hydrothermal synthesis method followed is shown in Figure 3.1. 10g spent catalyst (SC) and 5g $Na_2CO_3$, was taken in a platinum dish, mixed thoroughly and fused under static conditions at 800℃, for 2h in a furnace. Reaction mixtures were prepared by addition of aqueous NaOH solution and sodium aluminate (56% $Al_2O_3$, 44% $Na_2O$) to the fused mixture, during stirring at room temperature for 24 hours. Optionally, this mixture was aged for 24 h at room temperature, without stirring. The alkaline solution added at the beginning of the reaction was prepared so as to reach a molar ratio $Na_2O/Al_2O_3$ = 2:1 and $SiO_2$:$Al_2O_3$ =2:1, which is favorable for obtaining 4A zeolite as the principal final product. Hydrothermal crystallization was performed at varied temperatures from 80-100℃for 4 hours in closed reactors. The solid was isolated from the liquid phase by filtration, washed with DM water and dried at 110℃overnight.

Table 3.2: Gel composition used for Zeolite 4A synthesis

| **Particulars** | **Substance** | **Molecular weight (g/mol)** | **Mass used (g)** | **Moles** |
|---|---|---|---|---|
| **Solvent** | $H_2O$ | 18 | 75 | 4.16 |
| **Activator** | $Na_2CO_3$ | 106 | 5.3 | 0.05 |
| **Mineralizer** | NaOH | 40 | 2.244 | 0.0561 |
| **Aluminate Source** | $NaAlO_2$ | 82 | 4 | 0.0487 |
| **Aluminosilicate source** | Spent Catalyst | | 10 | 0.096$SiO_2$<br>0.026 $Al_2O_3$ |

Molar gel Compositions:$2SiO_2$:$Al_2O_3$:$2Na_2O$:$36H_2O$

In both the synthesis procedures, the raw materials were activated by magnetic stirring to produce a reaction gel with a specific molar composition. The hydrothermal reaction was carried out under similar conditions for both the approaches except the fusion part which was absent in case of synthesis without fusion. Table 3.2 shows the gel composition used and Table 3.3 shows synthesis conditions.

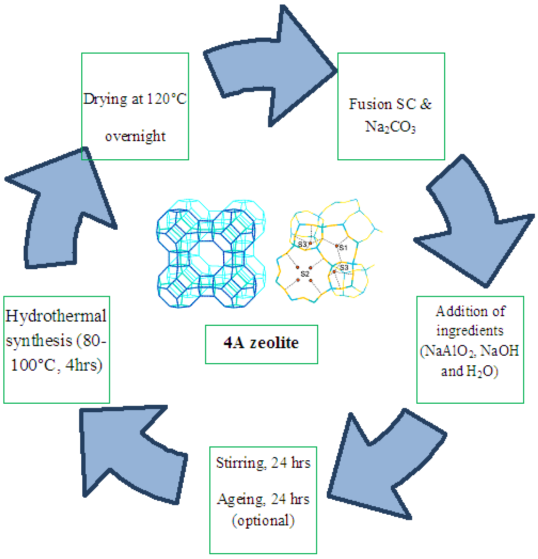


Figure 3.1: Hydrothermal Thermal Synthesis of 4A zeolite

Table 3.3: Conditions of Hydrothermal Synthesis for 4A

| **Sample Code** | **Si/Al** | **Stirring hrs** | **Ageing hrs** | **S T ℃** | **St hrs** |
|---|---|---|---|---|---|
| **MP005** | 1 | 24 | 0 | 80 | 4 |
| **MP006** | 1 | 24 | 24 | 80 | 4 |
| **MP007*** | 1 | 24 | 40 | 90-95 | 1.5-2.5 |
| **MP009** | 1 | 24 | 0 | 80 | 4 |
| **MP010** | 1 | 24 | 0 | 90-95 | 1.5-2.5 |
| **MP011** | 1 | 24 | 0 | 100 | 4 |
| **MP012** | 1 | 24 | 24 | 100 | 4 |
| **MP013** | 25/75 | 24 | 24 | 80 | 4 |
| **MP014** | 40/60 | 24 | 24 | 80 | 4 |
| **MP017** | 75/25 | 24 | 24 | 80 | 4 |
| **MP018** | 1 | 24 | 24 | 100 | 4 |
| **MP019** | 1 | 24 | 24 | 100 | 4 |
| **MP020** | 1 | 24 | 24 | 100 | 4 |
| **MP022** | 1 | 24 | 24 | 100 | 4 |
| **MP026**** | 1 | 24 | 24 | 100 | 4 |
| **MP040** | 1 | 24 | 24 | 100 | 4 |

MP007:Fusion with NaOH (NaOH:SC =1:1.2), **MP026:Ground sample

## 3.4 Adsorption Isotherms

The adsorption capacity of spent catalyst, reference 4A and synthesized 4A samples, in the form of powder, was carried out using standard McBain adsorption isotherm procedure as shown below. Water and benzene adsorptions are studied for the selected samples. Molecular size of Benzene is 6 Å[49] and Water is 2.85 Å. Data obtained was compared with reference commercial 4A. Figure 3.2 shows the McBain Adsorption Isotherm setup used for this test.

**Working of McBain Adsorption Isotherm**

1. Loading of adsorbent around 200mg.

2. Note the extension of quartz spring before and after loading of the adsorbent and keep it for activation.

3. Heat the adsorbent by evacuation upto $10^{-3}$mm Hg and 350℃for 4 hours and cool

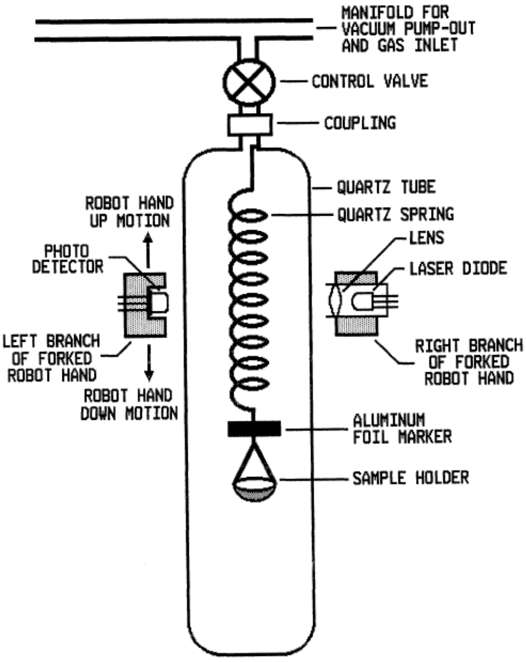


Figure 3.2: McBain Adsorption Isotherm Setup

it to room temperature by removing the electric heater.

4. Degas the water with liquid nitrogen or dry ice.

5. Introduce the water into the system by pulse for liquid and increase the pressure slowly. (Note: Pressure should not cross 1 atm).

6. Measure extension of spring after every pulse by using Cathetometer and calculate the amount adsorbed at different pressure.

## 3.5 Calcium exchange capacity

The calcium exchange capacity is an important parameter in the characterization of 4A zeolite. Solutions containing various concentration of calcium (10, 50, 100, 200, 500 and 1000 $\mu$gCa/ml) were taken in a conical flask with a constant volume/weight ratio (Vol. 10 ml and zeolite wt. 0.5g) at room temperature. The solutions were stirred intermittently and left for 24 hours to attain equilibrium after which the samples were centrifuged (REMI Laboratory Centrifuge), for 20 minutes at 3000 rpm and final concentration of calcium were analyzed using ICP-OES.

## 3.6 Toxic Metals Exchange

Due to good cation exchange capacity of 4A zeolite, it is used for toxic metal removal. In present study, equilibrium exchange (Figure 3.4) of various toxic metals like Cadmium (Cd), Copper (Cu) and Lead (Pb) from aqueous solutions was determined. Batch adsorption experiments were conducted using 0.5g of catalyst with 10 ml of solutions containing varied concentration of heavy metal ions (10, 50, 100, 200, 500 and 1000 $\mu$g/ml) at constant temperatures (25 ℃) separately in conical flasks. The solution was shaken intermittently and left for 24 hours to attain equilibrium. Then the samples were centrifuged (REMI Laboratory Centrifuge) for 20 minutes at 3000 rpm and final concentration of metals were analyzed using ICP-OES.

The percent adsorption (%) was calculated using the equation:

$$\% adsorption = \frac{C_i - C_f}{C_f} \times 100$$

Where $C_i$ and $C_f$ are the concentrations of the metal ion in initial and final solutions respectively.

## 3.7 Adsorption Uptake of toxic metal exchange

To determine the adsorption uptake of the toxic metal, a 2.5 g of catalyst (both synthesized 4A & reference 4A), was put into a 250 ml solution of the metal ions separately at initial concentration of 3000 $\mu$g/ml. Different samples were left to stand for 0, 0.5, 1, 2, 3, 4, 5, 6 and 24 hours in a magnetic stirrer at a constant speed of 300 rpm, at room temperature. The metal ions concentration of the filtrates was determined ICP-OES. The amounts of the metal ions adsorbed were gotten by difference between the initial concentration of the metal ions and the final concentration.

Adsorption uptake was calculated using the formula:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\prod^2} \sum \frac{1}{n^2} exp[\frac{-Dn^2\prod^2 t}{R^2}]$$

Where $M_t and M_\infty$ are the amounts adsorbed at time t and at infinite time, respectively, r is the particle radius [50]. The values $D/r^2$ were calculated by using the program in fortran.

## 3.8 Preparation of the catalyst by wet impregnation method

The ZnO/decoked spent catalyst and $In_2O_3$/decoked spent catalyst, containing various amounts of ZnO (10 and 20 wt %) and $In_2O_3$(5, 10 and 20 wt.%) were prepared by a standard wet impregnation method (Figure 3.3). The requisite quantity of zinc chloride (source of Zinc) and indium nitrate monohydrate (source of Indium) were dissolved in pure methanol separately. The solution was added in small a liquots of 1 ml each time to the 10 gm of decoked spent catalyst (DSC) with constant stirring with a glass rod or kneading it properly. The excess methanol was evaporated at room temperature in 2 to 3 hours and the resulting material was oven dried at 120℃overnight and subsequently calcined at 550℃in case of zinc chloride for removing excess chloride content and 650℃in case of indium nitrate for removing excess nitrate content for 4 h.

## 3.9 Catalytic Reaction

The liquid phase benzylation of *o*-xylene with benzyl chloride (BC)(Figure 3.4) was carried out in a 50 ml two necked flask attached to a condenser and a septum. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, benzene and BC were added in the required molar ratio to the activated catalyst. The catalysts were activated at 200℃in air for 2 h with a flow rate of 50 ml/min and cooled to room temperature prior to their use in the reaction. The reaction mixture

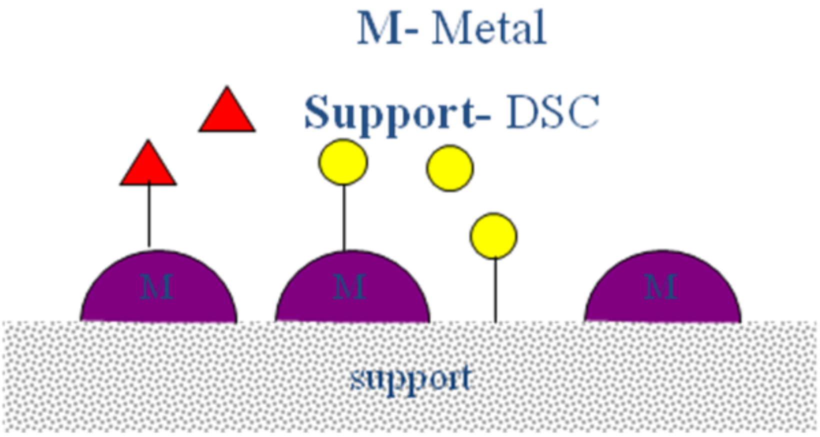


Figure 3.3: Metal Support Interaction

was magnetically stirred and heated to the required temperature under atmospheric pressure. In all the cases, the major product formed was mainly mono-benzylated compound along with polybenzyl and HCl as side products depending upon the condition used. In a typical run, *o*-xylene and benzyl chloride (20:1 molar ratio) were added to activate the spent catalyst (0.5 g). The product samples were analyzed periodically by a gas chromatograph (Thermo Finnigan Trace GC) equipped with a flame ionization detector and a capillary column (Restek-5). The products were also identified by injecting authentic sample and GC/MS (Thermo scientific Trace GC ultra). Finally, the percentage conversion (wt.%) of benzyl chloride is defined as the total percentage of benzyl chloride converted.

## 3.10 Characterization of Catalyst

The catalysts were systematically characterized by various techniques:

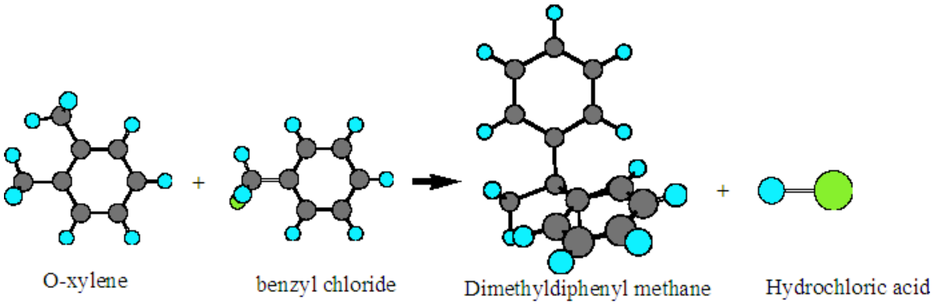


Figure 3.4: Reaction Scheme

### 3.10.1 XRD

X-ray diffraction (XRD) pattern were obtained with a D8 Advance Bruker Axs diffractometer with monochromated Cu K$\alpha$ radiation (40 kV, 100 mA) operated by using a step scan program (step width 0.02). The formation of 4A and crystallinity were monitored for all synthesized zeolites. Spent catalyst, synthesized 4A, reference 4A and prepared catalyst for catalysis application were scanned for $2\theta$ in the range 5-60Åwith step change of 0.01°.

### 3.10.2 FTIR

FT-IR spectroscopy is used to probe the structure of zeolites and monitor reactions in zeolite pores. Analysis of all the synthesized materials and prepared catalyst for catalysis application were performed by using FT-IR spectrometer (Nicolet 6700) using KBr pellets. Specifically, structural information can be obtained from the vibrational frequencies of the zeolite lattice observed in the range between 200 and 1500 $cm^{-1}$.

### 3.10.3 Surface acidity by $NH_3$ TPD

Temperature programmed desorption (TPD) of ammonia was carried out to evaluate acidic properties of the DSC and metal impregnated DSC using $NH_3$ as an adsorbate with a Chemisorb 2750 thermogravimetric system with a heat conductivity detector, TCD and FID. In a typical run, 0.05g of a calcined sample was placed in a quartz tubular reactor and heated at 650℃under a Argon flow of 20 ml/min for 1 h. The reactor was then cooled to 120℃; thereafter, $NH_3$ was passed over the sample for 30 min. The sample was subsequently kept in the flow of Argon at 120℃till saturation in order to eliminate the physisorbed ammonia.

### 3.10.4 Surface area and Pore volume

The BET surface area and pore volume were determined by $N_2$ physisorption at liquid $N_2$ temperature on a Micromeritics ASAP 2020 instrument. Prior to analysis, the samples were oven-dried at 20℃for 12 h and flushed with Argon gas for 2 h.

# Chapter 4

# Results and discussion

## 4.1 Effect of grinding

For complete utilization of silica available in spent catalyst, its solubilization in aqueous medium is a required priority. It is known that the smaller particles are easily solubilized. Hence, the sample grinding was chosen as a first step for reducing particle size. Among the various methods proposed for this purpose, attrition by "ball milling" has been proved to be of the most promising one [51]. It is expected to reduce particle size and thereby bringing structural changes in the material. Spent catalyst was subjected to ball milling and the particle size distribution was measured

Table 4.1: Particle size Distribution of MP008 and MP024 (wt%)

| | **Cumulative(Microns)** | | | | | | | **Range distribution** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample Name** | 20 | 25 | 30 | 35 | 45 | 88 | 120 **fines** | < 20 Bad **Fines** | < 45 **Medium Coarse** | 45-88 | >88 **Coarse** |
| MP008 | 22 | 26 | 32 | 37 | 49 | 65 | 76 | 22 | 49 | 16 | 3.4 |
| MP024 | 43 | 51 | 60 | 70 | 85 | 98 | 98 | 43 | 85 | 13 | 1.4 |

MP008- Unground Spent Catalyst
MP024-Ground Spent Catalyst

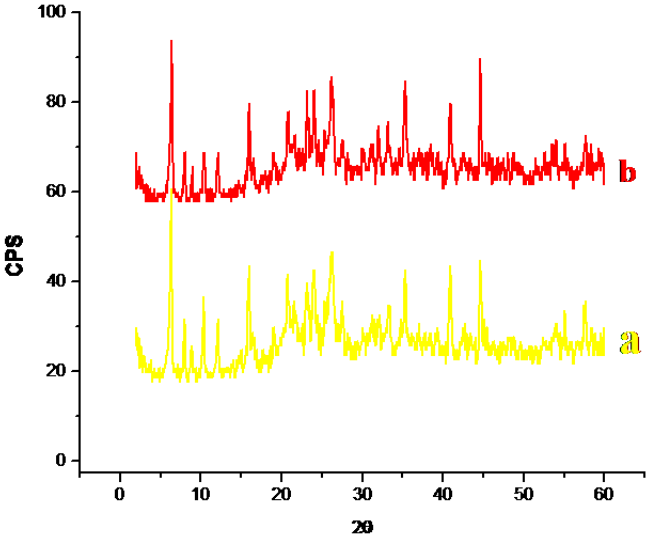


Figure 4.1: XRD of (a) Ground and (b) Unground spent catalyst

for both ground and unground samples. The impact of grinding is clearly seen in Table 4.1. About 50% increase in the number of fine particles (≤20 micron size) of the material was observed. Substantial decrease from 34% to 1.4% in coarse particle is observed on ball milling. However, their X-ray diffractogram in 15-30°$2\theta$ range did not show any structural changes (figure 4.1) on grinding, as it is observed in case of high energy ball milling [52]

## 4.2 Extraction of Si and Al

For silica to undergo zeolitization it needs to first react with alumina and soda for making sodalite cages. Since the silica source in the present case is derived from spent catalyst, its dissolution in solution phase is very important for a forward polymerization reaction. Spent catalysts are subjected to high temperature and pressure during their run length in the reactor and undergo structural changes. Also, the present spent catalyst contains a mixture of different crystalline zeolite phases like ZSM-5 and zeolite Y or zeolite X. Hence, a study was undertaken to extract maximum amount of silica from spent catalyst. It is known that the amorphous silica when stirred in presence of 0.1 M sodium hydroxide, more than 95% dissolved in less than 2h. The dissolution is progressed in two stages. The first stage is neutralization of acidic silanol groups by $OH^-$ ions. Charges $O^-$ sites are created that attract positive ions. The reaction is represented as:

$$H_{2x}SiO_{2+x} + 2xNaOH \rightarrow Na_{2x}SiO_{2+x} + 2xH_2O$$

Where 2x is the fraction of silicon atoms with silanol groups. The reaction can be regarded as exchange of $H^+$ ions with $Na^+$ ions, which is ionically bonded and which attract hydration spheres of water molecules that slightly swell the rigid silica structure. A second stage of reaction occurs when excess hydroxyl ions in alkaline solutions attack the siloxane bridges so that additional negatively charged $O^-$ reaction sites are created that also bind $Na^+$ ions. The silica structure loosens progressively as the siloxane bridges are broken, additional oxygen alkali sites become active and additional water is imbibed during an osmotic-like swelling of the loosened structure. This structure may become alkali-silicate solution or alkali-silicate hydrate gel, depending on moisture content. The $OH^-$ concentration and pH both decrease as silica dissolves. This reaction may be written in simplified form as:

$$Na_{2x}SiO_{2+x} + (2-2x)NaOH + xH_2O \rightarrow 2Na^+ + H^2SiO_4^{2-}$$

In present case most of silica is in crystalline phase and it is difficult to break siloxane bridges for dissolution. Also, it is observed that ball milling does not improve silica solubility. This could be due to inefficient reduction of crystallinity. Hence, the dissolution of silica in higher concentration of sodium hydroxide solutions was studied under two different temperatures and varied refluxing time. Since preliminary screening with low concentration of sodium hydroxide did not extract silica from spent catalyst (0.1 to 1M), minimum concentration chosen was 2M. Table 4.2 and 4.3, depicts the effect of various extraction conditions on Si and Al dissolution from un-ground spent catalyst.By increasing sodium hydroxide concentration (2M to 5M),

Table 4.2: Change in % Si and Al extraction with Concentration of alkali and temperature for 2 hours

| NaOH Conc., M | % Si, 80℃ | %Si, 100℃ | % Al, 80℃ | %Al, 100℃ |
|---|---|---|---|---|
| **2** | 16.0 | 13.024 | 1.3 | 2.0 |
| **3** | 17.6 | 12.5 | 1.7 | 3.0 |
| **5** | 15.0 | 12.4 | 1.4 | 2.3 |

Table 4.3: Change in % Si and Al extraction in 2M NaOH with time and temperature

| Time, min | % Si, 80℃ | %Si, 100℃ | % Al, 80℃ | %Al, 100℃ |
|---|---|---|---|---|
| **30** | 12.2 | 11.8 | 1.2 | 2.0 |
| **60** | 14.0 | 9.4 | 1.3 | 2.2 |
| **120** | 16.0 | 13.0 | 1.3 | 2.1 |
| **240** | 17.0 | 15.4 | 1.3 | 2.1 |

silica and alumina concentration did not increase substantially in aqueous solution. Increase in temperature from 80℃to 100℃showed decreased dissolution of silica where as alumina concentration had increased to some extent. Solubilization of silica in 2M NaOH for 2 hours at both the temperatures was the maximum. Very low amount of aluminum could be extracted under experimental conditions used. This could be due to the presence of refractory phases of silica and alumina. This indicated that without fusion, dissolution of silica even by grinding is difficult and all available silica may not take part in zeolitization.

## 4.3 Characterization of synthesized zeolite 4A

### 4.3.1 XRD of synthesized zeolite 4A

The main components of the spent catalyst are oxides of Si and Al and various metallic oxides as shown in Table 3.1. Synthesized Zeolite 4A also comprises of oxides of Sci, Al including sodium ions with traces of other metallic oxides as impurities. In case of spent catalyst, crystalline peaks of ZSM-5 and zeolite Y are identified (Figure 4.1). Numbers of synthesis were performed with varied parameters (Table 3.3). After the optimization, maximum crystallinity of zeolite 4A was obtained only after converting the spent catalyst to a highly reactive state using an activator (such as Noah or $Na_2CO_3$) at high temperature (Figure 4.2). Powder XRD of spent catalyst

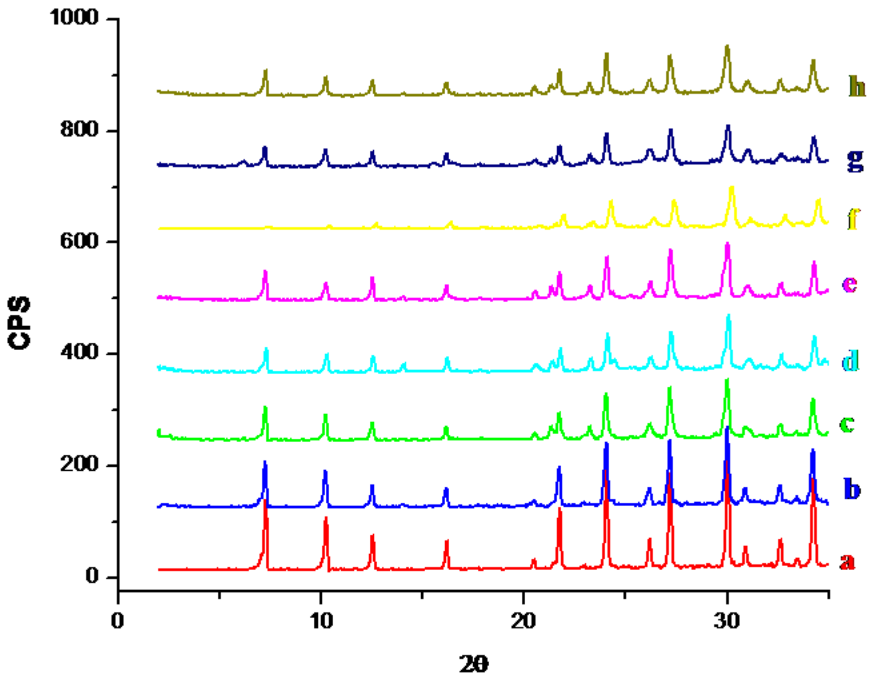


Figure 4.2: XRD of (a) reference sample (4A) (b) to (h) Synthesized 4A samples from spent catalyst

and zeolite 4A including reference 4A were scanned for $2\theta$ in the range 5-60°. The d-spacing values reported in the literature for zeolite 4A (11.99, 8.58, 7.01, 4.07, 3.68, 3.39, 3.26, 2.73, 2.60) were used as the basis of identification and quantification of crystalline phases. In each synthesis condition, formation of 4A has occurred as all characteristic peaks of zeolite 4A are seen similar to reference sample (a), however, the percentage crystallinity has varied relative to reference sample.

X-ray diffractograms of 4A synthesized from ground and un-ground samples were compared to see effect of grinding. Though, it is seen that the diffraction patterns for both samples ((f) and (g), respectively) are comparable, there was slight improvement in the peak intensities signifying improved crystallinity for ground sample (Table 4.4). This could be due to improved gel formation. Grinding followed by alkali fusion probably helps in better silica extraction as observed earlier.

It is observed that at the higher temperature, higher degree of crystallinity is achieved with increased yield of 4A (Figure 4.3 ). It is known that the rate of crystallization is greater if the synthesis temperature is increased and our results also showed similar trend [53], [54] . Synthesis of zeolite 4A depends on the rate of gel dissolution, the number of distribution of nuclei in the gel, and the crystal growth rate during hydrothermal treatment. All of them in turn depend on the other factors such as synthesis temperature, synthesis time, alkalinity, etc. Nucleation dominates in the initial stage of synthesis process, whereas crystal growth occurs throughout the pro-

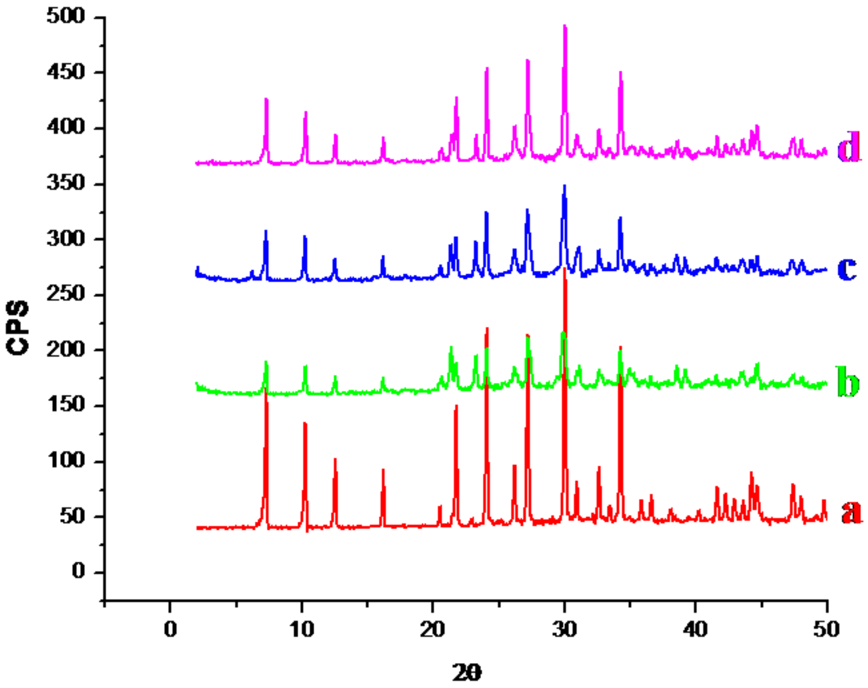


Figure 4.3: Effect of Synthesis Temperature (a) reference sample (4A), (b) 80℃, (c) step change 90℃, 95℃and (d) 100℃

cess. Li et. al, [55], [56] have developed a two-stage varying temperature synthesis to determine the nucleation period and nucleation rate for TPA-silicalite-1 crystallization. Hui and Chao [25] have also reported decreased synthesis time of 4A from coal fly ash by introducing step change in hydrothermal synthesis temperature compared to using constant temperature. However, synthesis from spent catalyst did not show similar effect in 4A synthesis. The major influence in present synthesis is silica solubilization from spent catalysts. Hence, the attempt of synthesis in absence of fusion step (figure 4.4) was not successful.

XRD method is used for estimating crystallinity [57], [58] of zeolite material using formula as shown below and the data are presented in Table 4.4 and4.5.

$$\%Crystallinity = \frac{\sum(relativeIntensitiesofSample)}{\sum(relativeIntensitiesofstandard)} \times 100$$

Table 4.4: % Crystallinity of Synthesized 4A

| $2\theta$ | **MP015** | **MP005** | **MP007** | **MP009** | **MP010** | **MP011** | **MP012** |
|---|---|---|---|---|---|---|---|
| **29.95** | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| **24.01** | 76.53 | 37.63 | 81 | 87.86 | 65.18 | 62.81 | 69.84 |
| **7.21** | 47.05 | 16.2 | 44.31 | 44.22 | 47.56 | 52.79 | 41.97 |
| **27.13** | 83.31 | 77.64 | 64.98 | 90.7 | 94.16 | 52.79 | 60.98 |
| **10.205** | 40.06 | 17 | 39.62 | 38.58 | 47.11 | 22.75 | 31.4 |
| **34.165** | 86.71 | 30.86 | 64.26 | 54.41 | 78.4 | 64.77 | 55.13 |
| **21.68** | 46.97 | 61.18 | 44 | 46.21 | 50.42 | 32.1 | 31.27 |
| **12.49** | 23.31 | 8.55 | 17.09 | 22.93 | 21.45 | 15.31 | 19.96 |
| **16.13** | 18.92 | 16.47 | 20.89 | 27.88 | 23.02 | 15.61 | 16.21 |
| **26.095** | 23.37 | 0 | 27.27 | 48.36 | 40.05 | 23.99 | 22.98 |
| **Total (I)** | 546.23 | 365.53 | 503.42 | 561.15 | 567.35 | 423.33 | 449.74 |
| **%Crysta- llinity** | 100 | 67 | 92.16 | 103 | 104 | 77.5 | 82 |

In order to see effect of impurity elements on zeolitization, synthesis of 4A was carried out after leaching of impurities from spent catalyst (MP022). Spent catalyst was treated with dilute hydrochloric acid under mild condition prior to silica extraction. Fusion was avoided in this experiment. It is observed that the impurities are removed substantially from spent catalyst, but the synthesized 4A had poor crys-

Table 4.5: % Crystallinity of Synthesized 4A

| **$2\theta$** | **MP013** | **MP014** | **MP017** | **MP018** | **MP019** | **MP020** | **MP022** | **MP026** |
|---|---|---|---|---|---|---|---|---|
| **29.95** | 87.29 | 75.95 | 83.81 | 100 | 100 | 100 | 32.76 | 100 |
| **24.01** | 0 | 63.49 | - | 67.25 | 93.03 | 55.87 | - | 67.99 |
| **7.21** | 3.42 | 24.13 | - | 32.2 | 46.08 | 6.06 | 5.58 | 28.86 |
| **27.13** | 51.44 | 74.57 | 52.19 | 73.56 | 87.75 | 60.23 | - | 88.34 |
| **10.205** | 7.65 | 28.93 | - | 24.39 | 24 | 6.63 | 24.99 | 30.01 |
| **34.165** | 0 | 69.13 | 100 | 67.5 | 72.38 | 80.6 | 28.32 | 54.02 |
| **21.68** | 100 | 42.28 | 81.85 | 41.65 | 48.23 | 33.38 | - | 37.78 |
| **12.49** | 11.54 | 26.89 | - | 23.46 | 39.29 | 6.64 | 3.51 | 33.94 |
| **16.13** | 17.71 | 28.85 | 25.51 | 20.77 | 22.68 | 11.05 | 19.88 | 22.52 |
| **26.095** | 79.53 | 33.12 | 92.82 | 21.88 | 31.83 | 23.7 | 37.83 | 47 |
| **Total (I)** | 358.58 | 467.34 | 436.18 | 472.66 | 565.27 | 384.16 | 152.87 | 510.46 |
| **%Crystallinity** | 66 | 86 | 80 | 86.5 | 103.5 | 70.33 | 28 | 93.45 |

tallinity (28%) compared to other samples. Probably in absence of fusion, reaction does not proceed due to starved silica source. This is further confirmed from its XRD pattern (Figure 4.4), where diffractogram showed presence of most peaks of spent catalyst. Synthesized 4A samples show more than 80% crystallinity, indicating presence of some impure amorphous phases. This could be due to the insolubility of spent catalyst. By removal of insoluble portion of spent catalyst after alkali extraction may give pure 4A zeolite as reported by Keka et al [19].

### 4.3.2 Adsorption Isotherm

4A zeolites are characterized for their water adsorption behavior. Adsorption of water was studied for the spent catalyst, synthesized 4A and reference 4A in the form of powder. The adsorption isotherms are shown in Figure 4.5(a). Water adsorption in case of reference 4A is 25 weight % at relative pressure of 80 wherein it's only 15% for the synthesized 4A. This has been attributed to the presence of impurity phase in synthesized 4A from spent catalyst. The unconverted spent catalyst may not show any water adsorption. Considering presence of ZSM-5, zeolite Y or X in spent catalyst, adsorption of benzene was also seen in spent catalyst as well as

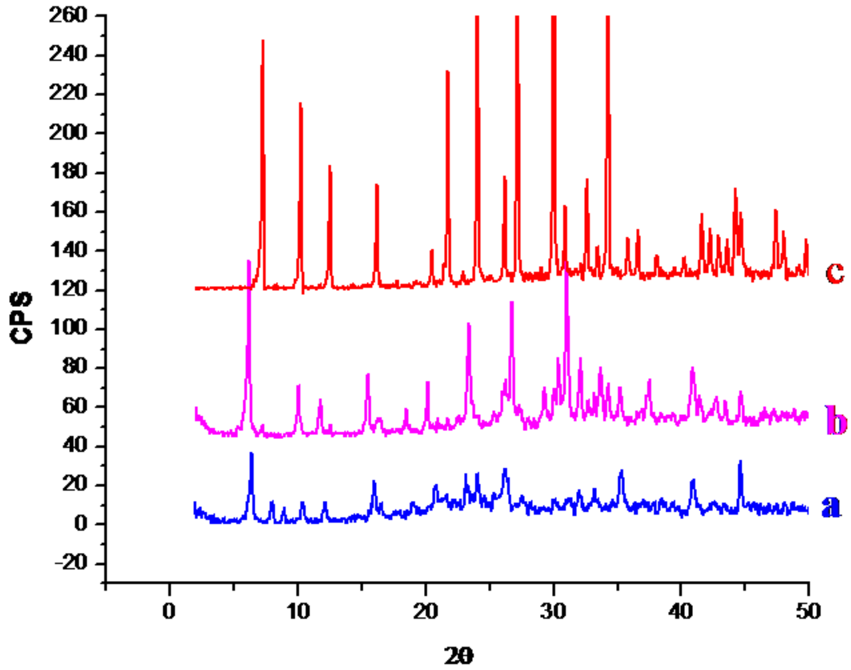
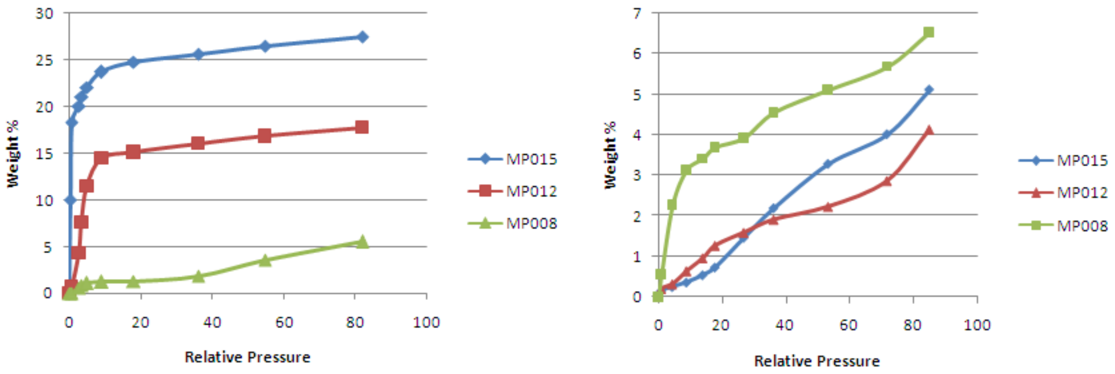


Figure 4.4: XRD (a) spent catalyst, (b) synthesized 4A (after removal of impurities) and (c) ref 4A

synthesized 4A from spent catalyst. There could be a chance of benzene adsorption if unconverted zeolite phases are present in the synthesized 4A. Experimental data showed that the benzene adsorption is absent in both synthesized and reference 4A as expected (Figure 4.5(b)) confirming indirectly that the zeolite impurity phases are absent in synthesized 4A. This is because the pore size of 4A zeolites is 4.2Åwhereas size of the benzene molecule is 6Å. Due to higher size of benzene molecule, it cannot enter 4A pores showing absence of benzene adsorption. Since spent catalyst is having mixed zeolite phases it has shown slight adsorption of benzene.

### 4.3.3 Calcium exchange capacity

zeolite 4A is now a days used as builder in detergent which at lower concentration enhances the effect of the surfactant by deactivating calcium, and magnesium ions,



(a) (b)

Figure 4.5: Adsorption Isotherms of spent catalyst (□), syn 4A (△) and ref 4A(◇) (a) Water (b) Benzene

which would otherwise use up surfactant molecules. It can be used as water softeners and work by complexation (sodium tripolyphosphate STP), precipitation (sodium carbonate) or ion-exchange (zeolites). Now a days the builders used are synthetic zeolites and most importantly zeolite 4A which exchanges one calcium ion with two ions of sodium and removes calcium from the washing water (figure 4.6). In order to check the suitability of the synthesized 4A zeolite from spent catalyst in detergent application, calcium exchange capacity (CEC) is found and is around 5.14 meq$CaCO_3$/g whereas it is 6.49 meq$CaCO_3$/g reference 4A. Hence CEC value of synthesized 4A is 80% of that of reference 4A. This result is in agreement with the crystallinity of XRD results.

## 4.4 Toxic Metals exchange

One of the major applications of 4A zeolite is for removal of toxic metals from waste water. In order to study cation exchange behavior of synthesized 4A, the adsorption of heavy metals like $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ as a function of their concentrations was carried out at room temperature. The metal concentration was varied from 10 to 500

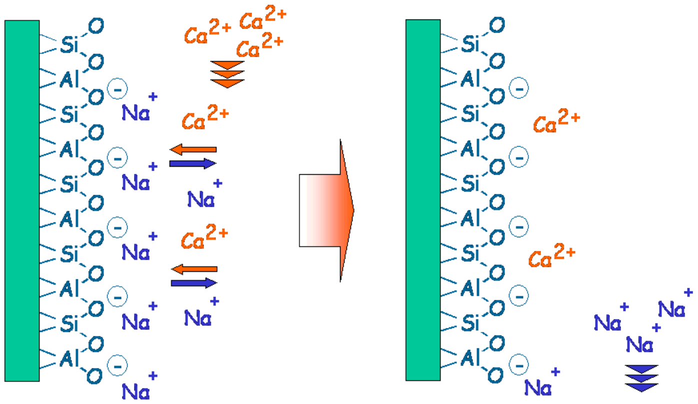


Figure 4.6: Calcium Exchange

mg/l keeping solid to volume ratio same. Figure 4.7 shows the ion exchange behavior of zeolite 4A. The ion exchange capacity (IEC) of zeolite 4A depends on the pore size and the exchangeable cations ($Na^{+}$) bonded to the framework of 4A . The metals used in this study have smaller sizes than the pore size of zeolite A. The results are

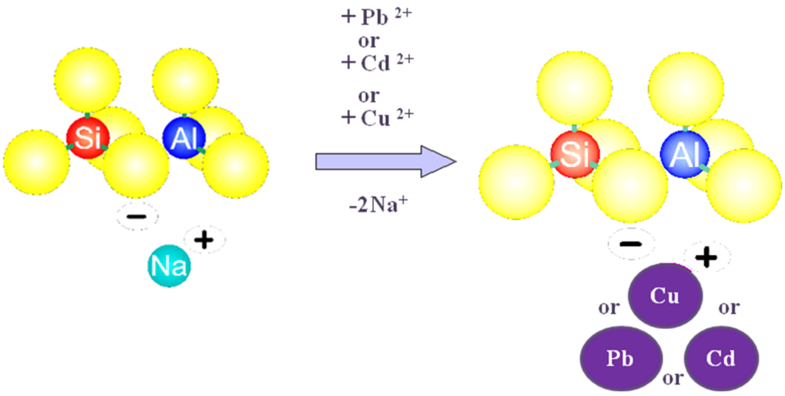


Figure 4.7: Toxic Metal Exchange

shown in figure 4.8. from aqueous solutions, at metal concentration, $\mu$g/ml almost 100% exchange of $Cu^{+2}$, $Cd^{+2}$ and $Pb^{+2}$ is observed. These results indicate that favorable sites energetically become involved with increasing metal concentrations in the aqueous solution. Ion exchange of metal ions on reference zeolite 4A, synthesized 4A and the spent catalyst as a function of their initial concentration: m =0.5 g, V = 10 ml, time = 24 h was studied. The heavy metal uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass, but also through channels of the lattice, and they had to replace exchangeable cations (sodium). Diffusion was faster through the pores for both reference 4A and

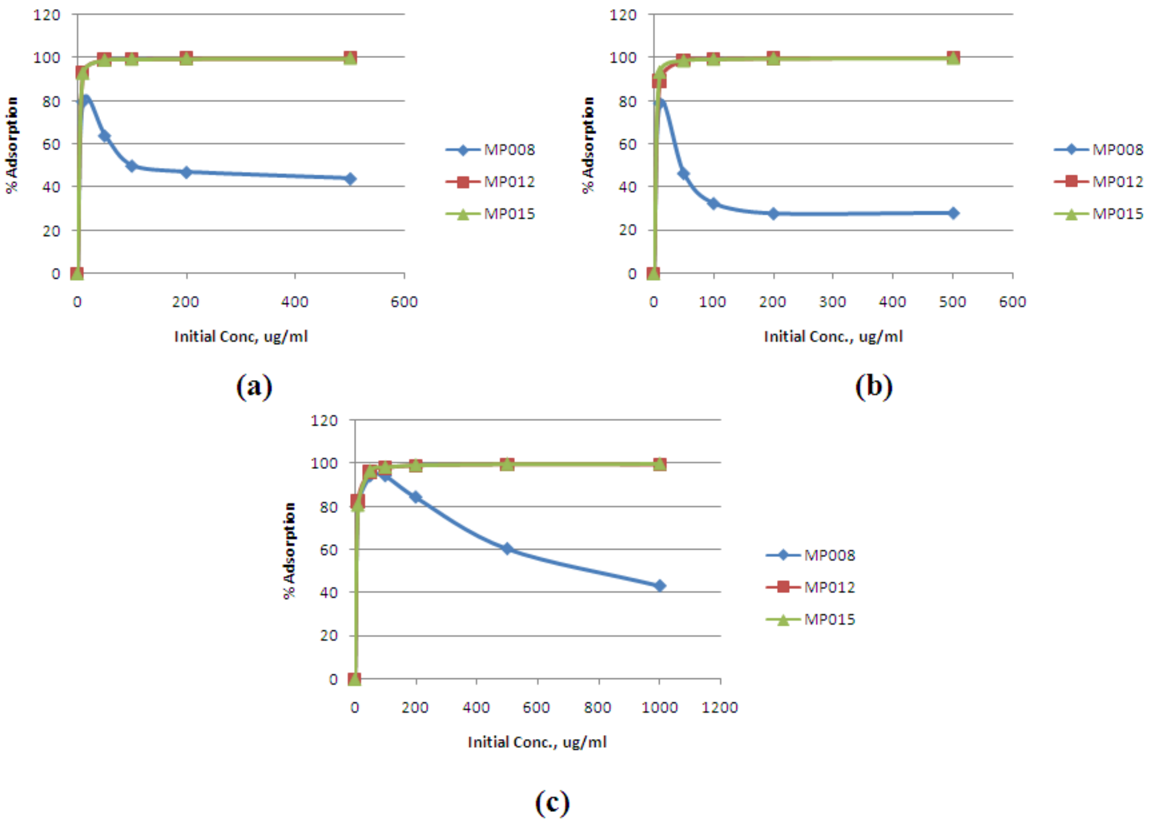


Figure 4.8: Toxic metal exchange (a) Cadmium (Cd), (b) Copper (Cu) and (c) Lead (Pb),spent catalyst (◇), syn 4A (□) and ref 4A(△)

synthesized 4A. In case of spent catalyst the percentage adsorption decreased with increase in metal concentration. There are several reasons for such behavior of the catalyst. Firstly there might be blockage or coke deposition in the pores because of which diffusion was faster for small concentration and then there was retardation when the ions moved only through the void spaces. The ion exchange capacity(IEC) of synthesized 4A for cadmium, copper and lead was found to be 0.178 mmol/g, 0.205 mmol/g and 0.222mmol/g respectively.

## 4.5 Adsorption uptake

The adsorption uptake (Table 4.6) of the toxic metals (Cd, Cu and Pb) has been calculated using a well known equation of intraparticle diffusion model. The results confirm that synthesized 4A can equally diffuse the toxic metals as reference 4A. Cadmium diffusion into synthesized 4A is 1.2 times lesser than the reference 4A because of the presence of impurity phases in synthesized 4A which is in agreement with crystallinity of the synthesized 4A. In case of copper and lead, the uptake is almost equal.

Table 4.6: Adsorption Uptake

| **Catalyst** | **Cadmium** | **Copper** | **Lead** |
|---|---|---|---|
| **Reference 4A** | $0.549\times10^{-4}$ | $0.7618\times10^{-4}$ | $0.9142\times10^{-4}$ |
| **Synthesized 4A** | $0.4648\times10^{-4}$ | $0.76097\times10^{-4}$ | $0.8914\times10^{-4}$ |

### 4.5.1 Determination of optimum contact time

Figure 4.9(a) shows IE of Cd, Cu and Pb at room temperature with continuous stirring condition. The equilibrium is reached within 60 to 90 minutes of contact time with exchange efficiency of 48%, 83% and 82% respectively in synthesized 4A zeolite which is almost similar to reference 4A zeolite (Figure 4.9(b)). The uptake of metals was rapid within the first 10 min of contact time. The removal rate gradually decreased with increase in contact time. Initially, the rate was higher because all sites on zeolite 4A were vacant and concentration was high, but decrease of sorption sites reduced the uptake rate.

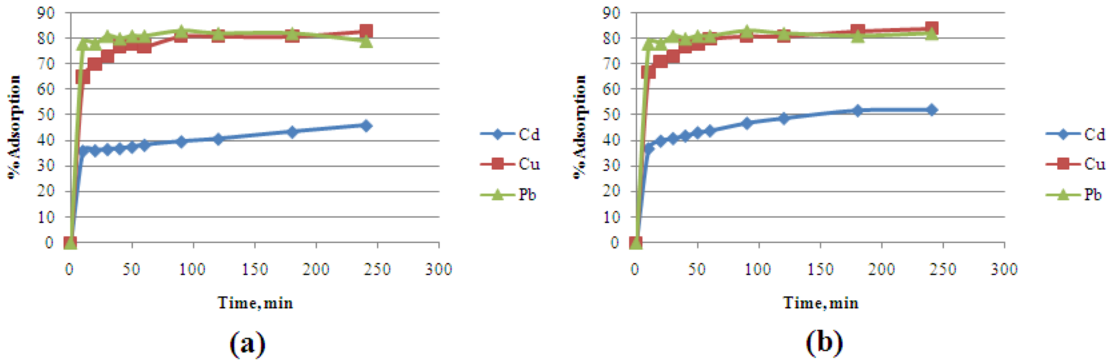


Figure 4.9: Optimum contact time of toxic metal with 4A (a) synthesized 4A and (b) reference 4A

Table 4.7: Ion exchange of heavy metals

| **Matrix** | **%removal of toxic metals** | | |
|---|---|---|---|
| | **Cadmium** | **Copper** | **Lead** |
| **DM Water** | 31 | 73 | 67 |
| **Wastewater** | 36 | 76 | 64 |

Metal exchange study was also carried out from the mixture containing all the three heavy metals (2000$\mu$g/ml each). Solutions were prepared in DM water as well as sample collected from one of the waste water stream from RIL plant. The order of metal exchange from the mixture was $Cu^{+2} > Pb^{+2} > Cd^{+2}$ (Table 4.7) under static conditons. No remarkable difference was seen in the exchange behavior from pure water or waste water matrix. Poor sorption of cadmium attributed with the fact that cadmium adsorbs rather weakly on organic matter and inorganic oxides[64].

## 4.6 Characterization of Supported Catalyst

The detail characterization of prepared catalyst by various techniques as explained below:

### 4.6.1 XRD of modified decoked spent catalyst

Figure 4.10 shows the XRD of DSC, 10% and 20% Zn loading on DSC. The crystalline peaks of DSC have been diminished by zinc loading. Jun Chen et al. reported that in case of ZSM-5 there is no change in its crystalline phase for more than 4% zinc loading on zeolites. They have demonstrated that ZnO clusters have been formed in the pores of zeolite and no macrocrystalline ZnO exists. Similar results were obtained by Choudary et al. with no phase change with metal (Fe, Zn, In and Ga) loading [45]. S. Mondal et al. reported that the (002) peak appears with maximum intensity at 34.55 and the other peaks at 31.85, 36.35, 47.6 and 56.85 can be associated with (100), (101), (102) and (110) peaks of ZnO, as is expected for hexagonal ZnO structure [59]. But in present case the peaks of ZnO are not appearing and phase change that had taken place with zinc loading is quite unpredictable may be due to complex structure of spent catalyst. In case of pure zeolite, Choudary et al. have reported that there

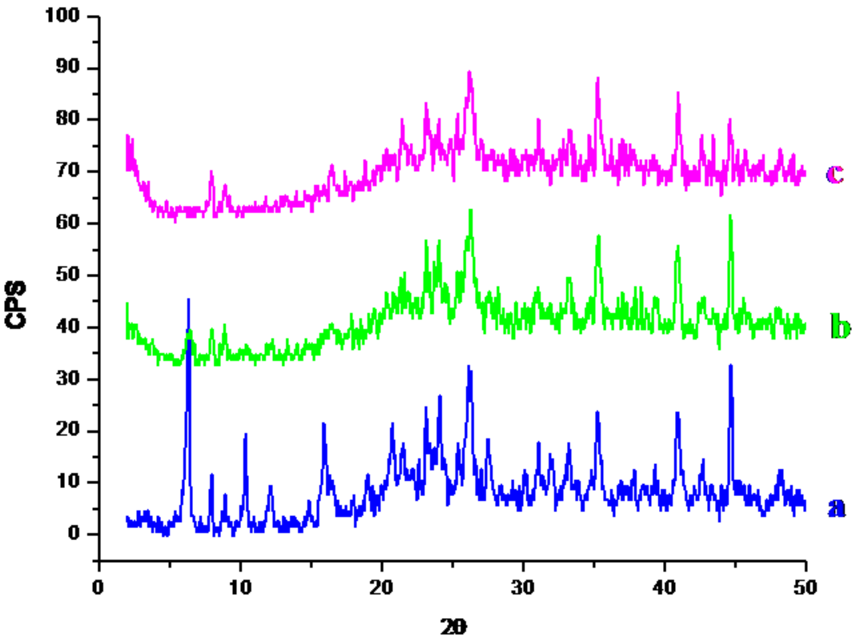


Figure 4.10: XRD of (a) DSC, (b) 10% zinc loaded DSC and (c) 20% zinc loaded DSC

is no structural or crystalline phase change with indium loading [45]. When indium supported on DSC the crystalline phases of the spent catalyst have diminished and new peaks are formed at d-spacing of 2.92, 1.79, and 2.53 which are attributed to the major peaks of $In_2O_3$ [60] at 222, 400 (cubic structure) and 440 planes respectively [61],[62]. These results indicate that indium is present on the surface only and not entered inside the pores of the spent catalyst(Figure 4.11).

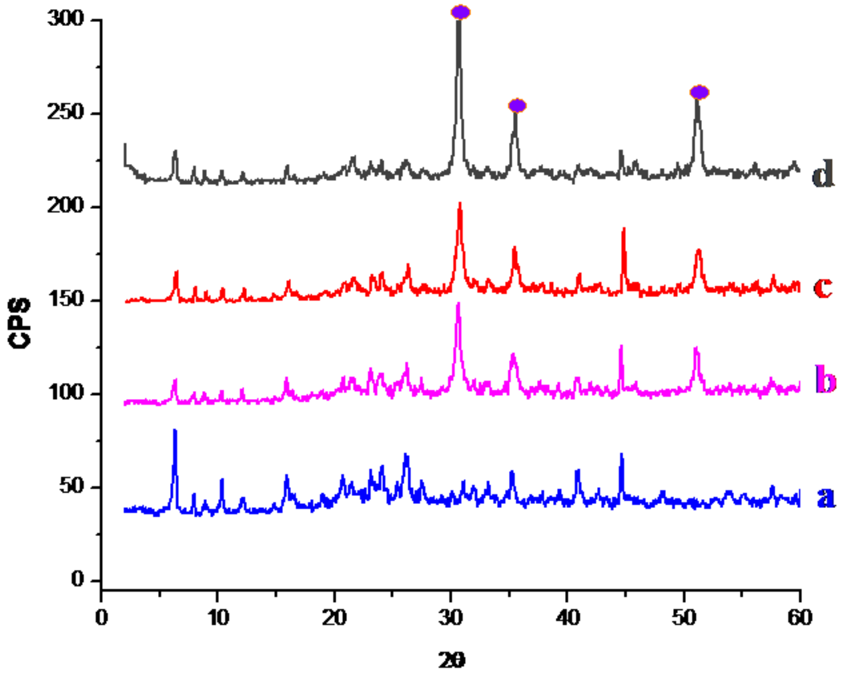
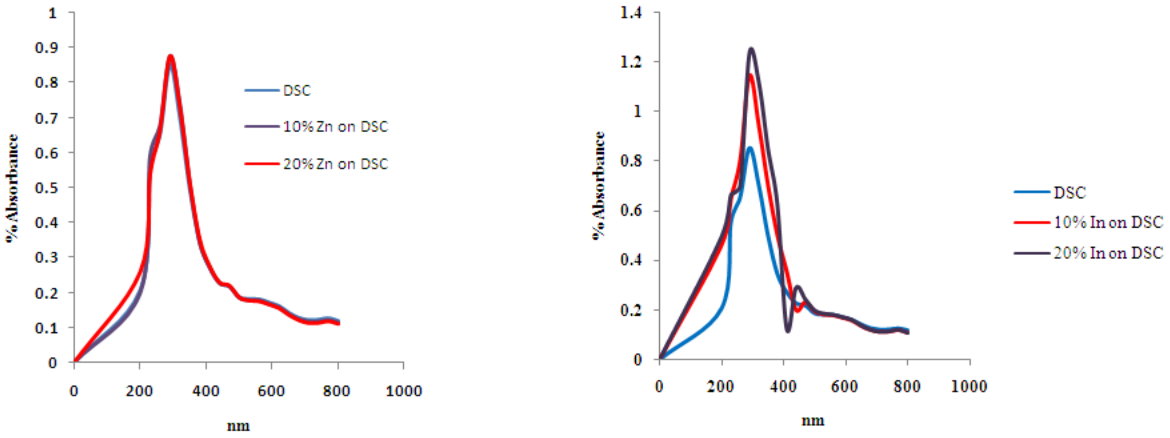


Figure 4.11: XRD of (a) DSC, (b) 5% Indium loaded DSC, (c) 10% Indium loaded DSC and (d) 20% Indium loaded DSC

### 4.6.2 UV-Vis Diffusive Reflectance Spectroscopy(DRS)

Figure 4.12 shows diffused reflectance spectra in the UV-Vis region for DSC, Zn /DSC and In/DSC. It is observed that DSC and Zn supported DSC exhibit strong absorption ligand to-metal charge transfer (LMCT) broad band at 295 nm. It indicates that Zn is available on the surface and not strongly bonded with support so there is no shift in absorption band due to d-d transition. The similar type of pattern is also observed in the case of Indium supported DSC. A faint absorption band around 440 nm was observed due to interaction of Indium with support on weaker side. Whereas according to Jun Chen et al., band gap of macrocrytalline ZnO, appears at absorption band at about 370 nm [63] with more than 4 wt% ZnO loading. However, no absorption band was observed at higher ZnO loading on DSC. This suggests that Zn exchange has not occurred inside the pores.



(a) (b)

Figure 4.12: Diffused Reflectance Spectra of (a) ZnO/DSC and (b) $In_2O_3$/DSC

### 4.6.3 BET Surface area and Acidity by ammonia TPD

BET surface area, pores volumes and acidity by ammonia TPD of the prepared catalyst are presented in Table 4.8. The total surface area and pore volume of decoked sample is 156.58 $m^2g^{-1}$ and 0.22 $cm^3g^{-1}$ respectively, which reduced to 49.94 $m^2g^{-1}$ and 0.186 $cm^3g^{-1}$ upon 20% Zn loading. The similar type of phenomena was observed in case of indium supported catalyst. It indicates that insertion of metal into the aluminosilicate framework leads to a decrease of the BET surface area and pore volume which can be explained by a change of the pore shape due to the change of

Table 4.8: Surface Acidity, Surface Area and Pore Volume

| **Catalyst** | $NH_3$ **Adsorption, mmol/g** | **Surface area,** $m^2$**/g** | **Pore volume,** $cm^3$**/g** |
|---|---|---|---|
| **DSC** | 0.2033 | 156.58 | 0.218 |
| **10% Zn on DSC** | 0.4245 | 73.97 | 0.175 |
| **20% Zn on DSC** | 0.3636 | 49.94 | 0.186 |
| **5% In on DSC** | 0.1599 | - | - |
| **10% In on DSC** | 0.102 | 139.94 | 0.189 |
| **20% In on DSC** | 0.085 | 123.6 | 0.112 |

the cell parameters.

Temperature programmed of ammonia desorption is used to estimate the acid property of the catalysts qualitative and quantitatively. It is known that ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts. Its strong basicity and smaller molecular size allows detection of acidic sites located in the narrow pores of the solids. Hence the total amount of $NH_3$ desorbed relates to the number of acidic sites and from the desorption temperature, the strength of acidic sites is suggested. The results of $NH_3$-TPD of the catalysts are tabulated in Table 4.8. The amount of acid or acidity is expressed as moles of $NH_3$ desorbed per unit weight of the solid. It is also clearly seen from table 4.8 that the acidity of DSC is 0.20 $mmolg^{-1}$ and it increases with 10% of zinc loading. However, further increase of zinc loading, no further increase in acidity was observed. This could be due to shift in strong acid sites leading to $NH_3$ desorption at higher temperature.

## 4.7 Catalytic Activity

The prepared catalysts were used for liquid phase alkylation of *o*-xylene with benzyl chloride under various reaction conditions. A systematic investigation of various operating parameters was also studied.

### 4.7.1 Effect of zinc loading on DSC

The DSC, 10% and 20% Zn-modified DSC are used for liquid phase benzylation of benzene at 80℃. The benzyl chloride conversion versus reaction time was plotted (Figure 4.13). Spent catalyst did not show any conversion but 10% and 20% zinc loading on DSC shows 30% and 75% respectively 6 hours of reaction time.

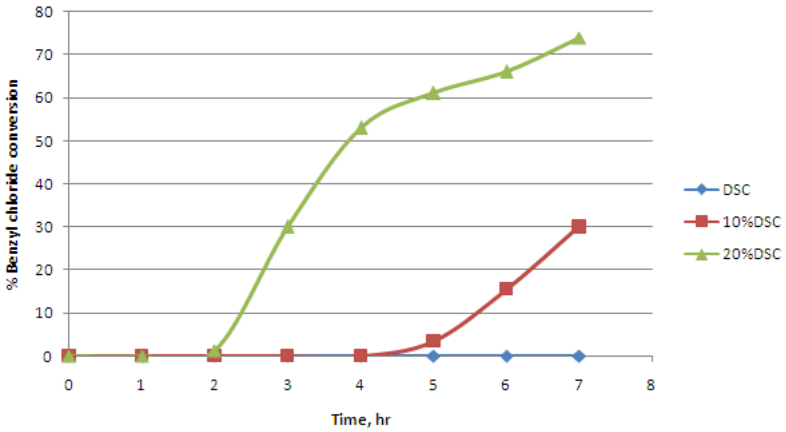
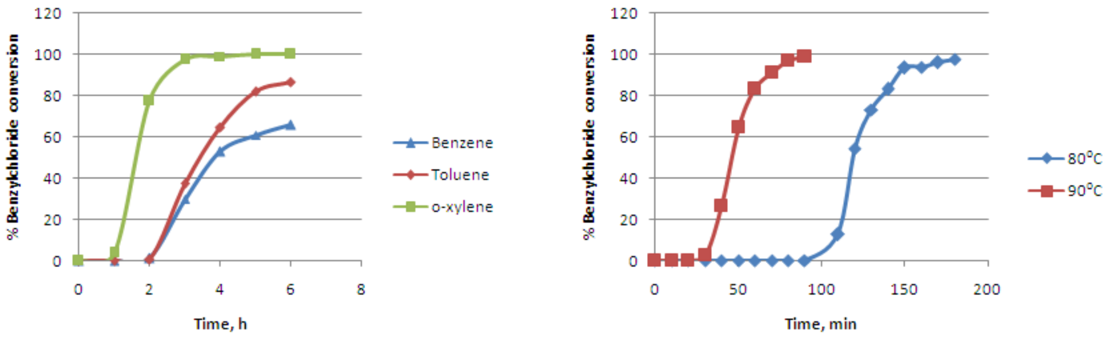


Figure 4.13: Effect of various loading of Zinc on DSC, DSC (◇), 10%Zn loading (□) and 20% Zn loading (△)

### 4.7.2 Effect of various aromatics and Temperature

A study has been done to find the effect of different electron substituent groups optimum reaction conditions (Catalyst loading = 0.5 g, Temperature = 80℃and stirring speed = 600 rpm, mole ratio 20:1) using 20% Zn loaded DSC as the catalyst. The order of benzylchloride Figure 4.14(a) conversion observed as benzene < toluene <*o*-xylene. According to the classical mechanism of the Friedel-Crafts type acid catalyzed benzylation reaction, the benzylation of an aromatic compound will be easier if one or more donating groups are present in the aromatic ring. These reactions show similar trend. Under identical conditions, the reaction was studied at two different temperatures. The results show that the catalytic performances of 20%



**(a)** **(b)**

Figure 4.14: Effect of (a) various aromatics, Benzene(△), Toluene(◇) and *O*-xylene(□) and (b) Temperature, 80°C(◇) and 90°C(□)

zinc loaded DSC increase with the reaction temperature (Figure 4.15(b)). The time necessary for 100% conversion of benzyl chloride changed from 180 min at 80C to 90 min at 90C and interestingly, no significant changes of the selectivity occurred. This was as expected classical mechanism. As temperature of 90C takes less time for the conversion, the reaction temperature was maintained 90C throughout the study. The similar type of reaction was studied with 5-10% In/DSC. The reaction rate was higher with In/DSC compared to zinc supported decoked catalyst.

### 4.7.3 Leaching Test with 5% In/ DSC Catalyst

The heterogeneous nature of the reaction needs to be proved since leaching is expected in a reaction involving oxidation catalysts owing to the solvolysis of the metal-oxygen bonds through which the metal is bonded to the DSC support. To test for leaching, a test reaction was conducted at 90°Cand stirring speed 600 rpm with mole ratio of 20:1 using 0.5g of 5% In/DSC. Table 4.9 shows the results of this study. 90% of benzyl chloride conversion had occurred after the filtration of the catalyst. That implies that indium had leached out into the solution and that must have catalyzed the reaction further as indicated by the results. Hence it can be concluded that the reactions performed were not heterogeneous catalytic reactions but they were homogeneous

Table 4.9: Leaching effect for 5% In/DSC

| **Time,min** | **% Benzyl chloride conversion** |
|---|---|
| 10 | 2.6 |
| 60 | 90 |

reactions catalyzed by dissolved indium. This indicates that DSC as such cannot be used as a support for liquid phase reactions. Its use as support demands further investigations to improve metal support binding.

### 4.7.4 Reaction mechanism

The tentative mechanism for the benzylation of *o*-xylene using on In/DSC is shown in Figure 4.15. As it can be observed, indium species have a key role in the catalytic activity. Considering the trend followed for the adsorption of *o*-xylene and benzyl chloride, it seems that the high catalytic activity of the In/DSC is related to the strong interaction of the benzyl chloride with indium oxide active sites.

According to Choudary and Jana [45], the adsorption takes place on tetrahedral

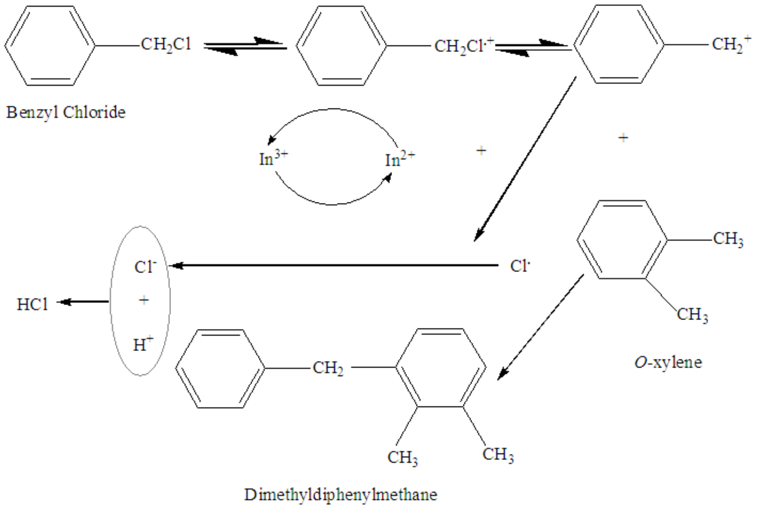


Figure 4.15: Reaction Mechanism

indium atoms by the formation of a benzyl cation ($C_6H_5CH_2^+$) and a chloride ion in a process involving the homolytic rupture of the C-Cl bond of this molecule catalyzed by $In^{3+}$, which suffer a redox cycle ($In^{3+}/In^{2+}$). This effect can explain that in this work, increasing on the amounts of the metal lead to most active catalysts.

Concerning to the interaction between *o*-xylene and metal species, although Choudary and Jana propose that indium oxide also participates in *o*-xylene activation [45], this possibility is not clear according to our experimental results, since both the strength of the adsorption and the specific interaction (which provides an insight about the chemical interaction between *o*-xylene and catalyst surface) is lower for the metal-loaded spent catalyst. This result lead to think that there is a high surface concentration of *o*-xylene in all the cases, and is the formation of reactive species from benzyl chloride the determinant step for this reaction. In this reaction the metal support interaction is weak so it is truly going by homogenous catalysis mechanism as shown in figure 4.15.

# Chapter 5

# Conclusions

High conversion of exhausted catalysts to zeolite A and its application in metal removal from water/wastewater constitute a valid alternative to disposal. Thorough milling of spent catalyst was found to modify reactivity and characteristics of the crystals produced. Depending on the synthesis conditions and activation treatments, it is possible to convert the exhausted catalysts into aluminum rich zeolite type A. About 80-85% conversion with 93% crystallinity is obtained for 4A synthesized with ground spent catalyst. The lowering in crystallinity is attributed to the unconverted spent catalyst. Substantial calcium exchange capacity was observed (5.14 meq$CaCO_3$/g)indicating its possible use in detergent applications. Ion exchange capacity of synthesized 4A for the removal of heavy metals like cadmium (Cd), copper (Cu) and lead (Pb) from water was found to be 0.178 mmol/g, 0.205 mmol/g and 0.222mmol/g respectively.

Though spent catalyst loaded with zinc used in liquid phase benzylation has not resulted appreciably but by converting the spent catalyst into ZSM-5 might produce good results.

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