Acylation of 2-Methoxynaphthalene over Ion-Exchanged Beta Zeolite

By

İsmail Cem KANTARLI

**A Dissertation Submitted to the
Graduate School in Partial Fulfillment of the
Requirements for the Degree of**

MASTER OF SCIENCE

**Department: Chemistry
Major: Chemistry**

**İzmir Institute of Technology
İzmir, Turkey**

September, 2002

ACKNOWLEDGEMENTS

I wish to give my thanks to my supervisors, Prof. Levent Artok and Assistant Prof.Selahattin Yılmaz for their valuable advice, help, and support during the course of the research. I would like to thank Mrs. H.Bulut for her help in the experimental studies and GC analysis throughout my thesis study, Assoc. Prof. A. Eroğlu and Mr. S. Yılmaz for atomic absorption and ICP analyses, Dr. H. Özgener for his help in the purification of authentic samples, and Miss B. Öztürk for FTIR analysis. Financial support by the Research Funding Office of Izmir Institute of Technology is highly appreciated.

ABSTRACT

Friedel Crafts acylation of 2-Methoxynaphthalene was carried out over various ion-exchanged β zeolites ($M^{n+}\beta$, where M^{n+}: In^{3+}, Zn^{2+}, Al^{3+}, Fe^{3+}, La^{3+}) with various anhydride (acetic, propionic and benzoic anhydrides), or acyl chloride (acetyl, propionyl and benzoyl chlorides) acylating reagents. The results suggested that selectivity towards the 6-substituted products was higher with the larger size anhydrides, propionic and benzoic anhydrides. The metal cation type within the zeolite significantly influenced the extent of conversion and product distribution. That La^{3+} exchanged zeolite displayed higher selectivity for the 6-position acylated product with anhydrides ascribed mainly to narrowing of channels by the presence of $La(OH)^{2+}$ ions that leave no room for the formation of more bulky isomeric forms and to enhanced Bronsted acidity of the zeolite. With acyl chlorides, the recovery of ketone products was found to be remarkably low. 1-Acyl-2-methoxynaphthalenes actively underwent deacylation when acyl chlorides were used as the acylation reagent.

ÖZ

Bu çalışmada 2-Metoksinaftalinin In^{3+}, Zn^{2+}, Al^{3+}, Fe^{3+}ve La^{3+} iyonlarıyla değişime uğramış β-zeolitleri üzerinde çeşitli anhidrit (asetik, propiyonik, ve benzoik anhidritler) ya da açil klorür (asetil, propiyonil, ve benzoil klorür) açilleme reaktifleriyle Friedel-Crafts açillenmesi incelenmiştir. Sonuçlar göstermiştir ki, propiyonil ve benzoiyik anhidrit gibi büyük boyutlu anhidritlerle 6-pozisyonundan açillenmiş ürüne olan seçimlilik daha yüksektir. Zeoilitin içindeki metal katyon tipi de dönüşümü ve ürün dağılımını önemli ölçüde etkilemektedir La $^{3+}$ ile değişime uğramış zeolit hacimli izomerlerin oluşumu için hiç yer bırakmayan $La(OH)^{2+}$ iyonunun varlığından dolayı daralan kanallar ve artan Bronsted asitliği yüzünden 6-pozisyonundan açillenmiş ürün için daha yüksek seçimlilik göstermiştir. Açil klorürlerle keton ürünlerinin geri kazanımının oldukça düşük olduğu saptanmıştır. Açil klorürler açilleyici reaktif olarak kullanıldığında 1-Açil-2-metoksinaftalin deaçillenmeye uğramıştır.

TABLE OF CONTENTS

LIST OF FIGURES vi
LIST OF TABLES vii

Chapter 1. INTRODUCTION..... 1

Chapter 2. FRIEDEL-CRAFTS ACYLATION OF AROMATICS.....4
2.1.Introduction..... 4
2.2.Friedel-Crafts Acylation Reactions with Homogeneous Lewis-Acid Catalysts..... 5
2.3.Friedel-Crafts Acylation Reactions over Heterogeneous Zeolite Catalysts..... 7
2.4.Friedel-Crafts Acylation of 2-Methoxynaphthalene..... 7

Chapter 3. BACKGROUND: ZEOLITE CHEMISTRY AND CATALYSIS..... 11
3. 1. Industrial Importance of Zeolite Catalysis..... 11
3. 2. Zeolite Chemistry..... 12
3. 2. 1. Chemical Structure..... 12
3. 2. 2. Surface Acidity..... 13
3. 2. 3. Pore Structure and Molecular Sieving..... 15
3. 3. Shape Selectivity..... 16
3 . 4. Ion Exchange..... 18

Chapter 4. EXPERIMENTAL STUDY..... 20
4. 1.Catalyst Preparation..... 20
4. 1. 1. Preparation of H-β Zeolite..... 20
4. 1. 2. Cation Exchange of Zeolites..... 20
4. 2. Zeolite Characterization..... 21
4. 3. Acylation Reactions..... 22
4. 3. 1. GC Method..... 23
4. 3. 2. Calculation of Reactant and Product Amount on GC..... 24
4. 3. 3. Calculation of 2-Methoxynaphthalene Conversion and Product
Selectivity, Product Yield, and Product Recovery..... 25
4. 4. Synthesis of Authentic Compounds..... 26

Chapter 5. RESULTS AND DISCUSSION..... 27

5. 1. Acylation of 2-Methoxynaphthalene with Anhydrides..... 27
5. 1. 1. Acylation of 2-Methoxynaphthalene with Acetic Anhydride..... 28
5. 1. 1. 1. Activity of Catalyst..... 28
5. 1. 1. 2. Effect of Cation Type on Acylation Reactions..... 28
5. 1. 1. 3. Test of Regenerability..... 30
5. 1. 2. Acylation of 2-Methoxynaphthalene with Propionic and Benzoic Anhydrides..... 32
5. 2. Acylation of 2-Methoxynaphthalene with Acyl Halides..... 33

Chapter 6. CONCLUSION..... 36

REFERENCES..... 37

LIST OF FIGURES

Figure 1.1.	(S)-Naproxen synthesis	1
Figure 1.2.	Acylation of 2-Methoxynaphthalene	3
Figure 2.1.	Protiodeacylation of 1-AcMN	9
Figure 3.1.	SiO_4 and AlO_4 building blocks of zeolites	13
Figure 3.2.	Formation of Bronsted and Lewis acid sites in zeolites	14
Figure 3.3.	Schematic presentation of the channel system of zeolite Beta	16
Figure 3.4.	Reactant selectivity	17
Figure 3.5.	Product selectivity	17
Figure 3.6.	Transition state selectivity	17
Figure 4.1.	Preparation of H-β zeolite	20
Figure 4.2.	Experimental set-up designed for acylation of 2-MN reactions	23
Figure 4.3.	A sample gas chromatogram of reactant and reaction products	24
Figure 5.1.	Acylation of 2-MN with acetic anhydride over H^+-β at 130 ^{0}C	27
Figure 5.2.	FTIR spectra for the pyridine adsorbed β zeolites	31
Figure 5.3.	Acylation of 2-MN with acetyl chloride over H^+-β at 130 ^{0}C	33

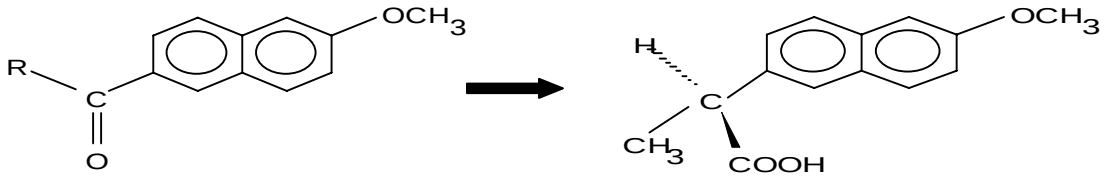
LIST OF TABLES

Table 4.1.	Physico-chemical properties of the ion-exchanged β-Zeolites used in this study	22
Table 5.1.	Acylation of 2-methoxynaphthalene by acetic anhydride over M^{n+} -β zeolite	29
Table 5.2.	Acylation of 2-methoxynaphthalene by propionic or benzoic anhydride over M^{n+} -β zeolite	32
Table 5.3.	Acylation of 2-methoxynaphthalene by acetyl chloride over M^{n+} -β zeolite	34
Table 5.4.	Acylation of 2-methoxynaphthalene by acyl chlorides over M^{n+} -β zeolite	35

CHAPTER 1

INTRODUCTION

Friedel Crafts acylation of aromatics is an essential method for synthesis of aromatic ketones, such as 2-acetyl-6-methoxynaphthalene and p-methoxyacetophenone, used largely as intermediates in the fine chemical industry (Olah, 1973). The selective acylation of 2-MN (2-methoxynaphthalene) is of particular interest. The acylation of 2-MN in the presence of a catalytic amount of conventional Lewis acids gives the major products 6-AcMN (6-acyl-2-methoxynaphthalene) and 1-AcMN (1-acyl-2-methoxynaphthalene). 6-AcMN is recognised to be an important intermediate for the production of an anti-inflammatory drug, (S)-Naproxen (Figure 1.1.) , when the acyl group is the acetyl or propionyl group (Davis et al. 1998;Harrington et al. 1997).



6-AcMN (S)-Naproxen

Figure 1.1. (S)-Naproxen Synthesis

The use of homogeneous Lewis acid catalysts is recognised with a number of disadvantages. A major disadvantage of these catalysts is that they are not regenerable and they are used in reactions in more than stoichiometric amounts. In addition to this, throughout the reaction a resultant intermediate complex occurs and the hydrolysis of this complex produces hazardous corrosive waste products such as acidic and salty waste waters (Smith et al., 1998). Another major disadvantage of these catalysts is the lack of elevated positional selectivity.

It was shown a decade ago that environmentally benign zeolites can be used as heterogeneous catalysts for the acylation of 2-MN by acetic anhydride and the selective formation of 2-acetyl-6-methoxynaphthalene was achieved with H-Beta catalyst (Harvey et al., 1992).

Since that time, various studies reporting the effect of reaction parameters on acylation of 2-MN over zeolites have appeared. Heinichen et al.(1999) studied the influence of postsynthesis treatment such as calcination and acid treatment of zeolite beta in the acylation of 2-MN with acetic anhydride and reported that calcination of zeolite β (beta) under high heating rate enhanced the catalytic activity of inner surface due to the formation of extraframework alumina species in the micropores and acid treatment of zeolite β enhanced the catalytic activity of outer surface due to the extraction of extraframework alumina species out of the micropores and due to the formation of silanol groups. Kim et al. (2000) studied the effect of zeolite type, solvent type, reaction temperature, amount of solvent, and amount of catalyst on the acylation of 2-MN with acetic anhydride. They observed that only zeolite β exhibited good regioselectivity to desired 2-acetyl-6-methoxynaphthalene and obtained the highest 2-MN conversion at 120 ^{0}C. Andy and his co-workers (2000) carried out surface poisoning experiments of acylation of 2-MN over zeolite β and reported that formation of 1-acetyl-2-methoxynaphthalene occurs on the external surface of zeolite. Das et al. (2000) studied the influence of type of acylating agent, reaction temperature, and zeolite structure in the acylation of 2-MN using H-Mordenite, H-β, and H-Y zeolites as catalysts and acetyl chloride and acetic anhydride as acylating agents. They reported that acetic acid formed in the reaction with acetic anhydride was not reactive, as separate experiments carried out with acetic acid showed that it has no acylation activity under the reaction conditions. Cassagrande and his co-workers (2000) studied the effect of zeolite pre-treatment, catalyst-substrate ratio, and reaction temperature on acylation of 2-MN with propionic and benzoic anhydrides over H-β zeolites.

Yet, to my knowledge, there is not any existing report that investigated the catalytic effect of ion-exchanged β- zeolites on acylation reactions of 2-MN, though it is known that the type and amount of metal cation on zeolite may influence the strength and distribution of acid sites. Gunnewegh et al. (1996) studied the acylation of 2-MN over Zn^{2+} exchanged MCM-41. In this study, it is reported that Zn-MCM-41/acetyl chloride combination is less favourable than the H-MCM-41/acetic anhydride combination for both selectivity and regenerability. The leaching of zinc is reported as another problem for the Zn-MCM-41/acetyl chloride combination as well.

In literature, a few studies in which ion exchanged –Y, mordenite and ZSM-5 zeolites were used in acylation of various arenes other than 2-MN, exist. Chiche and co-

workers showed that rare-earth-exchanged –Y could catalyse the acylation of alkylbenzenes with carboxylic acids (Chiche et al 1986; Gauthier et al.1989). In their study, para isomer is reported to be the predominant isomer produced, which is also observed in Friedel-Crafts reactions catalysed by conventional Lewis acids. Gaare and Akporiaye (1996) studied the acylation of anisole over lanthanum exchanged Y type zeolites. They found that LaY was very active in the acylation of anisole and reported that the yield increased with the level of La in zeolite. Laidlaw and coworkers (2001) reported that Zn- and Fe- exchanged zeolites (–Y, mordenite and ZSM-5) were very active on the benzoylation of toluene. The extensive leaching of Zn was observed in the reactions, while Fe mostly remained on the zeolite .

In this study, the catalytic activity of the cation-exchanged β-zeolite in acylation of 2-MN (Figure 1.2.), using various anhydride and acyl chloride reagents is reported. The metal cations loaded onto zeolite by ion-exchange method were In^{3+}, Zn^{2+}, Al^{3+}, Fe^{3+}, and La^{3+}. Acylation studies were also carried out over H^{+}-Y and M^{n+}-Y, however, the results from the –Y type zeolite are not presented in this study, since the conversion of 2-MN (20-30%) and selectivity to the 6-acylated isomer (20-30%) were substantially low.

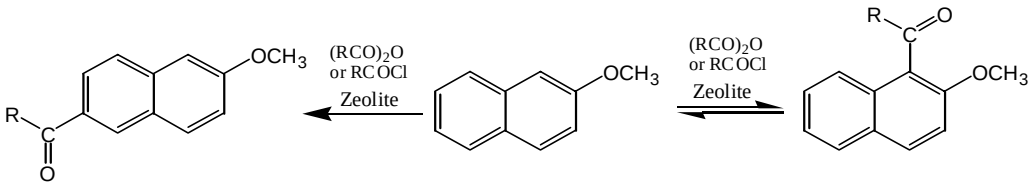


Figure 1.2. Acylation of 2-Methoxynaphthalene

Before covering the experimental methods, reporting and discussing the results obtained throughout this study, it is necessary to give a much more detailed background on Friedel-Crafts acylation of aromatics with either Lewis acids or heterogeneous catalysts and on zeolite chemistry and on their features such as acidity and shape-selectivity that makes them preferable in catalytic applications.

CHAPTER 2

FRIEDEL-CRAFTS ACYLATION OF AROMATICS

2.1. INTRODUCTION

The term “Friedel-Crafts (FC) chemistry” has been used to cover an ever-increasing number of reactions related to the first aluminium chloride reaction discovered by Friedel and Crafts in 1877. They observed by accident that, an alkylhalogenide or acylhalogenide reacted with benzene in the presence of anhydrous $AlCl_3$ forming alkyl- or acyl-substituted aromatic, respectively. They continued working on this subject and found out that a whole class of Lewis acids could catalyse this and many other related reactions such as dealkylation, polymerization, and isomerisation. As a result of their work, it became generally accepted that a reaction combining two or more organic molecules through the formation of carbon to carbon bonds under the influence of anhydrous $AlCl_3$ or related catalysts, is a Friedel-Crafts reaction.

Later on, Bronsted acids and Lewis-Bronsted acid associations were found to also catalyse these reactions, extending the original scope of the Friedel-Crafts reaction to any substitution, isomerisation, elimination, cracking, polymerisation or addition reaction taking place under the effect of Lewis or Bronsted acids. The principal relationship between these different reactions is their electrophilic reaction mechanism. There seems to be no fundamental reason to limit the scope of Friedel-Crafts reactions to the formation of C-C bonds. The formation of many other bonds such as C-N, C-O, C-S, and C-X is in harmony with the general Friedel-Crafts mechanistic principle. Nevertheless, since the Friedel and Crafts were exclusively limited to the substitution of aromatic substrates, it is proper to use the name Friedel-Crafts for those reactions involving the formation of a new carbon-carbon bond by electrophilic substitution on an aromatic ring in the presence of Lewis or Bronsted acid as catalyst (Espeel, 1999).

The $R-\overset{\overset{\displaystyle O}{\|}}{C}-$ group is named as acyl group. Acylation reaction is a reaction whereby an acyl group is introduced into a compound. In this context, the Friedel-Crafts

acylation reaction is the reaction whereby an acyl group is effectively introduced into an aromatic ring.

In Friedel-Crafts acylation reactions, either acyl chlorides or carboxylic acid anhydrides are used as acylating reagents. The product of the reaction is an aryl ketone.

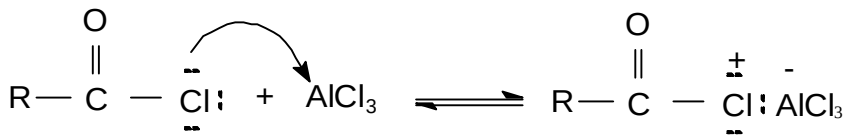
In the following sections Friedel-Crafts acylation reactions and their mechanisms are explained according to the type of catalyst used.

2.2.FRIEDEL-CRAFTS ACYLATION REACTIONS WITH HOMOGENEOUS LEWIS-ACID CATALYSTS

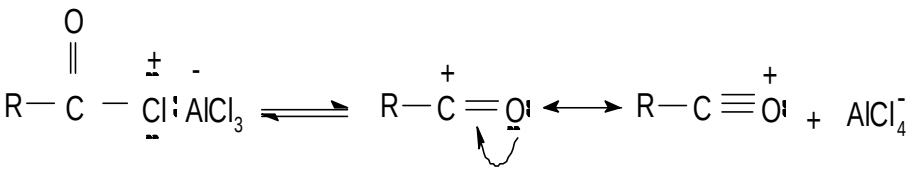
If the aromatic compound to be acylated is not highly reactive, it is a necessity to add at least one equivalent of a Lewis acid catalyst to the reaction mixture.

In the case of Lewis acid catalysts such as $AlCl_3$, the first step in Friedel-Crafts acylation reaction appears to be the formation of an electrophilic acylium ion from an acyl halide in the following way (Solomons,1992):

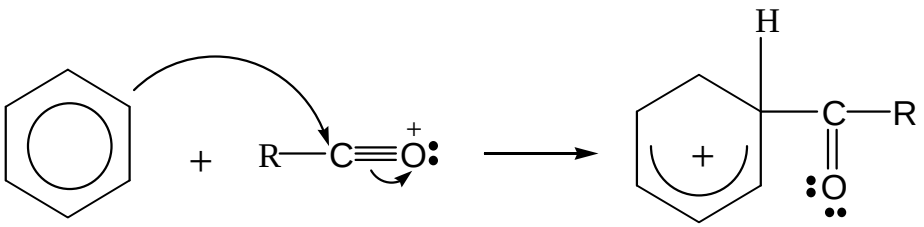
Step 1.

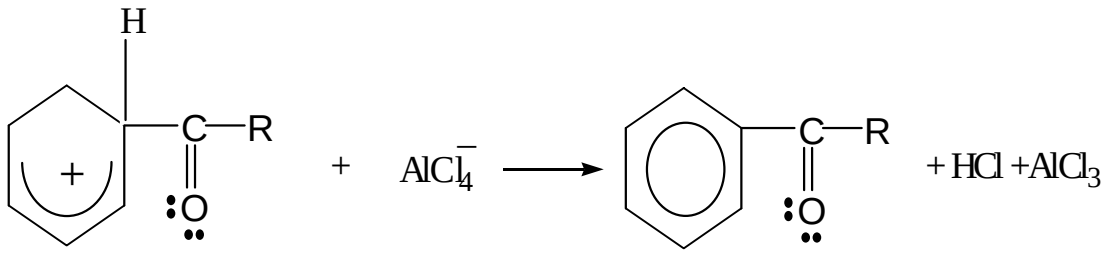


Step 2.

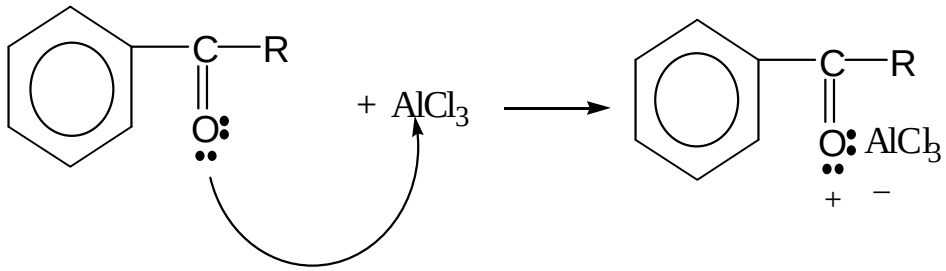


The remaining steps in Friedel-Crafts acylation reactions are as follows:

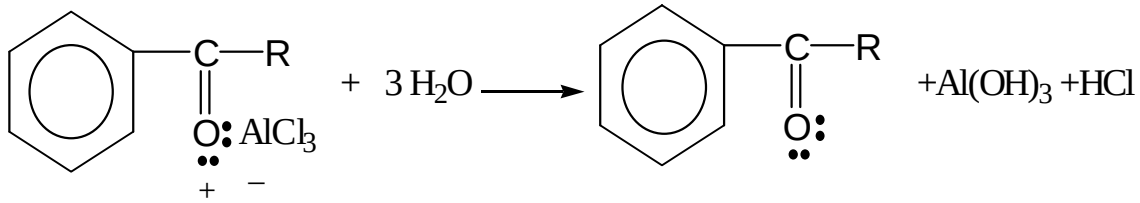




In the last step, $AlCl_3$ (Lewis acid) forms a complex with the ketone(a Lewis base):



After the reaction is over, treating the complex with water liberates the ketone:



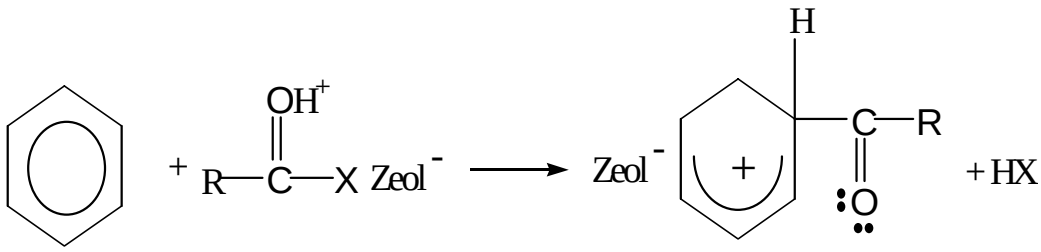
As it is clear from the mechanism, the Lewis acid catalyst can not be regenerated and formation of corrosive waste product such as HCl occurs as a result of the hydrolysis of intermediate complex.

2.3. FRIEDEL-CRAFTS ACYLATION REACTIONS OVER HETEROGENEOUS ZEOLITE CATALYSTS

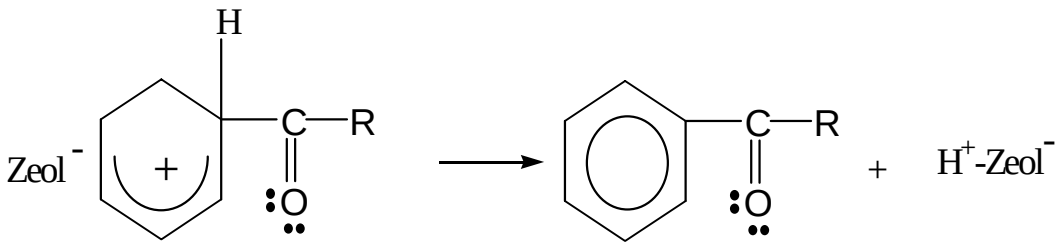
In heterogeneous zeolite-catalysed Friedel-Crafts acylation reaction, a mechanism similar to Lewis acid catalysed reaction is assumed to apply, in which the adduct is formed by the interaction of the surface acid sites with an acylating agent. The plausible mechanism is given below (Das, 2000):

(1)

(2)



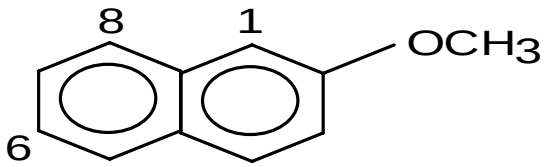
(3)



2.4. FRIEDEL-CRAFTS ACYLATION OF 2-METHOXYNAPHTHALENE

In the Friedel-Crafts acylation of 2-MN, the presence of the electron-donating methoxy group must be taken into account in order to figure out the reaction. The

presence of this electron-donating group activates the 1-, 6-, and 8- positions of the naphthalene ring.



2-Methoxynaphthalene

The 1-position is more active than the other two positions and the 6-position is more stable than the other two positions, so acylation of 2-MN generally occurs at this kinetically favored 1-position at low temperatures and at the thermodynamically favored 6-position at high temperatures. At high temperatures, in the reaction mixture, migration of the acyl group from 1- to 6-position which is named as transacylation and protiodeacylation of the acyl group at the 1-position of 1-AcMN are possible. These two reactions may result in the formation of the thermodynamically favored product which is 6-AcMN. Steric hindrance to acylation is reported in the order 1- > 8- > 6-position (Das, 2000). Therefore, the isomerisation of the sterically hindered ketone 1-AcMN to sterically less hindered isomers like 6-AcMN and 8-AcMN (8-Acyl-2-methoxynaphthalene) will be favored.

In homogeneous catalytic systems, the acylation of 2-MN results in a mixture of 1-AcMN and 6-AcMN initially, and later 1-AcMN is converted to 6-AcMN in a long reaction time (Gore, 1964; Giordano et al.,1990). Since the homogeneous catalyst provides free catalytic sites, acyl group at the sterically hindered 1-position migrates to the more stable 6-position. On the other hand, in heterogeneous catalytic systems, most of catalytic sites are fixed on external surfaces and inner pores. Therefore, the selectivity of the products will be changed in accordance with the restriction imposed on the sites. Gunnewegh et al., in 1996 and Choudary et al., in 1998, reported that over fixed catalytic sites without a geometric restriction 1-AcMN converted back only to 2-MN even at high temperatures (Figure 2.1.). S.D.Kim and co-workers (2000), on the other hand, reported that over H-Beta, by contrast, 1-AcMN reacted to yield not only 2-MN but also 6-AcMN at temperatures higher than 120 ^{0}C, when acyl group is the acetyl group. They also tested deacylation of 6-AcMN over H-Beta and

found out that deacylation of 6-AcMN occurs at 180 ^{0}C but not at 120 ^{0}C. 6-AcMN did not convert back to 1-AcMN .

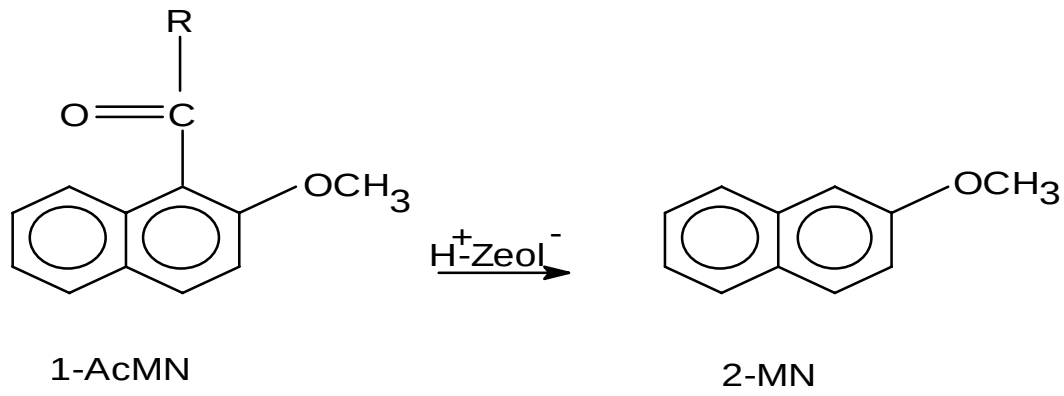


Figure 2.1. Protiodeacylation of 1-AcMN

In heterogeneous catalytic systems, diffusion characteristics of reactant and product molecules must also be taken into account while trying to figure out the selective acylation of 2-MN. Bharathi investigated the diffusion characteristics of acetylated 2-MN inside the large pore zeolites. He calculated the three largest dimensions of 2-MN, 1-Ac-2-MN (1-acetyl-2-methoxynaphthalene), 6-Ac-2-MN (2-acetyl-6-methoxynaphthalene), and 8-Ac-2-MN (8-acetyl-2-methoxynaphthalene) as (10Å x 6Å x 2,8Å), (10,3Å x 8,1Å x 4,1 Å), (12,3Å x 6,2Å x 2,8Å), and (10,5Å x 7,8Å x 2,8Å), respectively. Moreover, he studied the chemical interaction between the zeolite guest-host molecules using energy minimization calculations by carrying out the diffusion of these molecules along the a-direction in the 12-membered channels of mordenite, L, and β zeolites. For zeolite β, the diffusion energy barrier found for 2-MN, 1-Ac-2-MN, 6-Ac-2-MN, and 8-Ac-2-MN were 9.4, 275.18, 16.5, and 320.2 kJ mol^{-1}, respectively. The diffusivity parameter found for 2-MN,1-Ac-2-MN, 6-Ac-2-MN, and 8-Ac-2-MN were 0.965, 0.762, 0.971, and 0,797, respectively. The diffusivity value is always between 0 and 1, and values closer to 1 indicate higher diffusivity. Both of these results imply that the pore dimensions, shape of the pores and their correspondence to the size and shape of the molecules determine the diffusion characteristics of molecules. These results also imply that there will be high selectivity for the diffusion of 6-Ac-2-MN in the case of zeolite β, since it has the highest diffusivity and the diffusion energy barrier for it is the smallest compared with those of other molecules. Thus, zeolite β

seems to be a suitable catalyst for the shape selective acylation of 2-MN to 6-Ac-2-MN (Bharathi et al., 1999).

CHAPTER 3

BACKGROUND: ZEOLITE CHEMISTRY AND CATALYSIS

3.1. INDUSTRIAL IMPORTANCE OF ZEOLITE CATALYSIS

Zeolites exist in nature and have been known for almost 250 years as aluminosilicate minerals**.** Most common examples of zeolites are clinoptilolite, faujasite, offretite, ferrierite, and chabazite**.** Today most of these and many other zeolites are of great interest in many fields. Out of these fields, catalysis is the most essential application of zeolites in terms of financial market size, but not in terms of tons of production per year (Weitkamp et. al, 1999).

Zeolites exhibit unusually high activity for various acid catalyzed reactions. The properties that makes zeolites proper for heterogeneous catalytic applications are given in literature as follows:

1. Zeolites have porous crystal structures made up of channels and cages that allow a large surface area thus a large number of catalytic sites. They have pores with one or more discrete sizes between 0,2 and 2 nm (Tosheva, 2001).
2. They have exchangeable cations allowing the introduction of cations with various catalytic properties. If these cationic sites are exchanged to H^+, they can have a high number of strong acid sites (Bhaita, 2000)
3. Since they are solid, they can easily be removed from products and therefore they are environmentally benign. No waste or disposal problems is observed with zeolites (Espeel et al., 1999).
4. Their molecular sieve action can be used to control which molecules have access to and which molecules can depart from the active sites which is defined as shape-selectivity.

But unfortunately from the catalytic perspective, naturally occuring forms of zeolites are of limited value, because (Weitkamp, 2000)

1. They almost always contain undesired impurity phases,
2. Their chemical composition changes from one deposit to another and even from one stratum to another in the same deposit,
3. Nature has not optimized their properties for catalytic applications”

Studies on synthesis of new zeolite structures and their catalytic applications exhibited an amazing growth with the advent of synthetic zeolites in the period from 1948 to 1959. Initially, new zeolite-based catalysts were investigated for applications in the petrochemical industries and with the introduction of synthetic faujasites zeolites X and Y on an industrial scale in fluid catalytic cracking of heavy petroleum distillates in 1962, zeolite catalysis has undergone rapid and dynamic advances (Weitkamp, 1999). Today about 100 zeolites which do not have natural counterparts are known and some of them have great practical importance in many applications.(Bhatia, 2000). In addition to increased use in petrochemicals manufacture, zeolite catalysis is expanding into the areas of specialty and fine chemical synthesis. It is possible with the establishment of a relationship between the acid properties of the zeolite catalysts and the outcome of the reaction that a drug molecule or one of its intermediates will be synthesized over a zeolite-based catalyst in the near future (Davis, 1998).

3.2. ZEOLITE CHEMISTRY

3.2.1. Chemical Structure

Zeolites are hydrated aluminosilicates that are built from an infinitely extending three-dimensional network of SiO_4 and $[AlO_4]^{-1}$ tetrahedra. These tetrahedra join together in through shared oxygen atoms with various regular arrangements, to form hundreds of different three-dimensional crystal frameworks (Breck, 1974). The zeolite framework contains channels, channel intersections and/or cages. Inside these voids are water molecules and small cations (Weitkamp, 2000). Since the trivalent aluminum is bonded to four oxygen anions, each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation, generally from the group IA or IIA (Tosheva, 2001). The chemical composition of zeolites may be represented by the emprical formula:

$$A^{m+}_{y/m} \left[(SiO_2)_x . (AlO_2^-)_y \right] . \; z\,H_2O$$

where A is a cation with the charge m, (x + y) is the number of tetrahedra per crystallographic unit cell and x/y is the so-called framework silicon / aluminum ratio n_{Si} / $n_{Al.}$ SiO_4 and AlO_4 building blocks of zeolites are given in Figure 3.1.

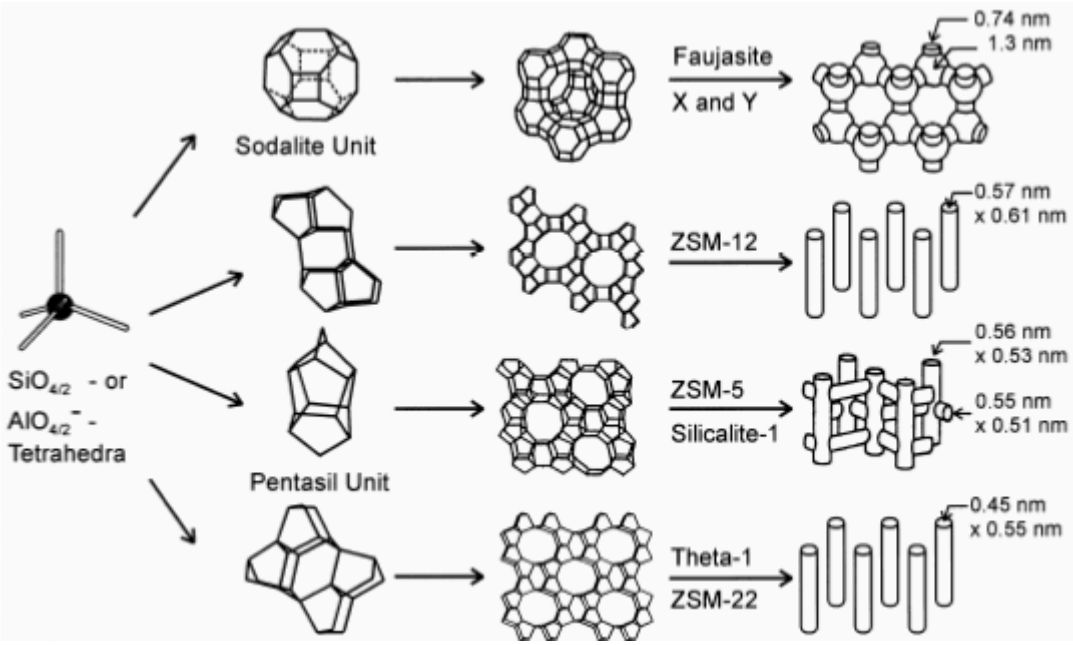


Figure 3.1. SiO_4 and AlO_4 building blocks of zeolites (Weitkamp, 2000)

According to the increasing framework Si / Al ratio, zeolites are categorized as: (i) low Si / Al zeolites (1 to 1.5, zeolite A, zeolite X); (ii) intermediate Si / Al zeolites (~ 2 to 5, mordenite); (iii) high Si / Al zeolites (~ 10 to 100, ZSM-5, Beta); and (iv) silica molecular sieves (silicalite-1). As the Si / Al ratio of a zeolite increases, its cation content decreases, its thermal stability increases, and its surface selectivity changes from hydrophilic to hydrophobic. Silica molecular sieves (silicalite-1) have a neutral framework, are hydrophobic in nature, and have no ion exchange or catalytic properties, since $[AlO_4]^{-1}$ tetrahedra do not exist in the framework structure (Tosheva, 2001).

3.2.2. Surface Acidity

The feature that enables the separation of zeolites from all-silica minerals, is the substitution of metals other than silicon such as aluminum into the crystalline

framework. The replacement of SiO_4 tetrahedra by the $[AlO_4]^{-1}$tetrahedra in the zeolite framework results in excess negative charge that needs to be neutralized by cations. Compensation of the negative charge by associated cations like H^+ , Na^+ , K^+ , Ca^{2+} , and NH_4^+ generates the acid sites. The catalytic activity of the zeolites is attributed to the existence of these acid sites and the proton affinity at the charged framework. The catalytic activity of acid sites is either Bronsted or Lewis in character(Hindle, 1997). If the acid site is of Bronsted type, it acts as a proton donor. If the acid site is of Lewis type, it acts as an electron acceptor. A description of acidity in general, and surface acidity more specifically, requires the determination of the nature, the strength, and the number of acid sites.

If the charge compensating cation associated with the tetrahedral aluminum is ammonium, heating the zeolite between 300-400°C would cause the zeolite surface obtain the capacity to act as a proton donor and therefore act as a Bronsted acid. If the zeolite is heated to a temperature higher than 450°C, formation of Lewis acid site and zeolitic water would occur (Weitkamp, 2000). Ward proposed that two Bronsted acidic sites are needed for the formation of a single Lewis (electron acceptor) acidic site (Figure 3.2.) (Ward, 1996).

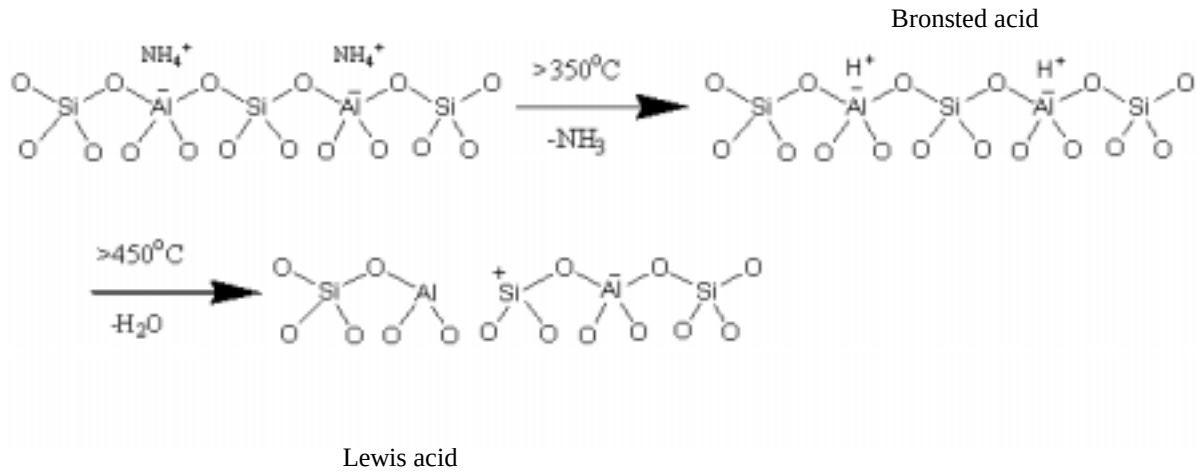


Figure 3.2. Formation of Bronsted and Lewis acid sites in zeolytes

The chemical nature of the Bronsted acid sites is the same regardless of the method used for their generation. The proton attached to a framework oxygen atom connected to neighbor silicon and aluminum atoms results in the so-called bridged

hydroxyl group which is the site responsible for the Bronsted acidity of zeolites (Corma, 1995). On the other hand, the precise chemical nature of Lewis acid sites is less clear. For some time, they were looked upon as tricoordinated aluminum and / or tricoordinated, positively charged silicon in the framework (Weitkamp, 2000). However, Kühl, in 1977, was able to show that silicon in dehydroxylated zeolites remains tetracoordinated and much of the aluminum is converted to octahedral rather than trigonal coordination. Kühl concluded that $[(AlO)^{+}]_{n}^{n+}$ units removed from the zeolite framework act as true Lewis sites (Kühl, 1977).

3.2.3. Pore Structure and Molecular Sieving

There are mainly two types of pore structures of zeolites. One of them provides an internal pore system comprised of interconnected cage-like voids, e.g. Zeolite A and Zeolite Y. The other one provides a three dimensional system of uniform channels, e.g. ZSM-5 has set of straight parallel pores intersected by a set of perpendicular zigzag pores or a one-dimensional channel system composed of only straight parallel pores as in ZSM-22 (See Figure 3.1.).

In most of the zeolites, crystalline voids make up from 20 to 50% of the crystal volume (Breck, 1974).

The diameters of the windows or pore leading into the voids vary according to the arrangement of the tetrahedral units. The size of aperture depends on the number of oxygen atoms present in the ring. The apertures can have 8, 10, or 12 oxygen atoms and zeolites are classified according to this number of oxygen atoms as 8, 10, or 12 oxygen membered ring zeolites. The size of the aperture is also dependent on the sizes of nearby cations, which may partially block it.

Zeolite Beta, familiar with its disordered framework, has a three-dimensional intersecting, 12-membered ring channel system. Two mutually perpendicular straight channels, with a cross-section of 0.76 x 0.64 nm, run in the a- and b-directions. A sinusoidal channel of 0.55 x 0.55 nm runs parallel to the c-direction (Jansen, 1997). Schematic presentation of the channel system of zeolite Beta is given in Figure 3.3.

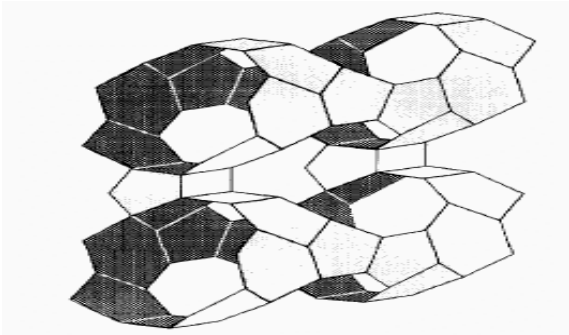


Figure 3.3. Schematic presentation of the channel system of zeolite Beta (Jansen, 1997)

Molecular sieving is the selective adsorption of molecules, whose dimensions are below a certain critical size, into the intracrystalline void system of a molecular sieve. The use of kinetic diameter of a molecule is very popular for comparison with zeolite pore dimensions. But, it is not only the kinetic diameter of a molecule that determines whether it is adsorbed in a given zeolite or not, but also the shape of the molecule in relation to the shape of the pore openings (Weitkamp et al., 1999)

3.3. SHAPE SELECTIVITY

As acidic, basic, or redox catalysts, zeolites essentially act in a way similar to their homogeneous counterparts. However, because of their specific nature, these solid microporous materials sometimes show a behavior not observed in the homogeneous phase. Shape selectivity of zeolites is such kind of a behavior.

In zeolites , most of the active sites are located in the well-defined and molecularly sized pores and cages. Throughout a reaction, the transforming molecules are continuously exposed to steric limitations imposed by the zeolite structure, possibly changing the course of the reaction and finally resulting in product distributions showing deviations from those obtained in the homogeneous phase. In this context, molecular shape selectivity can be described as the restrictions imposed on guest molecules by size and shape of the zeolite pores. There are three types of molecular shape selectivity observed associated with zeolites (Espeel et al., 1999):

1)Reactant selectivity implies that those molecules with high diffusivity will react preferentially and selectively, while molecules excluded from the zeolite interior will only react on the external surface of the zeolite (Figure 3.4.).

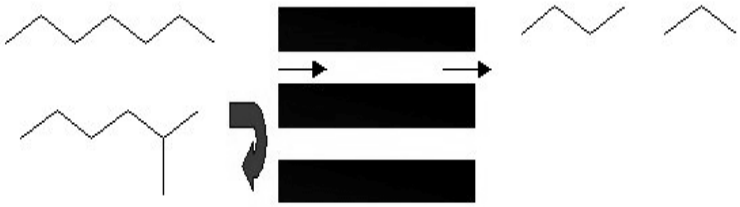


Figure 3.4.Reactant selectivity (www.keele.ac.uk/depts/ch/postgrad/spc/webpage3.html)

2)Product selectivity implies that products with high diffusivity will be preferentially desorbed, while the bulkier molecules will be converted and equilibrated to smaller molecules which will diffuse, or eventually react to form larger species which will block the pores (Figure 3.5.).

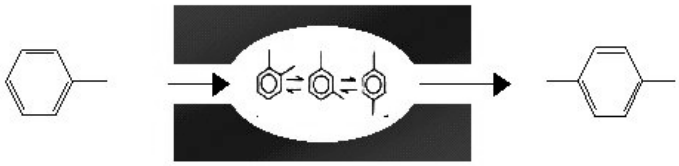


Figure 3.5. Product selectivity (www.keele.ac.uk/depts/ch/postgrad/spc/webpage3.html)

3)Transition state selectivity takes place when certain reactions are prevented as the transition state necessary for them to proceed is not reached because of the space restrictions (Figure 3.6.).

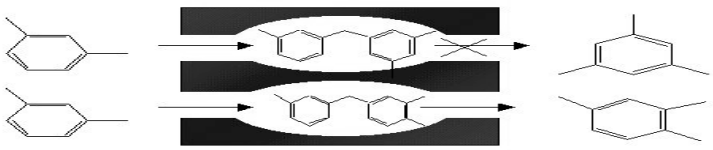


Figure3.6.Transition state selectivity (www.keele.ac.uk/depts/ch/postgrad/spc/webpage3.html)

Modification of the shape selective properties of zeolites is possible with different approaches for catalytic purposes. Most of these approaches not only change the shape selective but also the acid properties of zeolites. It is in fact impossible to change these properties independently. These approaches are given as follows:

(i) Cation exchange: Small cations like H^+ and Na^+ can be replaced by larger cations such as K^+ , Rb^+ , Cs^+ , using the ion-exchange method. This replacement results in the narrowing of the pore diameter of the zeolite channels in addition to a change in the number and strength of the Bronsted acid sites.

(ii) Deposition of inorganic oxides: By deposition of inorganic oxides in the pores of the zeolite, the effective pore diameter is reduced and the steric constraints on reactants, transition state or products are enhanced. Deposition of these oxides also changes the acidic and basic properties of the zeolite.

(iii) Crystal size: The crystal size of zeolite catalysts can be varied by adapting the synthetic conditions. By increasing crystal size, the fractional amount of sites on the outside of the crystal in comparison to the total amount of sites decreases and consequently the center of catalytic activity shifts from extra to intrazeolitic.

(iv) Deactivation of the external surface: For small crystals, the active sites on the external surface largely contribute to the catalytic activity of the material. In the case of Bronsted acid sites, they can be deactivated by deposition of inorganic oxides or neutralized by chemical reaction with organosilanes which are too bulky to diffuse through the intracrystalline voids. By silylation, the hydrophobicity of the materials is enhanced.

(v) Deposition of organic bases: Deposition of organic bases in the intracrystalline voids narrows the pore apertures and so enhances the steric constraints on molecular diffusion.(Espeel et al.,1999)

3.4. ION EXCHANGE

The cations of zeolites are distributed within the same intercrystalline pore systems as the zeolitic water and can be mobile like the zeolite water as a result of the open structure of zeolite. But, unlike the water, cations are not free to leave the crystals, if they are not replaced by their electrochemical equivalent of other cations since neutralization of the anionic charge of the aluminosilicate framework is required. The nature of the cations in a zeolite structure can be easily and simply changed. A variety

of ionic forms can be prepared using alkali and alkaline earth or transition metals and rare earth ions. Sometimes, the exchange reaction may go to completion or fail to do so, depending on the nature of the ion, the zeolite, and the temperature. Changes in ionic nature may result in marked changes of zeolite properties like thermal stability, sieving, and sorptive and catalytic function (Bhatia, 2000).

Usually, ion exchange is applied by simply contacting the zeolite with a salt solution of a different cation at ambient temperature, or at elevated temperature if an accelerated exchange rate is desired. The exchange reaction, in which one type of cation is replaced with another, assumes an equilibrium state that is specific to the particular zeolite and particular cations (Kühl, 1999).

CHAPTER 4

EXPERIMENTAL STUDY

4.1. CATALYST PREPARATION

4.1.1. Preparation of H-βZeolite

Zeolite Beta in pronated form (H-β) was obtained by the calcination of NH_4-β-zeolite (Zeolyst International, CP-814E, SiO_2/Al_2O_3 mole ratio: 25) at 550°C for 10 h in air atmosphere (Figure 4.1.).

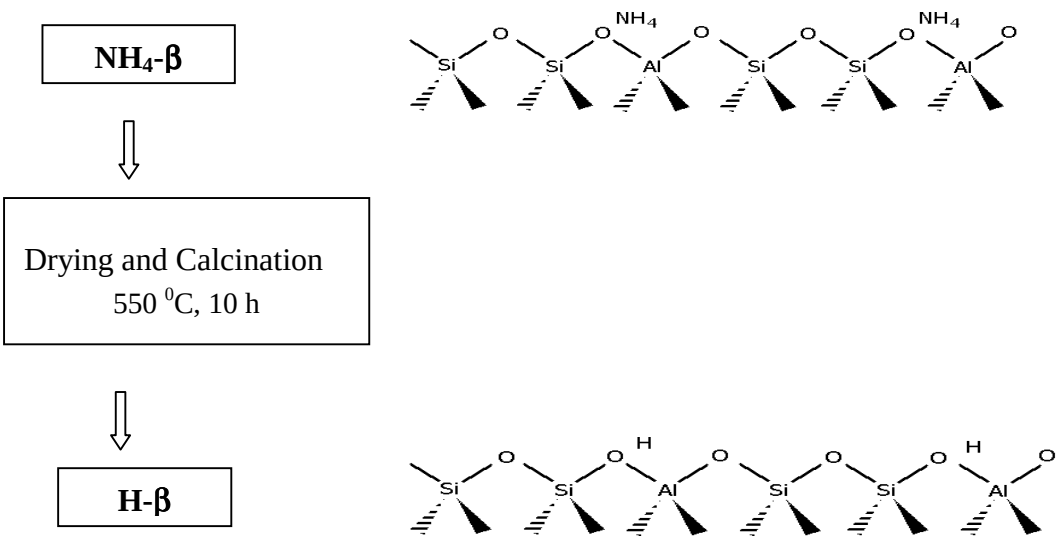


Figure 4.1. Preparation of H-β Zeolite

4.1.2. Cation Exchange of Zeolites

Metal cations were loaded onto the zeolite by stirring 5 g of NH_4-β zeolite in a 40 ml solution of 0.3 M of the proper metal chloride or metal nitrate at 80°C for 4 h. Following the ion-exchange process, the zeolite suspension was filtered, washed thoroughly by deionised water and finally dried at 120°C overnight**.**

4.2. ZEOLITE CHARACTERIZATION

BET surface areas of calcined zeolite samples were measured on a Micrometrics ASAP-2010. The cation content of samples was determined by flame atomic absorption method using Solaar M atomic absorption system and by ICP-emission method using Varian-96 Inductively Coupled Plasma Atomic Emission Spectrometer. By ICP-emission method La^{3+} and In^{3+} content of zeolites were determined. By atomic absorption method Zn^{2+} and Fe^{3+} content of zeolites were determined. For the cation content analysis, the dissolved zeolite samples were prepared according to the microwave digestion method which is summarised below:

Over 50 mg of zeolite sample, a mixture of 3 mL HNO_3, 2 mL HF, and 1 mL $HClO_4$ were added and this mixture was heated in the Ethos Plus Microwave Labstation furnace according to the following heating program: The mixture was heated to 120 ^{0}C and hold at this temperature for 3.5 minutes under 500 W power. Then it was heated to 150 ^{0}C and hold at this temperature for 3.5 minutes under 600 W power. As the next step, it was heated to 190 ^{0}C and kept at this temperature for 4 minutes under 550 W power. Then, the sample was held at the same temperature under 600 W power this time. At the end of the program, the solutions were diluted to a final volume of 25 ml. The solutions prepared for ICP analysis were diluted according to a dilution factor of 100. The solutions prepared for atomic adsorption analysis were diluted according to a dilution factor of 2. For ICP analysis, 1, 5, and 10 ppm of $La^{3+}$and In^{3+} cations containing standard solutions were prepared. For atomic absorption analysis, 1, 2, and 5 ppm of Zn^{+2} cation and 1, 2, 5, and 10 ppm of Fe^{3+} cation containing standard solutions were prepared.

The characteristics of catalysts are given in Table 4.1.

Bronsted and Lewis acidities of zeolites were examined by FTIR analysis of pyridine-sorbed zeolites following a procedure given by Kaneda. After calcination of each zeolite catalyst, it was placed in a glass vessel. Then pyridine-saturated nitrogen stream was passed through the glass tube for 1 hour. Then, the apparatus was heated to 150 ^{0}C and kept at this temperature under a nitrogen stream for 2 hours in order to remove excess pyridine. The resulting zeolite (1 mg) was mixed with potassium bromide (100 mg), ground with agate mortar, extruded to a disk, and subject to FTIR measurement. IR Spectra of samples were recorded between 1400-1700 cm^{-1}

wavelength (resolution:2 ; number of scans:200) by a Nicolet Magna 550 FTIR spectrometer and processed with a computer equipped with it. The specific peaks of interest were at 1543 and 1448 cm^{-1} in these spectra. According to the literature these peaks could be assigned as C=C stretching of pyridine adsorbed at Bronsted and Lewis acid sites, respectively (Kaneda et al., 1998).

Table 4.1.Physico-chemical properties of the ion-exchanged β-zeolites used in the study

$M-^{n+}-$	Metal Cation Content, wt%	BET surface area (m^2/g)	Micropore Volume (cm^3/g)
H^+	-	584	0.192
In^{3+}	2.1	461	0.160
Zn^{2+}	1.9	452	0.148
Al^{3+}	ND[a]	445	0.145
Fe^{3+}	3.4	459	0.145
La^{3+}	0.7	395	0.133

[a]ND:Not Determined

4.3. ACYLATION REACTIONS

Acylation reactions were carried out in a 50 ml three necked round-bottom flask connected to a condenser in an oil bath under nitrogen atmosphere (Figure 4.2). The freshly activated (550°C, 10 h) 1 g of catalyst was added quickly into the flask while still hot. 10 mmol 2-Methoxynaphthalene(Merck, purity >99%), 20 mmol acylating reagent and 4.5 mmol tetradecane(Merck, purity >99%) as an internal standard were dissolved in 20 ml nitrobenzene(Merck, purity >99%) which was previously dried over $CaCl_2$ and distilled before use, and then introduced into the reaction flask through a dropping funnel. As acylating agent acetic anhydride (Merck, purity >98%), propionic anhydride (Fluka, purity >98%), benzoic anhydride (Fluka, purity >98%), acetyl chloride (Fluka, purity >98%), propionyl chloride (Merck, purity >98%), and benzoyl chloride (Riedel, purity >99%) molecules were used.

Figure 4.2. Experimental set-up designed for acylation of 2-MN reactions

The reactions were performed for 24 h at 130°C unless otherwise stated. Aliquots of samples were taken periodically and analysed by GC and GC/MS techniques. The identity of products was confirmed by comparison of their GC and GC/MS spectra with those of authentic samples. GC/MS spectra of samples was taken with Varian Star 3400 CX gas chromatograph and Varian Saturn 2000 GC/MS/MS mass spectrometer.

4.3.1 GC Method

The samples were analysed by GC (Shimadzu GC-17A) on a 30-m fused silica capillary column(5% Dimethylsiloxane, 95% phenyldimethylsiloxane) and with a FID detector. The GC program applied throughout the analysis is as follows: the column temperature was 40 ^{0}C at the beginning of the program and it was heated with a rate of 10 ^{0}C/min up to 250 ^{0}C. The column was kept at 250 ^{0}C for 5 minutes. Throughout the

analysis the injector and detector temperatures were kept constant at 330 ^{0}C and 340 ^{0}C, respectively. The analysis was performed on split mode with a split ratio of 1/50.

A sample gas chromatogram of the reactant and reaction products according to the given temperature program is given in Figure 4.3.

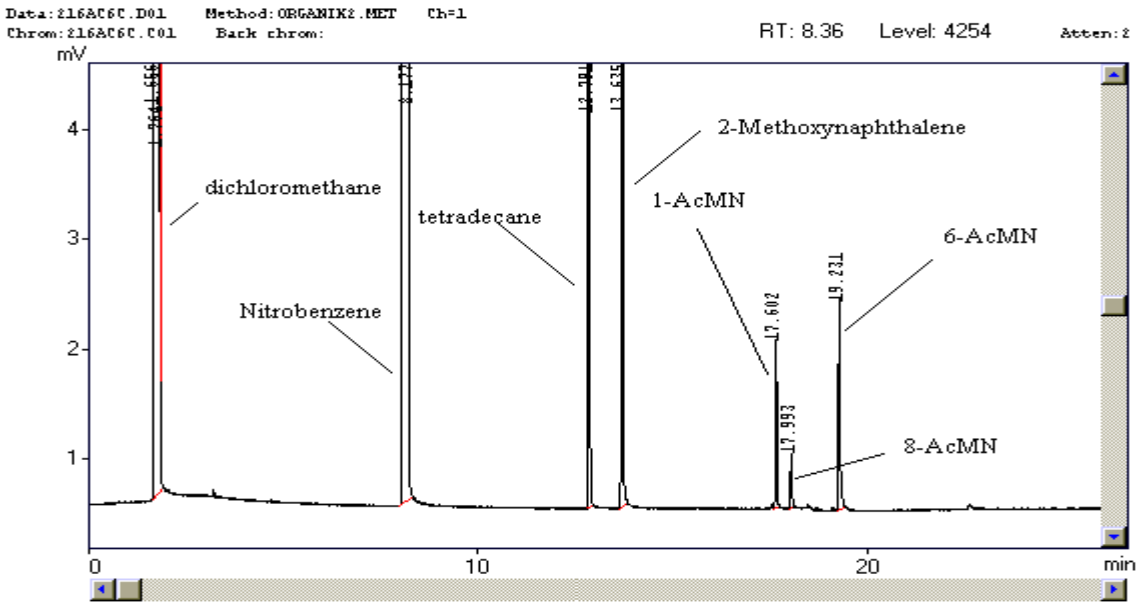


Figure 4.3. A sample gas chromatogram of reactant and reaction products

4.3.2 Calculation of Reactant and Product Amount on GC

For the calculation of amount of reactant and products, initially response factor of each reactant and product for the set temperature program of GC was determined. As internal standard tetradecane was used. The amount of internal standard does not change throughout the reaction, so the response factor of each compound was determined according to the amounts and areas under the peaks of internal standard and standard compound of interest. For the determination of response factor of a compound , a known amount of standard compound together with a known amount of internal standard dissolved in the reaction solvent and diluted with dichloromethane is injected to GC. After the analysis is completed according to the set temperature program, the following equation is used for the determination of response factor:

$$\text{R.F.} = \left(\frac{\text{internal standard area}}{\text{compound area}} \right) \times \left(\frac{\text{compound amount}}{\text{internal standard amount}} \right) \qquad (4.1.)$$

In order to calculate the amount of both reactant and products at any time of reaction, aliquots of reaction sample taken from the reaction flask at that time were injected to GC. At the end of GC analysis, taking the amount of tetradecane and the area under the tetradecane peak into account, the following equation was used in order to calculate the amount of reactant and products at that time:

$$\text{amount of compound} = \left(\frac{\text{internal standard amount}}{\text{internal standard area}} \right) \times \text{R.F.} \times \text{compound area} \qquad (4.2.)$$

4.3.3. Calculation of 2-MN Conversion and Product Selectivity, Product Yield and Product Recovery

2-MN conversion at any time is calculated using the following equation:

$$(2-\text{MN Conversion})_t\ \% = \frac{\left((2-\text{MN})_i - (2-\text{MN})_t\right)}{(2-\text{MN})_i} \times 100 \qquad (4.3.)$$

where $(2\text{-MN})_i$ is the weight of 2-MN at the beginning of the reaction and $(2\text{-MN})_t$ is the weight of 2-MN at time t.

Selectivity of an isomer at any time was calculated using the following equation:

$$\text{Selectivity}\ \% = \frac{(\text{mol of isomer})_t}{(\text{total moles of isomers})_t} \times 100 \qquad (4.4.)$$

where $(\text{mol of isomer})_t$ is the weight of isomer at time t and $(\text{total moles of isomers})_t$ is the sum of moles of all isomers at time t.

Product yield of a molecule was calculated according to the following equation:

$$\text{Product Yield} = \frac{(\text{moles of product})_t}{\text{initial moles of } 2-\text{MN}} \qquad (4.5.)$$

Product recovery at any time of reaction is calculated according to the following equation:

$$\text{Product Recovery} = \frac{(\text{Total of Product Yield})_t}{(2\text{-MN Conversion})_t\,\%}\, x\,100 \qquad (4.6)$$

4.4. SYNTHESIS OF AUTHENTIC COMPOUNDS

1-Acyl-2-methoxynaphthalenes were synthesised by acylation of 2-MN over a stoichiometric amount of $AlCl_3$ with the corresponding acyl chloride compound. Dry dichloromethane solution of 2-methoxynaphthalene was cooled down to -15°C. Acyl chloride was added gradually and stirred for an hour at -15°C. At the end of reaction, to the mixture was added dilute HCl solution and the product was extracted by dichloromethane and purified by recrystallisation using petroleum ether and by column chromatography on silica gel using hexane-dichloromethane(8:2) as eluent.

2-Acetyl-6-Methhoxynaphthalene was commercially available. However, other 6-Acyl-2-Methoxynaphthalene compounds were recovered from zeolyte catalysed acylation of 2-MN through column chromatography using hexane-dichloromethane (8:2) as eluent.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. ACYLATION OF 2-METHOXYNAPHTHALENE WITH ANHYDRIDES

Some general remarks can be drawn on the basis of the results from acylation reactions performed with anhydrides. Regardless of the structure of anhydride and metal type on the zeolite used, 1-acyl and 6- acyl methoxynaphthalene products were the major acylation products, while selectivity of other acylated isomers was <10% overall. Except the reactions with propionic acid, 8-acyl isomer of other ketone products comprised the most (3-5%). Overall ketone selectivity was generally >95%. No indication of protiodeacylation reaction (Harvey et al. 1992;Al-Kaabi et al.1998) or intermolecular trans-acylation reactions (Fromentin et al., 2000), which were reported to be principal reaction types responsible for deacylation of 1-acyl-2-methoxynaphthalene primary product, were observed in the presence of anhydrides.(See Figure 5.1.)

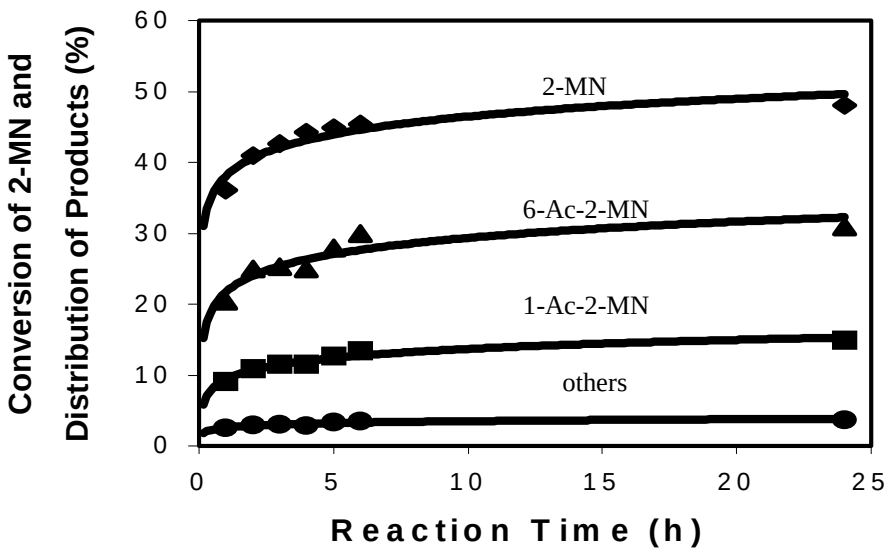


Figure 5.1. Acylation of 2-MN with acetic anhydride over H^+-β at 130°C

5.1.1. Acylation of 2-Methoxynaphthelene with Acetic Anhydride

5.1.1.1. Activity of Catalyst

Figure 5.1 shows the reaction run for the acylation of 2-MN with acetic anhydride over H^+-β at 130°C. Apparently the conversion was almost ceased after 6 h of reaction time and there appears to be no interconversion between product types. This case of 2-MN conversion with H^+-β can be generalised for other cation exchanged beta zeolites. If 2-MN conversion values at 2nd and 24th hours in Table 5.1. are examined, it can be seen that, except Zn^{2+}-β zeolite, longer reaction times slightly increased the 2-MN conversion at 130 ^{0}C. So for longer reaction times, rate of 2-MN conversion is almost ceased and catalyst seems to deactivate.

With the H^+-β and In^{+3}-β zeolites, the elevation of reaction temperature to 160°C increased the conversion rate, though the maximum 2-MN conversion was comparable to that obtained at the lower reaction temperature after 24 h of reaction. The acylation reactions were terminated at this conversion level due to catalyst deactivation. The elevation of reaction temperature did not show any significant effect on the product selectivity as well.

5.1.1.2. Effect of Cation Type on Acylation Reactions

The results of acylation reactions of 2-MN with acetic anhydride over ion exchanged β zeolite are presented in Table 5.1. Longer reaction times slightly lowered the 6-Ac-2-MN product selectivity, while the 1-Ac-2-MN selectivity increased slightly in general when reactions were performed with acetic anhydride.

Ion exchanging the β zeolite influenced its catalytic activity for acylation reactions. At 130°C, although the conversion rate and maximum conversion of 2-MN were the highest with In^{3+}-β, this catalyst gave rise to the lowest selectivity for 6-Ac-2-MN. The conversion of 2-MN with other cation-exchanged zeolites was either comparable to or less than that observed with H^+-β zeolite. The greatest selectivity for 6-Ac-2-MN product was obtained with La^{3+}-β zeolite. However, the conversion of 2-MN was lower with this catalyst than with H^+-β. Although the 6-Ac-2-MN selectivity was lower with In^{+3}-β zeolite compared with La^{3+}-β zeolite which shows the highest

6-Ac-2-MN selectivity, 6-Ac-2-MN yield was the highest with In^{3+}-β zeolite. Zn^{2+} -exchanged zeolite displayed the lowest activity to the acetylation reaction and gave the lowest 6-Ac-2-MN yield.

Table 5.1.Acylation of 2-methoxynaphthalene by acetic anhydride over M^{n+}-β zeolite.

Cation	Time	Conversion	Product Selectivity%		Product Yield%	
M^{n+}-	(h)	%	1-AcMN	6-AcMN	1-AcMN	6-AcMN
H^{+}	2	40	28	65	11	26
	24	48	30	62	14	30
H^{+a}	2	47	27	68	13	32
	24	47	30	63	14	30
In^{3+}	2	46	37	56	17	26
	24	58	41	53	23	31
Zn^{2+}	2	20	28	66	6	13
	24	36	29	64	11	23
Al^{3+}	2	34	27	65	9	22
	24	46	30	63	14	29
Fe^{3+}	2	32	29	64	9	21
	24	43	32	61	14	26
La^{3+}	2	34	19	75	7	26
	24	41	21	73	9	30
$H^{+}(II)^{b}$	2	34	26	67	9	23
	24	49	34	60	17	29
In^{3+a}	2	56	41	53	23	30
	24	61	43	50	26	31

[a]at 160°C

[b]second catalytic cycle

The regio-selectivity of acylation reactions should be influenced by the geometry of channels within zeolite. The introduction of larger cations reduced the

effective size of exchanged zeolites (Table 4.1.), La^{3+} loaded zeolite having the lowest BET surface area. However, intrinsic activity of cations can also play direct role in conversion of 2-MN and regio-selectivity of the products. It was reported that different metal halide compounds revealed different regio-selective activity to the acylation of 2-MN when used in catalytic amounts (Art et al., 1994).

FTIR analyses of pyridine adsorbed samples revealed that H^{+}-, In^{3+}, Fe^{3+} Al^{3+}- and La^{3+}-β zeolites contained Bronsted acidity, while Zn^{2+} exchanged β zeolites contained both Bronsted and Lewis acid sites (Figure 5.2). The specific peaks of interest were at 1543 and 1448 cm^{-1} in these spectra and assigned as C=C stretching of pyridine adsorbed at Bronsted and Lewis acid sites, respectively. The zinc exchanged zeolite possessed the highest proportion of Lewis sites compared with other zeolites. It has been reported that La^{3+}exchange enhances the Bronsted acid strength of zeolites (Gaare et al. 1996; Lee et al. 1987). Bronsted acid sites appear to be more important in polarisation of anhydride into a more electrophilic species which then attacks the benzene ring resulting in the formation of ketone.

5.1.1.3. Test of Regenerability

The regenerability of H^{+}-β zeolite was checked for a second catalytic cycle using acetic anhydride as acylating agent at 130°C . The previously used zeolite sample was calcined at 550°C for 10 h again and used as catalyst in acylation reactions taking all other parameters same. The reactions were carried out for 24 h.

Use of H^{+}-β zeolite in the second catalytic cycle decreased the 2-MN conversion rate, though the maximum 2-MN conversion was comparable to that obtained in the first catalytic cycle. Use of H^{+}-β zeolite in the second catalytic cycle did not have any significant effect on the product selectivity. Therefore, H^{+}-β zeolite can be considered regenerable.

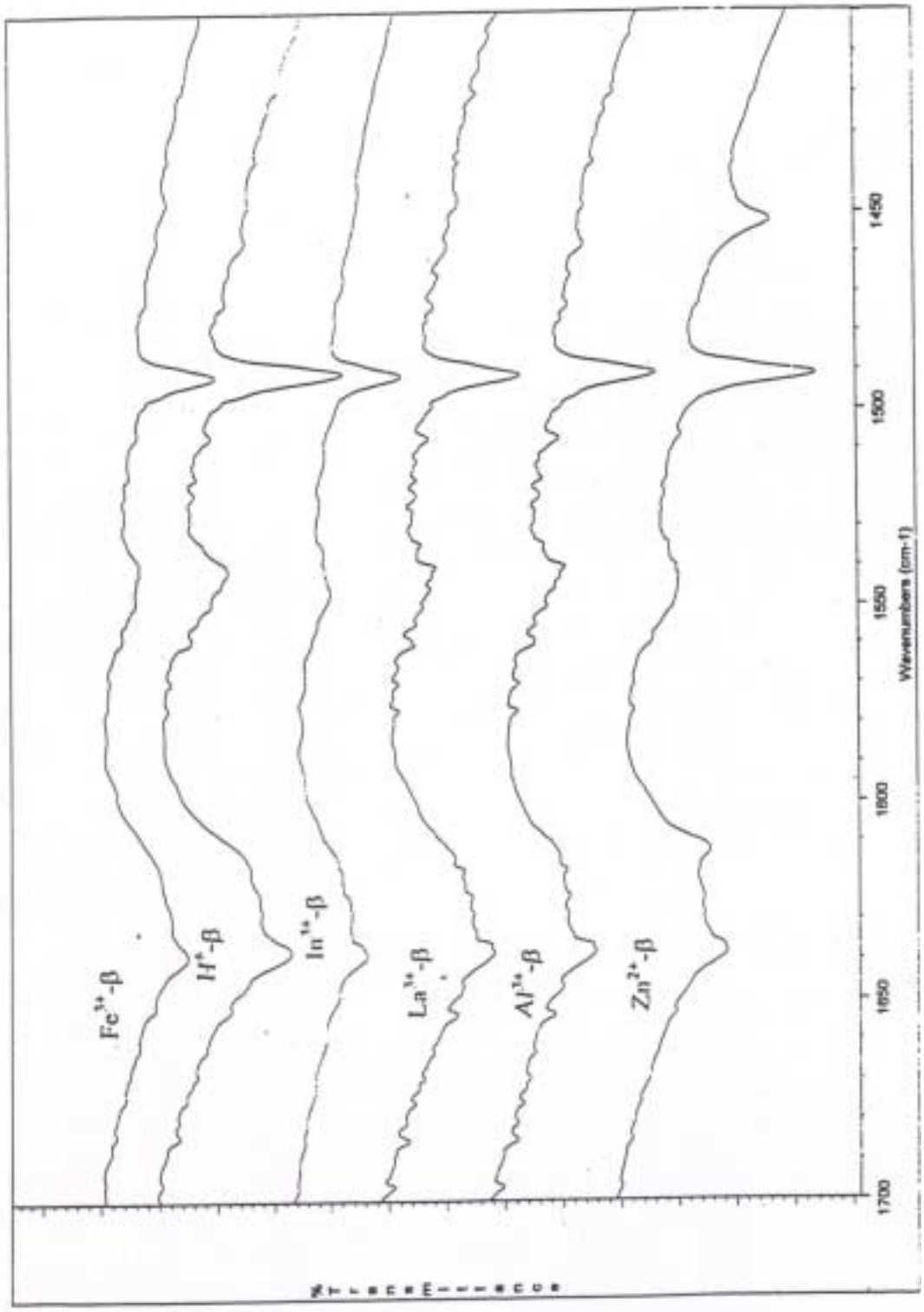


Figure 5.2. FTIR spectra for the pyridine adsorbed β zeolites

5.1.2 Acylation of 2-Methoxynaphthalene with Propionic and Benzoic Anhydrides

Table 5.2. presents the results from the acylation of 2-MN with propionic anhydride or benzoic anhydride. The comparison of the data given in Tables 5.1. and 5.2. indicates that regio-selectivity of products is dependent on the anhydride structure used. The higher ether conversion and selectivity to the acylation at 6-position were achieved with propionic and benzoic anhydrides than with acetic anhydride over H^+-β. Yet, benzoic anhydride afforded a slower reaction rate. This may be due to slower diffusion of bulkier benzoic anhydride. Molecular size of 1-acyl products should follow the order benzoyl>propionyl>acetyl. Hence, the formation of more bulky isomers, such as 1-acyl isomer, should be disfavoured owing to sterical constraints placed by the geometry of straight channels within the zeolite, which has 7.6 x 6.4 Å opening.

Table 5.2.

Acylation of 2-methoxynaphthalene by propionic or benzoic anhydride over M^{n+}-β zeolite

Anhydride	M^{n+}-	Time (h)	Conversion%	Product Selectivity% 1-AcMN	6-AcMN
Propionic	H^+	2	36	12	75
		24	50	11	75
	In^{3+}	2	**35**	13	75
		24	**56**	13	75
	La^{3+}	2	28	7	81
		24	43	7	79
Benzoic	H^+	2	23	20	74
		24	64	22	72
	In^{3+}	2	29	71	29
		24	45	60	38
	La^{3+}	2	2	12	88
		24	3	9	91

With propionic anhydride, the overall selectivity to the 1- and 6- position acylation was lower (85-87%), this being due to the formation of a diacylated ether

product (3-4%) and increased selectivity to an acylated isomer with unknown structure (6-7%). Analogous to those with acetic anhydride, somewhat higher conversion was achieved over Inβ, yet product distribution was comparable. The conversion was lower and 6-position acylation was more selective over La^{3+}-β.

The conversion of 2-MN with benzoic anhydride over In^{3+}-β was lower compared to that achieved with H^{+}-β, and the selectivity trend altered in favour of 1-benzoyl-2-methoxynaphthalene product with the catalyst. In the case of La^{3+}-β, the conversion was only <3%. These results indicate that penetration of bulky anhydride through catalyst pores is highly restricted with the presence of cations and eventually blocked with the presence of La^{3+}.

5.2. ACYLATION OF 2-METHOXYNAPHTHALENE WITH ACYL HALIDES

Activity of catalysts was distinctly different for acylation reactions with acyl chlorides as compared to the reactions with anhydrides. Some distinct features were observed when the reactions were performed in the presence of acyl halides: the product recovery was substantially low with acyl halides and excluding the reaction performed over Fe^{3+}-β with acetyl chloride, 1-acyl substituted product was significantly lowered as the reaction proceeded (Figure 5.3. and Tables 5.3. and 5.4.).

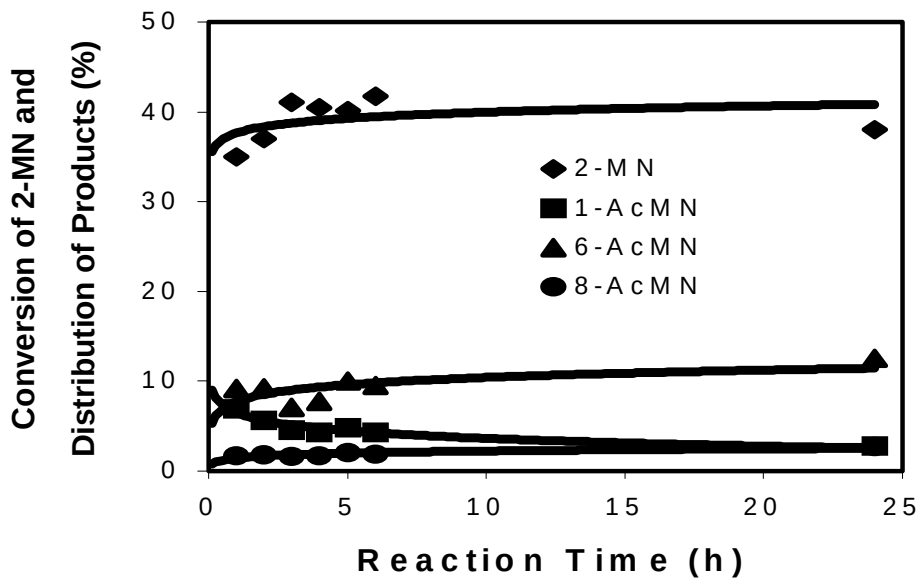


Figure 5.3. Acylation of 2-MN with acetyl chloride over H^{+}-β at 130°C

The reaction mixture appeared dark brown or black, while it was yellow for the reactions with acid anhydrides. These indicate that catalytic activity was altered by the interaction of some primary or secondary reagents present within the reaction medium that favoured condensation reactions and deacylation of 1-acyl isomer.

Excluding La^{3+}-β, metal exchanged β zeolites resulted in higher conversion than those attained with H^{+}-β after 24 hour of acylation reaction with acetyl chloride. However product recovery determined by GC was significantly low. The results with Zn^{2+}-β appear to be interesting. The higher conversion over Zn^{2+}-β which has relatively higher Lewis acidity accompanied lower 1-Ac-2-MN and higher 8-Ac-2-MN selectivity (Table 5.3). Conversion values with La^{3+}-β were comparable to those achieved with H^{+}-β. Nevertheless, the product recovery was the highest.

Table 5.3.

Acylation of 2-methoxynaphthalene by acetyl chloride over M^{n+}-β zeolite.

	Time		Product	Product Selectivity%		
M^{n+}-	(h)	Conversion%	Recovery%[a]	1-AcMN	8-AcMN	6-AcMN
H^{+}	2	37	50	29	11	61
	24	38	50	19	14	68
In^{3+}	2	44	28	25	15	60
	24	46	25	8	15	73
Zn^{2+}	2	60	37	8	23	69
	24	59	43	2	28	70
Al^{3+}	2	34	59	27	9	62
	24	46	47	16	12	71
Fe^{3+}	2	32	59	29	4	64
	24	43	44	32	11	61
La^{3+}	2	37	75	39	8	53
	24	39	74	26	10	64

[a]Based on 2-methoxynaphthalene consumed.

With propionyl chloride formation of a molecule with an unknown isomeric form and a molecular weight of 232 was determined. Its relative selectivity was 35 and 28% at the second hour of reaction and 27 and 12% after 24 h, with H^{+}-β and Zn^{2+}-β, respectively. On the other hand, 1-acyl substituted product selectivity was negligible with Zn^{2+}-β analogous to the case with acetyl chloride (Table 5.4).

Table 5.4.

Acylation of 2-methoxynaphthalene by acyl chlorides over M^{n+}-β zeolite.

Acyl chloride	M^{n+}-	Time (h)	Conversion%	Product Recovery[a]	Product Selectivity% 1-ACMN	6-ACMN	8-ACMN
Propionyl	H^+	2	45	74	18	41	6
		24	53	64	12	47	6
	Zn^{2+}	2	**69**	45	1	56	11
		24	74	45	2	72	13
Benzoyl	H^+	2	66	59	50	38	5
		24	79	50	30	56	6
	Zn^{2+}	2	72	77	38	46	5
		24	81	51	22	61	6

[a]Based on 2-methoxynaphthalene consumed.

The 1-acyl selectivity was still high for the reaction with benzoyl chloride. In comparison, Zn^{2+}-β is more active in deacetylation and selective formation of 6-acyl-2-methoxynaphthalene directly. Probably, most of the 1-benzoyl-2-methoxynaphthalene product forms at the outer surface of the catalyst mainly over Zn^{2+}-β and that it is improbable for this isomer to penetrate to active centres within the narrow sized channels to undergo deacylation which accounts for the higher recovery of 1-benzoyl-2-methoxynaphthalene.

CHAPTER 6

CONCLUSION

On the basis of the mentioned results, it can be stated that cation-exchanging the β-zeolite remarkably alters its activity in acylation of 2-MN and product regio-selectivity as well. La^{+3}-β yielded higher 6-acyl-2-methoxynaphthalene selectivity. However 2-MN conversion was lower with ion-exchanged β and even negligible with La^{+3}-β when benzoic anhydride was used as acylating reagent probably due to size incompatibility between the cation blocked channels and transition states, and lesser diffusibility of the anhydride. With acetic anhydride, H^{+}-β zeolite showed the same catalytic activity in the second catalytic cycle in the acylation reaction. Overall ketone selectivity for the acylation reactions with acyl chloride reagents was found to be significantly low due to facile formation of carbonaceous materials. 1-Acyl-2-methoxynaphthalenes were noticed to undergo deacylation in the presence of acyl chloride, while no such attitude occurred with anhydrides.

REFERENCES

Al-Ka'bi, J.; Farooqi, J.A.; Gore,P.H.; Nassar, A.M.G.; Saad, E.F. ; Short, E.L. ; Waters, D.N.; J. Chem. Soc., Perkin Trans. 2, (1998) 943.

Andy, P. ; Martinez, J. G.; Lee, G. ; Gonzalez, H. ; Jones, C. W. ; Davis, M. E. ; "Acylation of 2-Methoxynaphthalene and Isobutylbenzene Over Zeolite Beta" J. Catal. 192 (2000) 215

Art,S.P.; Okura, K. ; Miura, M.; Murata,S.; Nomura, M.; "Acylation of 2-Methoxynaphthalene with Acyl Chlorides in the Presence of Catalytic Amount of Lewis Acids" J. Chem. Soc., Perkin Trans. 1 (1994) 1703-1707.

Bharathi, P.; Waghmode, S.B.; Sivasanker, S.; Vetrivel, R.; "Molecular Modelling Studies on Zeolite Catalysts for Shape-Selective Electrophilic Substitution: I Acylation of 2-Methoxynaphthalene" Bull. Chem. Soc. Jpn. 72 (1999) 2161-2167.

Bhatia, S., Zeolite Catalysis:Principles and Applications, CRC Press, Inc. 2000, Florida

Breck, D.W., Zeolites Molecular Sieves:Structure, Chemistry and Use, Wiley, NY, 1974

Casagrande, M. ; Storaro, L. ; Lenarda.M. ; Ganzerla, R. ; " Highly Selective Acylation of 2-Methoxynaphthalene catalyzed by H-BEA Zeolite" App. Catal. A General, 201 (2000) 263

Chiche, B. ; Finiels, A. ; Gauthier, C. ; Geneste, P.; "Freidel-Crafts Acylation of Toluene and p-Xylene with Carboxylic Acids Catalyzed by Zeolites" J. Org. Chem. 51 (1986) 2128.

Choudary, B.M. ; Sateesh, M.; Kantam, M. L.; Prasad, K.V.R. ; "Acylation of Aromatic Ethers with Acid Anhydrides in the Presence of Cation-Exchanged Clays" Applied Catal., A: General 171 (1998) 155.

Corma, A.; "Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions" Chem. Rev. 95 (1995) 559-614

Das, D. ; Cheng, S. ; "Friedel Crafts Acylation of 2-Methoxynaphthalene over Zeolite Catalysts" App. Catal. A General 201 (2000) 159.

Davis, M.E.; "Zeolite Based Catalysts for Chemical Synthesis" Microporous and Mesoporous Materials 21 (1998) 173-182

Espeel, P.; Parton, R.;Toufar, H.;Martens, J.; Hölderich, W.;Jacobs, P.; "Zeolite Effects in Organic Catalysis" In: Catalysis and Zeolites, Fundementals and Applications ,(Eds) J. Weitkamp,; L Puppe, Springer-Verlag Berlin Heidelberg 1999

Fromentin, E.; Coustard, J.-M.; Gisnet, M.; "Mechanism of 1-Acetyl-2-methoxynaphthalene Isomerisation over a HBEA Zeolite" J. Catal., 190 (2000) 438.

Gaare, K. ; Akporiaye, D. ; "Modified Zeolites as Catalysts in the Friedel-Crafts Acylation" J. Mol. Catal., A: Chemical 109 (1996) 177.

Gauthier, C. ; Chiche, B. ; Finiels, A. ; Geneste, P. ;J. Mol. Catal. 50 (1989) 219.

Giardano, C.; Villa M.; Annunziata R.; Synth. Commun. 20 (1990) 383

Gore, P,H.; In: G.A.Olah (Ed.);Friedel Crafts and Related Reactions, Vol.III, Wiley Interscience, New York (1964) 64

Gunnewegh, S.; Gopie, S. ; Bekkum, H.V. ; "MCM-41 Type Molecular Sieves as Catalysts for the Friedel-Crafts Acylation of 2-Methoxynaphthalene" J. Mol. Catal., A: Chem. 106 (1996) 151

Harrington, P. J. ; Lodewijk, E. ;Org. Proc. Res. Dev. 1 (1997) 72.

Harvey, G.; Mader G.; " The Shape-Selective Acylation of 2-Methoxynaphthalene Catalyzed by Zeolites Y, Beta, and ZSM-12" Collect. Czech. Chem. Commun. 57 (1992) 862-868.

Heinichen, H.K. ; Höldrich, W.F. ; "Acylation of 2-Methoxynaphthalene in the Presence of Modified Zeolite HBEA" J. Catal. 185 (1999) 408

Hindle, S.;Transfer report Aug.1997 Dept. Of Chem Manchester Un. (source:http://mch3w.ch.man.uk./theory/staff/students/mbdtssh/trans/zeolites.html)

Jansen, J.C.; Creyghton, E.J.; Njo, S.L.; Koningsveld, H.V.; Bekkum, H.V.; "On the Remarkable Behaviour of Zeolite Beta in Acid Catalysis" Catalysis Today 38 (1997) 205-212

Kaneda,K. ; Wada, T. ; Murata, S. ; Nomura, M.; "Hydrocracking of Dibenzothiophenes Catalyzed by Palladium- and Nickel-Coloaded Y-type Zeolite" Energy Fuels12 (1998) 298.

Kim, S.D. ; Lee, K.H. ; Lee, J.S. ; Kim, Y.G. ; Yoon, K.E. ; "The Regioselective Acylation of 2-Methoxynaphthalene to 2-acetyl-6-methoxynaphthalene over Zeolite Beta" J. Mol. Cat., A: Chem. 152 (2000) 33

Kühl, G.H.; J.Phys. Chem.Solids 38 (1977) 1259

Kühl, G.H.; "Modification of Zeolites" In: Catalysis and Zeolites, Fundementals and Applications ,(Eds) J. Weitkamp,; L Puppe, Springer-Verlag Berlin Heidelberg 1999

Laidlaw, P. ; Bethell, D. ; Brown, S. M. ; Hutchings, G. J. ; "Benzoylation of Substituted Arenes Using Zn-and Fe-exchanged Zeolites as Catalysts" J. Mol. Catal., A: Chemical 174 (2001) 187-191.

Lee, E.F.T.; Rees, L.V.C.,; Zeolite 7 (1987) 545.

Olah, G.A. ;Friedel Crafts-Chemistry, Wiley, New York, 1973.

Smith, K.; Zhenhua, Z.; Hodgson, P.K.G.; "Synthesis of Aromatic Ketones by Acylation of Aryl Ethers with Carboxylic Anhydrides in the Presence of Zeolite H-β (H-BEA) in the Absence of Solvent" Journal of Molecular Catalysis A: Chemical 134 (1998) 121-128.

Solomons, G.; Organic Chemistry John Wiley and Sons New York1992

Tosheva, L.; "Molecular Sieve Macrostructures Prepared by Resin Templating", Doctoral Thesis, Lulea University of Technology 2001.

Ward, J.W.; J.Catal. 11,238,1996.

Weitkamp, J.; "Zeolites and Catalysis" Solid State Ionics 131 (2000) 175-188

Weitkamp, J.; Puppe, L.; (Eds); Catalysis and Zeolites, Fundementals and Applications Springer-Verlag Berlin Heidelberg 1999, preface

Weitkamp, J.; Ernst, S.; Puppe, L.; "Shape-Selective Catalysis in Zeolites" In: Catalysis and Zeolites, Fundementals and Applications ,(Eds) J. Weitkamp,; L Puppe, Springer-Verlag Berlin Heidelberg 1999

www.keele.ac.uk/depts/ch/postgrad/spc/webpage3.html