The Study of Aldol Condensation of Ketones Using Zeolites as Catalysts

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Synopsis

Recently there is a concerted effort to replace the homogeneous catalysts that give undesirable by-product with environmentally friendly heterogeneous catalysts (Choudary et al., 1999). Zeolites are important class of heterogeneous catalysts with some potential advantages.

In this investigation, zeolites HZSM-5 (Si/Al: 22), HZSM-5 (Si/A: 45), H-Beta and H-USY were evaluated as catalysts for aldol condensation reactions of acetone and cyclohexanone and the results compared with those using H_2SO_4. Cross-aldol condensation reactions of acetone and benzaldehyde were also performed. The adsorption of acetone, cyclohexanone and other ketones by these zeolites were also determined by a liquid chromatography method.

The three zeolites, HZSM-5, H-Beta and H-USY were screened at 170°C and further at 140°C and 100^0C at different reaction times on the self-condensation of acetone and cyclohexanone. Although lower acetone conversions were obtained over HZSM-5, the best selectivity for mesityl oxide was obtained over this zeolite compared to H-Beta and H-USY. An increase in the formation of mesitylene with time was detected over the latter zeolites. In the case of cyclohexanone self-condensation, H-USY gave better yield of 2-cyclohexylidene-cyclohexanone (52%) compared to HZSM-5 (Si/Al: 45; yield of 21%). HZSM-5 (Si/Al: 45) was chosen as the best zeolite after the first screening.

Further studies were done to investigate the effect of temperature on these reactions. Results revealed that the selectivity in the acetone aldol condensation was slightly influenced by increase in temperature, with significant increase in conversion. Cyclohexanone condensation was clearly temperature sensitive, with an increase in the yield of 2-cyclohexyxlidene-cyclohexanone from 3% at 100^0C to 20% at 170^0C respectively. Acetone condensation over H_2SO_4 offered total conversion of less than 3% whereas cyclohexanone conversion of 22% was obtained.

A high selectivity (80mol%) for benzalacetone was obtained in the condensation of acetone and benzaldehyde over HZSM-5. This was ascribed to the shape selective effect by medium pore zeolite, HZSM-5.

In the mixed aldol condensation of acetone and cyclohexanone over different zeolites and at different acetone/cyclohexanone ratio, cyclohexanone conversion was higher than that of acetone at all these conditions. After screening the same zeolites mentioned before, a high selectivity for mixed aldol product of acetone and cylohexanone, 1-cyclohexylidene-2-propanone was best

obtained over HZSM-5 (65 mol%). This was obtained at 3:1 mol/mol (acetone/cyclohexanone) ratio at 170^{0}C. This zeolite was further used in the investigation of acteone to cyclohexanone ratio at the same temperature. The other ratios used, 1:1 and 1:3 mol/mol (acetone/cyclohexanone) indicated that 2-cyclohexylidene-cyclohexanone was more favored over 1-cyclohexylidene-2-propanone. The other products obtained were mesityl oxide, mesitylene, 2-(1-methylethylidene)-cyclohexanone and 2-cyclohexyledene-cylohexanone, which were obtained, in lower amounts compared to 1-cyclohexylidene-2-propanone.

The attempt to explain the product distribution in the mixed aldol condensation reaction, where cyclohexylidene-2-propanone was preferred over 2-(1-methylethylidene)-cyclohexanone involved measurements of liquid adsorption of acetone and cyclohexanone over HZSM-5, H-Beta and H-USY. Similar adsorption coefficient (K) of acetone and cyclohexanone and other ketones using methanol, acetone and cyclohexanone as solvents revealed no preferential adsorption on all zeolites.

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Reaction Schemes

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Nomenclature

FT-IR	Fourier-Transform Infra-Red
GC	Gas Chromatography
SEM	Scanning Electron Microscopy
TEM	Tunnelling Electron Microscopy
XRD	X-Ray Diffraction
USY	Ultra Stable Y
ZSM	Zeolite Socony Mobil
p.s.i	pounds per square inch

Chapter 1

Introduction and Literature Review

1. Introduction

The use of mineral (homogeneous) acids and bases in organic reactions is common in many synthetic and industrial applications. While these homogeneous catalysts are often effective, they can produce undesirable side products and some amounts of environmentally hazardous residues (Martin-Luengo and Yates, 1995). Further disadvantages of using some homogeneous catalysts are (1) increased formation of undesired compounds, (2) their highly corrosive nature towards reaction vessels, (3) metal salt wastes, (4) difficulty in separating the catalyst from the product and (5) difficulties in controlling reaction rates and in some cases heat production. There is a concerted effort currently to develop environmentally friendly solid catalysts for clean processes in the fine chemical industry (Choudary et al., 1998). Heterogeneous catalysts have potential to meet these requirements with advantages like (1) simplified separation of the catalyst from the product, (2) little or absence of acidic and basic waste stream and (3) the possibility of regenerating catalyst (Saha and Streat, 1998).

Zeolites are an important class of heterogeneous catalysts that provide the advantages mentioned above and offer the additional possibility of controlling selectivity in certain reactions. For example, the active Brønsted acid sites in zeolites are for the major part located in the interior of the crystals. Consequently, in many acid-catalysed reactions of hydrocarbons over zeolites, the extent of reaction is determined by size of zeolite pores, dimensionality of the pore system and the shape and size of hydrocarbons (Jacobs et al., 1986).

As illustrated in Figure 1, the different types of shape selectivity can be classified as follows, 1) primary or reactant selectivity, where the size or shape of the reactant determines whether it can enter the zeolite pores and whether reaction can take place, 2) transition state selectivity, where only the reactive intermediates that can be accommodated inside the pores will subsequently form a product, and 3) product selectivity, which occurs when products of different sizes or shapes are formed within the interior of the zeolite crystal and some of the products are too bulky to diffuse out. In some reactions, secondary products or polymers may form from the end products that may be too bulky to diffuse out and thus cause the deactivation of catalyst through pore blockage.

Van Bekkum et al. (1997) reported that for the study of reaction mechanisms, it is important to distinguish between reactions occurring in the micro-pores and those occurring at the

external surface. They further claim that for strictly shape selective catalysis to occur, only the micro-pore system (large internal surface) is of interest, and the external active sites must be minimised in different ways. The incentive in reducing the external active sites is reduction in coke formation, which may cause deactivation of the catalyst by inhibiting the access to the micro-pores. Coke formation was described by van Bekkum et al. (1991) as the build-up of very bulky poly-aromatic compounds in a pore like structure like zeolites materials.

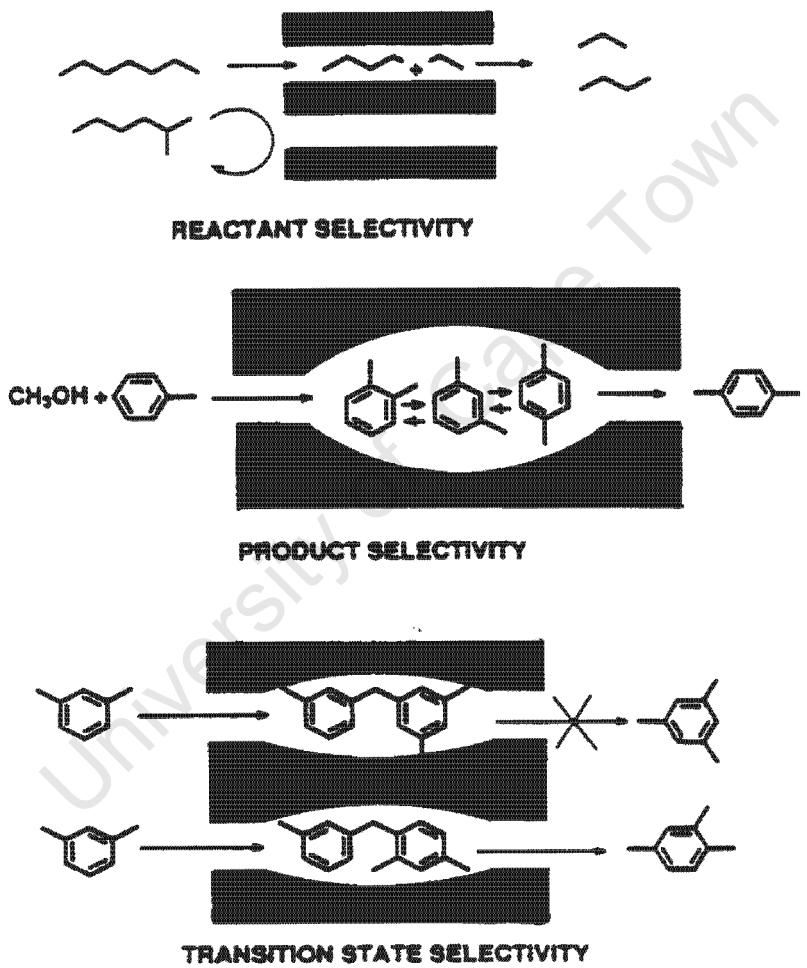


Figure 1 **Schematic representation of different types of shape selectivity**

In this study zeolites are investigated as selective catalysts for simple aldol reactions. The structure and properties of zeolites are reviewed, and an overview given of what is known about the mechanism and efficiency of the aldol reaction. In addtion, some factors affecting heterogeneous reactions are discussed, with particular empahsis on adsorption phenomena.

1.1 Zeolites – Broad Definitions

Augustine and Posner (1995) defined zeolites as crystalline aluminosilicates with defined structure and having a net negative charge compensated by counterions. The first synthetic zeolites were developed by Union Carbide (zeolite A, X and Y) and Mobil (zeolite ZSM-5) and all of them are used in the petroleum industry (Martin-Luengo and Yates, 1995).

Van Bekkum (1991) described the general characteristics of zeolites as;

a) High internal surface areas (> 600m^2/g)
b) High adsorption capacity
c) Well defined crystalline structure
d) Good thermal stability
e) Uniform pores with one or more discrete sizes - giving rise to shape selectivity
f) Highly acidic sites when ion exchanged with protons

1.1.1 Structure of Zeolites

Zeolites are divided into families of one-, two- and three dimensional pore structures. A 2-dimensional zeolite, ZSM-5, is widely used in the selective petrochemical reactions.
The active protons or Brønsted acid sites in zeolites which determine their activity are for the major part located in the interior of the crystals (Jacobs et al., 1986).
The zeolites with high concentrations of H^+ are hydrophilic and have strong affinities for polar molecules small enough to enter the pores. Those with low H^+ concentration are hydrophobic and take up organic compounds easily from water-organic mixtures. The stability of the framework also increases with increasing their Si/Al ratios. Zeolites with

high Si/Al ratios are stable in the presence of concentrated acids, but those with low Si/Al ratio are not. The trend is reversed in the case of basic solutions.

The interactions of the -OH groups with the bases like pyridine, measured by infrared spectroscopy demonstrate that the -OH groups located near the AlO_4 tetrahedra are strong Brønsted acid sites. Upon heating the hydrogen form of the zeolite to high temperatures, water is released and coordinatively unsaturated Al^{3+} ions are formed which are Lewis acid sites. Figure 2 below shows segments of zeolites in the sodium, calcium and proton form respectively, where the charges on the framework are accounted for.

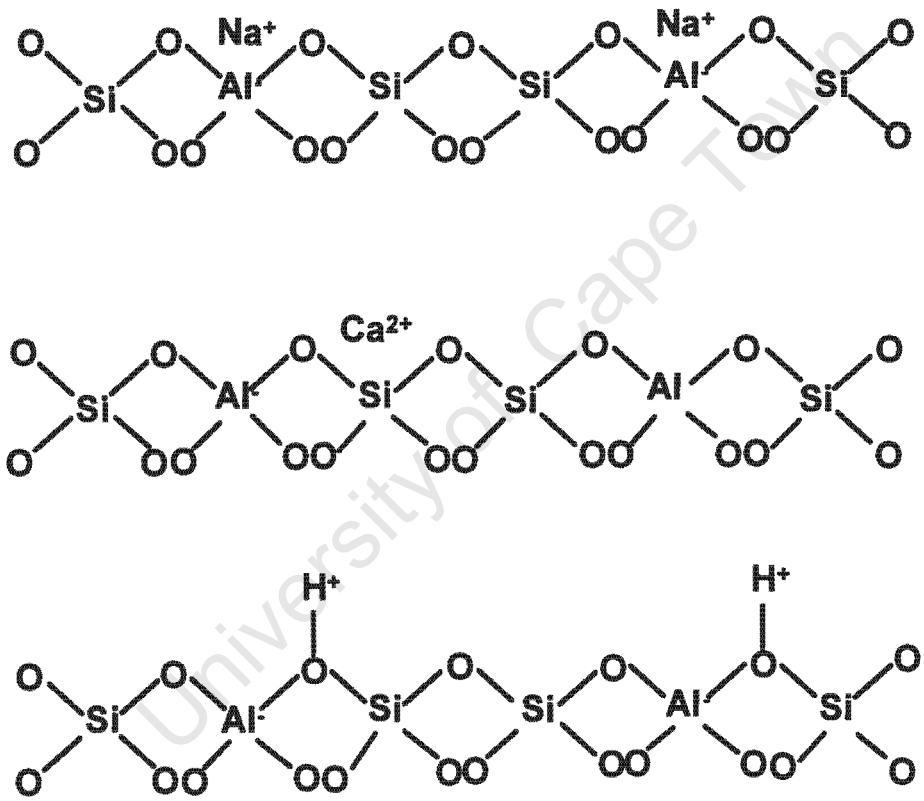


Figure 2 Simplified representation of the zeolite structure in different forms

1.1.1.1 ZSM-5

ZSM-5 is an example of a medium pore zeolite with ten-membered rings, which are 5Å in diameter. The channel system of this zeolite consists of vertical channels with the size of 5.3Å x 5.6Å which are perpendicular to zigzag-formed channel having dimensions of 5.1Å x 5.5Å (Niu and Hofmann, 1995). ZSM-5 belongs to the group of pentasils zeolites. On the basis of its pore structure, it is the most important zeolite from the catalytic and industrial point of view. It is resistant to coke formation especially on bimolecular reactions involving large molecules. Coke formation is inhibited because of narrow pores due to steric constraints on the transition states, which can selectively prevent the occurrence of secondary reactions (Bhattacharya and Sivasanker, 1995).

ZSM-5 is synthesised from an aqueous gel prepared from sodium aluminate, silica sol, NaOH, H_2SO_4 and tetrapropylammonium bromide. The composition of the solid is approximately $1.8(TPA)_2O\text{-}1.2Na_2O\text{-}1.3Al_2O_3\text{-}100SiO_2\text{-}7H_2O$. The ionic aluminosilicate structure incorporates Si^{4+}, Al^{3+}, and O^{2-}. Zeolite ZSM-5 has an unusual hydrophobicity because of high Si/Al content and thus is ideal for many applications such as separation of hydrocarbons and polar compounds like water and alcohols. The structure of ZSM-5 is represented below in figure 3.

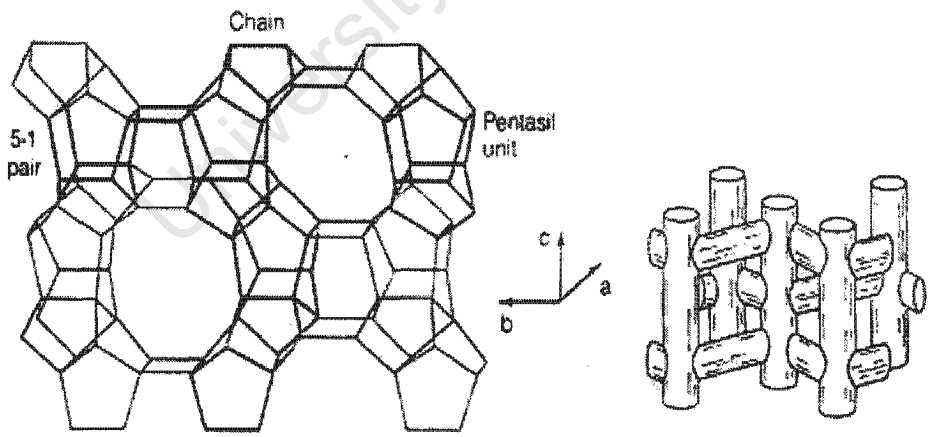


Figure 3 Structure of ZSM-5

1.1.1.1.2 Faujasites

The main application of the faujasites, zeolites X and Y, is in catalytic cracking of petroleum molecules, primarily in the gas-oil fraction giving smaller gasoline-range molecules. These zeolites consists of sodalite cages that are connected to four other sodalite cages, each connected by six oxygen ions linking hexagonal faces of two sodalite units. The super-cage in this structure, which is surrounded by 10 sodalite units, is large enough to accommodate a sphere with a diameter of 1.2nm.

Zeolite Y is a large pore zeolite with twelve-membered rings of about 7.4 Å diameter. It has a three-dimensional channel pore structure. The three-dimensional pore structure is large enough to admit reactant molecules like the hydrocarbons in gas oil, but the 0.74nm pore apertures are small enough and as such transport restrictions are sometimes expected.

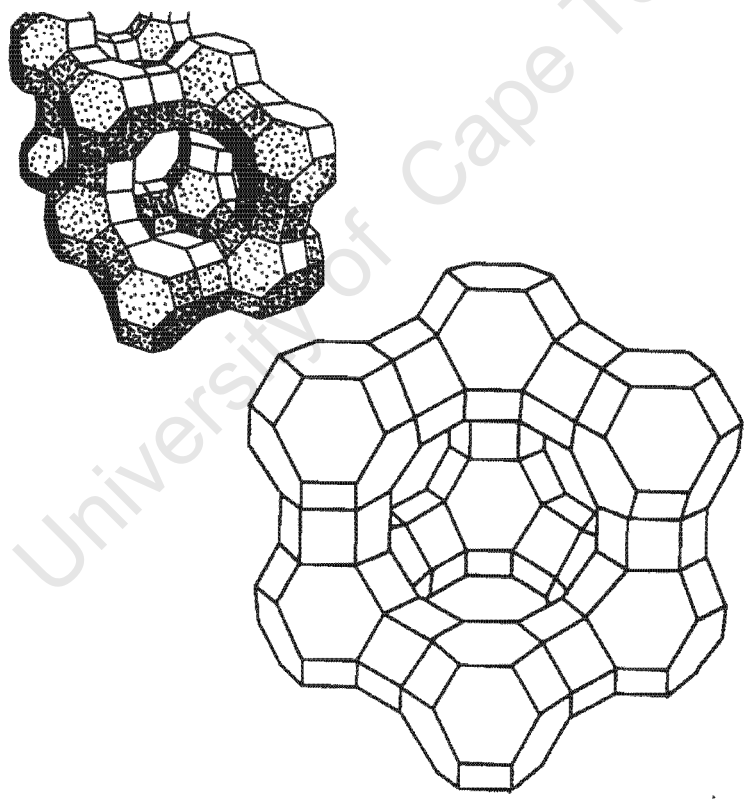


Figure 4 **Structure of H-USY**

1.1.1.3 Zeolite Beta

Zeolite Beta is a 12-membered ring belonging to large pore system zeolites. It has intersecting channels and has a pore size of 7.6 X 6.4Å and 5.5 X 5.5Å.

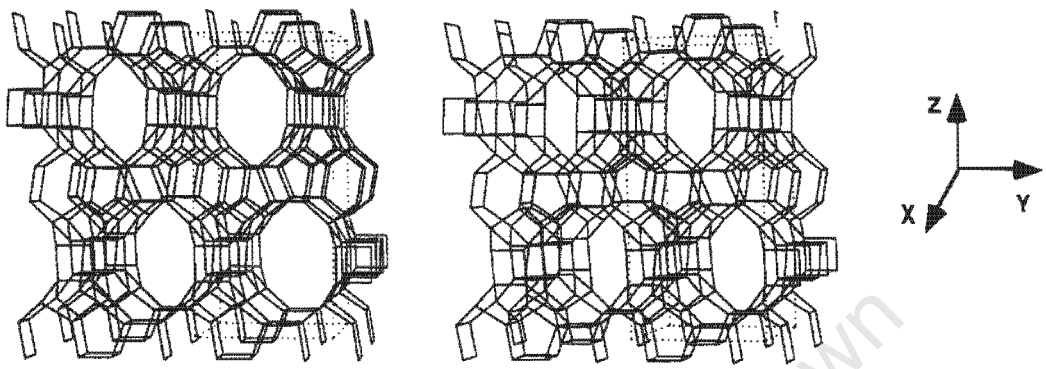


Figure 5 Structure of H-Beta

1.1.2 Characterisation of Zeolites

Physico-chemical properties play an important role in the activity and deactivation of zeolite catalysts. The main purpose of characterising zeolites is to define the nature of active sites suitable to catalyse a particular chemical reaction (Leofanti et al., 1997).

1.1.2.1 X-ray Diffraction

XRD is the most established characterisation technique used mainly for structure determination, crystal phase identification (finger print analysis), crystal size determination (line broadening) and crystal content in catalyst sample. Characterisation of fresh and spent zeolites by XRD methods is performed to compare their crystallinity. The greatest difficulty about XRD, which requires careful attention, is the quantitative determination of the crystallite size and degree of crystallinity (Leofanti et al., 1997).

1.1.2.2 Transmission Electron Microscopy and Scanning Electron Microscopy

Transmission electron microscopy (TEM) analysis offers the advantage of direct observation of the catalyst morphology. This characterisation method is also used in the determination of catalyst particle size. It is possible to distinguish between amorphous and crystalline forms of the catalysts. The technique involves taking micrographs (1-3s at high magnitude) of the catalyst samples of less than 50 to 100nm in thickness to allow for sufficient transmission.

Scanning electron microscopy (SEM) is the most versatile technique to study the morphology and particle size distribution of zeolites (van Bekkum et al., 1991). The image of the specimen is formed by recording secondary electrons or backscattered electrons emitted from the area irradiated by the scanning electron probe. The drawback in using SEM is its resolution, 5-10nm compared to a resolution of 0.3nm obtained in using TEM.

1.1.2.3 Infra-Red Spectroscopy

The lattice vibrations of many zeolites can be observed in the range of 300 to 1300 cm^{-1} in the infrared spectrum. Infrared spectroscopy can also be used in the characterisation of zeolite acidity, specifically for the analysis of OH groups and adsorbed bases (van Bekkum et al., 1991). This method is also used to determine the framework structure, and to examine the surface characteristics of solid sample. IR spectra can be obtained with pressed pellets, mulls, wafers or KBr pellets.

1.1.2.4 The BET Method

The Brunauer-Emmet-Teller (BET) is the method widely used for the determination of the total specific surface area and porosity of a catalyst from physisorbed isotherm data. The assumption that is made is that under steady state conditions of dynamic equilibrium, the rate of adsorption of nitrogen in each layer is equal to the rate of its evaporation from that layer. The two stages involved in the application of BET include the derivation of

monolayer capacity n_m. This is defined as the amount of adsorbate required to form a complete monolayer of a surface of unit mass of the adsorbent. The second stage would then involve specific surface area a_s(BET) from the monolayer capacity value. Nitrogen is generally considered the most suitable adsorbate for the determination of the surface area of non-porous, macro-porous or meso-porous solids.

1.2 Catalytic Reactions using Batch Reactor

The batch reactor is ideal for small-scale experimental studies on reaction kinetics and has the advantage of flexible operation. The reactants are initially charged into the vessel, mixed and left to react for a certain period and then the resultant mixture of products are discharged. Laboratory scale autoclaves are normally used as batch reactors for the initial screening of catalysts in the area of fine chemicals. The advantages of using small-scale batch method of catalyst testing are;

a) Lower cost of construction and installation of equipment
b) Less consumption of materials and less waste products to be disposed
c) Increased intrinsic safety which includes reduction in fire hazards, explosives and emission of toxic materials.

Some of the disadvantages of batch reactors that are reported by van Bekkum et al. (1991);

a) Reaction and deactivation cannot be separated since reactor operates at non-steady state
b) Requires long heat-up and cool-down periods
c) Temperature and pressure cannot be separated
d) Catalyst poisoning may accumulate
e) External diffusion control is only absent at higher stirring rates

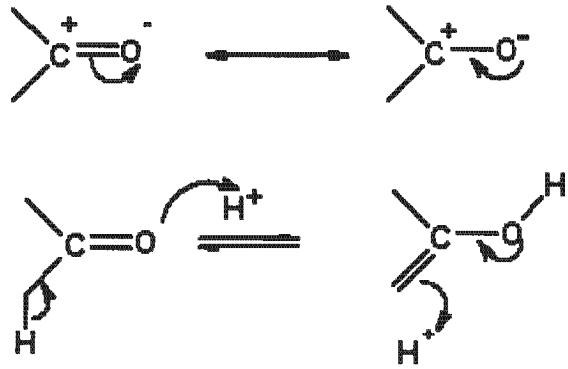
1.3 Aldol Condensation Reaction

The aldol condensation is one of the most versatile reactions in organic synthesis and frequently used in the formation of a new C=C bond. This reaction is normally catalysed by a base or an acidic medium, where a base-catalysed route is usually preferred over acid-catalysed processes because of higher yields and better selectivities. Although the mechanisms towards the products are different, both processes, acidic or basic, may give similar products. Enolate formation is an essential step for a base catalysed aldol condensation and the attack of an enolate on a carbonyl group is frequently the rate-determining step.

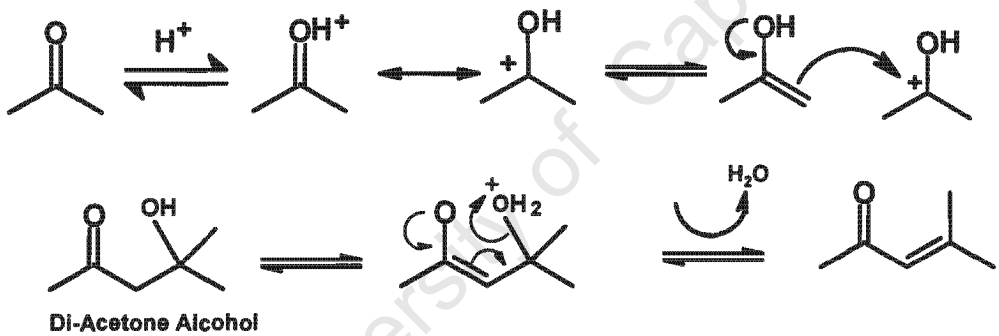
The mechanism and kinetics of the aldol condensation of ketones and aldehydes are well documented in the homogeneous medium but not well understood using heterogeneous catalysts. In an acid-catalysed reaction it is believed that an acid performs two functions; it catalyses the conversion of carbonyl compound into an enol form and it provides a protonated carbonyl compound with which the enol can react (Scheme 1). As a result the acid-catalysed reaction is regarded as a nucleophilic addition to a carbonyl group or as electrophilic addition to an alkene (Morrison and Boyd, 1983).

The end products obtained from aldol condensation reactions, α, β-unsaturated ketones or aldehydes, which are useful as intermediates in many synthetic processes.

Aldol condensation can occur between two molecules of a ketone or aldehyde. The two key features of the carbonyl group present in both ketones and aldehydes and is the polarisation with oxygen (δ-) and carbon (δ+), and the acidity of the proton α to the carbonyl which allows for enolization.



Many aldol condensation reactions involve addition, initiated by attack of a nucleophile on the positive carbon. Using the example of acetone self-condensation shown in scheme 1 below, this attack can be catalysed by acids that protonate the oxygen and in turn increases the positive charge on the carbonyl carbon atom.

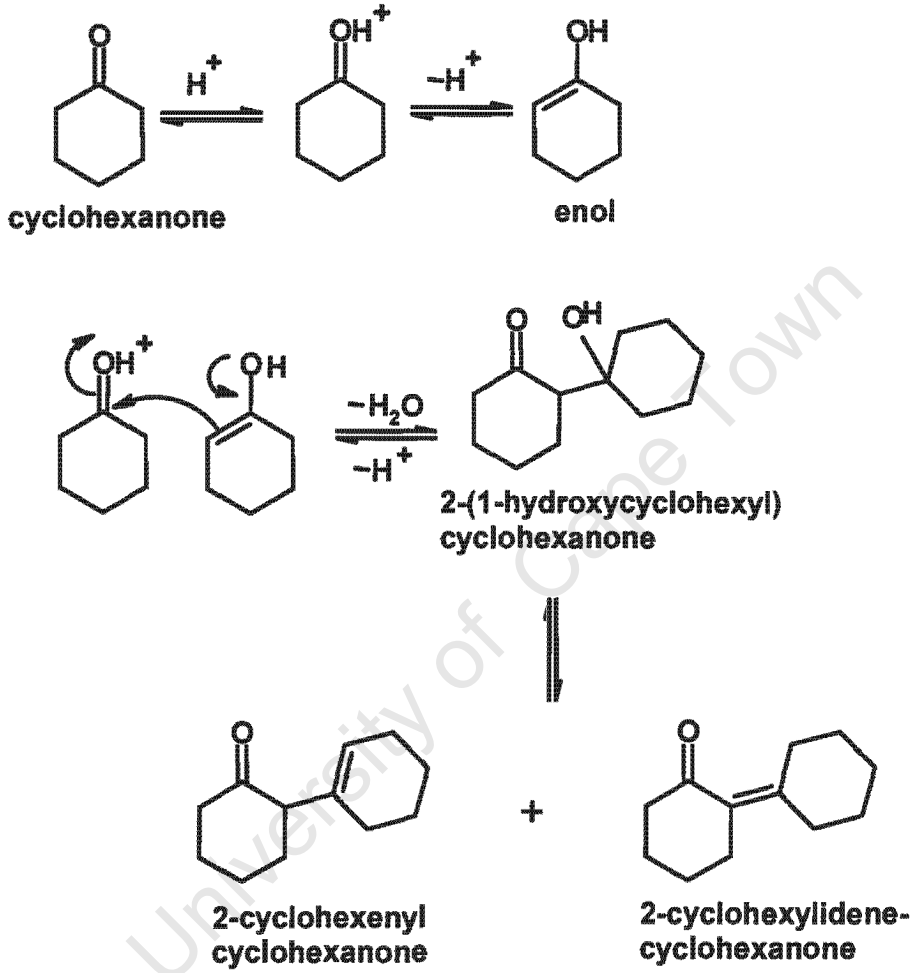


Scheme 1 Mechanism of self-condensation of acetone to form mesityl oxide

Aldol condensation reaction also occurs on cyclic ketones like cyclopentanone and cyclohexanone. A self-condensation of cyclohexanone yields a mixture of 2-cyclohexylidene-cyclohexanone, 2-cyclohexenyl-cyclohexanone and 2-(1-hydroxycyclohexyl)-cyclohexanone as the main products over potassium hydroxide catalyst (Efimova et al, 1989). Efimova et al. (1989) also established that at lower temperatures, the reaction is limited to the aldol condensation stage where the formation of a ketol 2-(1-hydroxycyclohexyl)-cyclohexanone takes place at a high rate. It is also important to note

that the nature of the solvent does not affect equilibrium between ketone and ketol (β-hydroxy ketone).

The kinetics of the process between 30 and 70^{0}C showed that the accumulation of the reaction products depended on the reaction temperature. Scheme 2 shows the mechanism of acid-catalysed self-condensation of cyclohexanone and the main products.



Scheme 2 **Mechanism of self-aldol condensation of cyclohexanone**

Although the formation of 2-(1-hydroxycyclohexyl)-cyclohexanone was independent of the presence of water in the system, it was found that water does inhibit its crotonization (aldolization) process and thus reduction to overall products (Efimova et. al., 1989).

Some of the important aspects of aldol condensation reactions pointed out by Jones (1987) and Ingold (1969);

- Most aldol condensation reactions are accompanied by multitude of side reactions and that make their kinetic data analysis difficult to measure.
- The rate limiting step for the overall condensation can either be additions or dehydration where dehydration is relatively more rapid with acid catalysis than with base.
- Many aldol condensation reaction additions are known to be exothermic and therefore thermodynamically favoured by low temperatures.
- The difficulty in establishing equilibria is that many aldols and ketols are easily dehydrated to α,β-unsaturated carbonyl compounds, like diacetone-alcohol to mesityl oxide or to form phorone.

The present investigation is centred on acetone, cyclohexanone and cyclopentanone condensation reactions. The properties of these ketones may reveal their activity in the presence of a catalyst to give α,β-unsaturated ketones. Newman (1956) indicated that cyclohexanone should be represented as existing in its chair conformation shown below.

Ketones and aldehydes with α-hydrogen exist as an equilibrium mixture of tautomers called the keto form and enol form. The keto form usually predominates, but the enol form can be stabilised by an intra-molecular hydrogen bonding or conjugation.

The table below shows the enolizations extent of some of ketones in a solvent.

Table 1 Percent enolization of ketones in a common solvent (Newman, 1956)

Ketone	% enol in liquid
Acetone	0.00025
Cyclohexanone	0.028
Cyclopentanone	0.0048

- The extensive enolization of cyclohexanone compared to cyclopentanone is due to a double bond exo-cyclic behaviour in a cyclohexanone system that is unstable with respect to migration into the ring and this tendency is less pronounced in cyclopentanone systems.
- The difference in stability (strain-energy) of the cyclopentanone and cyclohexanone systems are very small.
- The difference between high enolization of cyclopentanone than acetone is due to a loss of free rotation of acetone system upon enolization compared to cyclic ketones.

There are many uses of products from acetone self-condensation. For example, α,β-unsaturated compounds like mesityl oxide, isophorone, phorone, mesitylene and 2-hexenal, are frequently hydrogenated to yield solvents and plasticisers (Reichle, 1980).

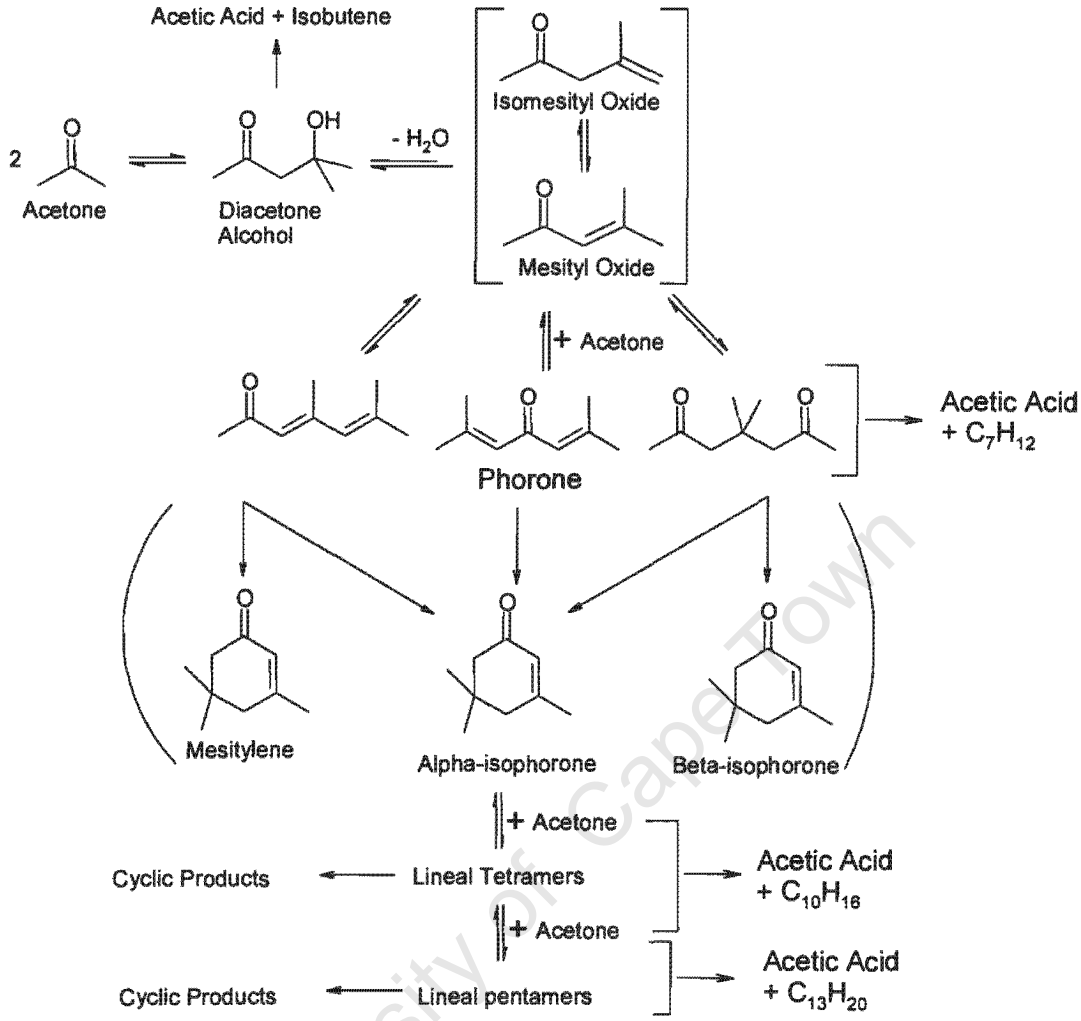
Another useful product, a self-condensation product of cyclohexanone, 2-cyclohexylidene-cyclohexanone, can be dehydrogenated on a Pt-KOH-γ-Al_2O_3 catalyst to give *o*-phenylphenol which has industrial applications in the synthesis of dyes, pharmaceutical drugs, and thermally stable and incombustible fibers (Saha and Streat, 1998).

1.4 Literature Review: Heterogeneous Catalysis of Aldol Condensation

1.4.1 Acid-catalysed Aldol Condensation Reaction of Acetone

An example of an acid catalysed reaction is that of acetone, which is a weak base, that, in acidic medium is in equilibrium with its conjugate acid. The conjugate acid loses one proton from carbon to form an enol which is a strongly electron-donating olefin due to the hydroxyl group attached to C=C bond. The olefin is therefore reactive towards electrophilic reagents such as the conjugate acid of another acetone molecule with which it forms di-acetone alcohol (Hine, 1956).

The α,β-unsaturated ketones formed in the aldol reaction of acetone can undergo further reaction. For example, mesityl oxide can react with protonated acetone to form phorone and then isophorone. Scheme 3 below shows a complete acetone self-condensation reaction investigated by Paulis et al. (1999) using a Nb_2O_5 catalyst. They found that an increase in calcination temperature decreased the specific surface area and consequently the catalytic activity. Selectivity towards mesitylene was significantly decreased and a (alpha)-mesityl oxide to (beta)-mesityl oxide ratio of 4 stayed the same.



Scheme 3 **Reaction Scheme of Gas Phase Aldol Condensation of Acetone (Paulis et al., 1999)**

Jones (1987) and Ingold (1969) indicated that there was a difference in the activity of acetone compared to cyclic ketones (cyclohexanone and cyclopentanone). Although the type of catalyst was not reported, their investigation indicated that acetone carbonyl group was; 1) less rapidly attacked by nucleophiles, 2) its electron releasing character of methyl group compared with hydrogen/acetone adduct was less stable and 3) its carbonyl group was more hindered. This finding is in agreement with the findings of Newnman (1956) that indicated

that only 0.00025% of acetone is enolized compared to 0.028% and 0.0048% of cyclohexanone and cyclopentanone respectively. The self-aldol condensation reaction of acetone is readily reversible, and the equilibrium is not always favourable to the product (Tencer et al., 1991).

Recently much effort has concentrated on understanding the mechanism of this reaction using zeolites as heterogeneous catalysts. Zeolites offer active sites and restricted pore channels in which this reaction can take place. The most important requirement of chemical reactions catalysed by solid acids and/or bases according to Iglesia et. al. (1997), is that reactants, intermediates and/or activated complexes interact with the catalyst's active site.
In the self-condensation reactions of acetone over acidic zeolites, acetone is converted via a series of Brønsted acid site aldolizations and dehydration reactions into isophorone or via dimerization and cracking into isobutene. In this process, β-hydroxy ketone (di-acetone alcohol) is quickly dehydrated to an α,β-unsaturated ketone. Furthermore, secondary reactions such as double bond migration, hydrogen transfer and cracking takes place in more acidic zeolitic materials at higher temperatures and also at long reaction times. The nature of secondary products in aldol condensation reactions can also be determined by the Si/Al content of zeolites which give rise to acid site density (Jacobs et al., 1985).
The size of reactant and transition state or products and choice of solvent zeolite may determine selectivity towards a single or more products. It was also determined by Haw et. al, (1993) that the choice of cation or framework to tailor acidity, basicity or redox properties of the zeolite affects the activity of aldol condensation reaction of ketones.

An example of a successful heterogeneous catalysed reaction is the synthesis of 4-methyl-2-pentanol from mesityl oxide, a self-aldol condensation product of acetone over Cu or Ni catalysts, was reported by Pittman and Liang, (1980). The yield of mesityl oxide from the aldol condensation of acetone is at equilibrium and limited to 20% over Nafion-H or Amberlite IR-120 as catalysts at 60, 100, and 140^{0}C after 24 hours as investigated by Pittman and Liang (1980).
A disadvantage mentioned earlier in using shape selective zeolites for aldol condensation is the deactivation of catalyst that may occur due to water eliminated during dehydration of di-acetone alcohol in the case of acetone condensation. In zeolites, the water molecules given off after dehydration are said to be competing for available active site. This phenomenon

was investigated by Fripiat and Panov (1998), where a minute liquid sample, exposed to a single statistical mono-layer of acetone, proved by the disappearance of spinning sidebands of the ^{13}C NMR spectra that water given off during the condensation reaction competes for available active sites.

A different behaviour was observed by Tichit et al. (1998), where a controlled amount of water added to Mg-Al layered double hydroxide catalyst led to an increase in the activity using these materials and hence higher selectivity of di-acetone alcohol.

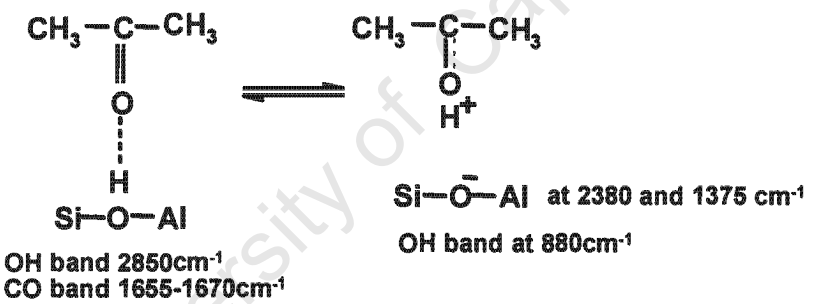
Different studies have also concentrated on understanding the mechanism by which aldol condensation reactions happen in zeolites. Many of these investigations also make use of different techniques like in-situ ^{13}C-NMR. These experiments are normally performed over a short time scales. The advantage of using these methods is that the motions of adsorbed species over a wide range of frequencies can be monitored so that the nature of adsorption and the reaction mechanism information can be obtained (Bell and Gold, 1982). Measurements are made at temperatures lower than 25^0C since at room temperature the heat of adsorption is sufficient to cause a reaction, proven by formation of a product (Bell and Gold, 1982). It was observed that the strength of initial complex between the starting ketone and the Brønsted acids sites of the zeolite can be determined quantitatively by the significant changes in the isotropic chemical shift of the carbonyl carbon. The extent of proton transfer may vary from almost complete proton transfer for mesityl oxide and crotonaldehyde to almost absence of proton transfer for chloro-acetone (Corma and Garcia, 1997).

A pulse-quench catalytic reactor has also received attention in the study for the mechanism of acetone self-condensation. This equipment has all the characteristics of a standard micro-reactor including continuous and pulse introduction of the reactants and gas chromatographic analysis of volatile products. Haw et al. (1998) used a pulse-quench catalytic reactor with a resolution of 200ms to study the self-condensation of acetone over zeolite H-ZSM-5 under conditions identical to most reaction studies. They observed the formation of 4-hydroxy-4-methylpentan-2-one (di-acetone alcohol) and 4-methyl-pent-3-en-2-one (mesityl oxide) using gas chromatography.

There are also numerous studies that concentrated on the use of infrared spectroscopy in order to understand the adsorption complex of acetone on catalyst surface complexes. The reactivity of ketones on solid catalysts is not easily understood mainly because they are less

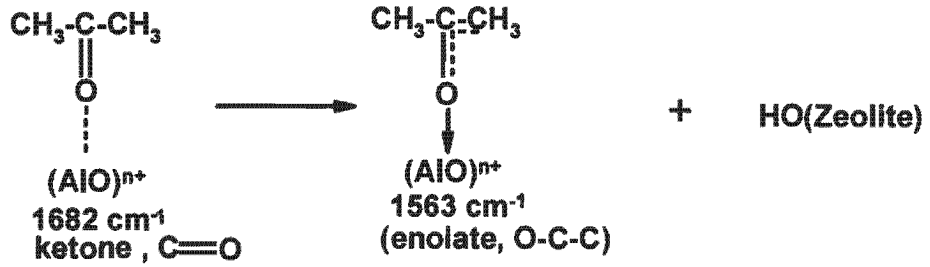
sterically crowded around the oxygen than other molecules like ethers (Weitkamp et al. 1997). Weitkamp et al. (1997) further asserted that the carbonyl-stretching mode in these molecules responds sensitively to intermolecular interactions with Lewis acid sites and Brønsted acid sites. Infrared shifts of $150cm^{-1}$ to lower frequencies are induced when acetone is co-ordinated to cationic centres while H-bonding leads to shifts of $20\text{-}40cm^{-1}$. The much-reported classic study undertaken by Bosacek and Kubelkova (1990) reported the use of both FT-IR and ^{13}C-NMR spectroscopy and indicated that the bridging hydroxyls are involved in the formation of protonated ketones. The adsorption of acetone was found to be greater over HZSM-5 than over zeolite HY, due to different acidic strengths of these zeolites as indicated by higher vibration frequencies of their OH groups and formation of products at room temperature over HZSM-5 (Bosacek and Kubelkova, 1990). A sharp increase in intensity of infrared bands of mesityl oxide over H-Y zeolite as temperature was increased from 25^0C to 180^0C indicated a dependence of this reaction on temperature.

Bosacek and Kubelkova (1991) also suggested the interaction between adsorbed acetone in zeolite HZSM-5 framework in scheme 4 below;



Scheme 4 **Complex formed between acetone and Brønsted acidic sites of zeolite (Bosacek and Kubelkova, 1991)**

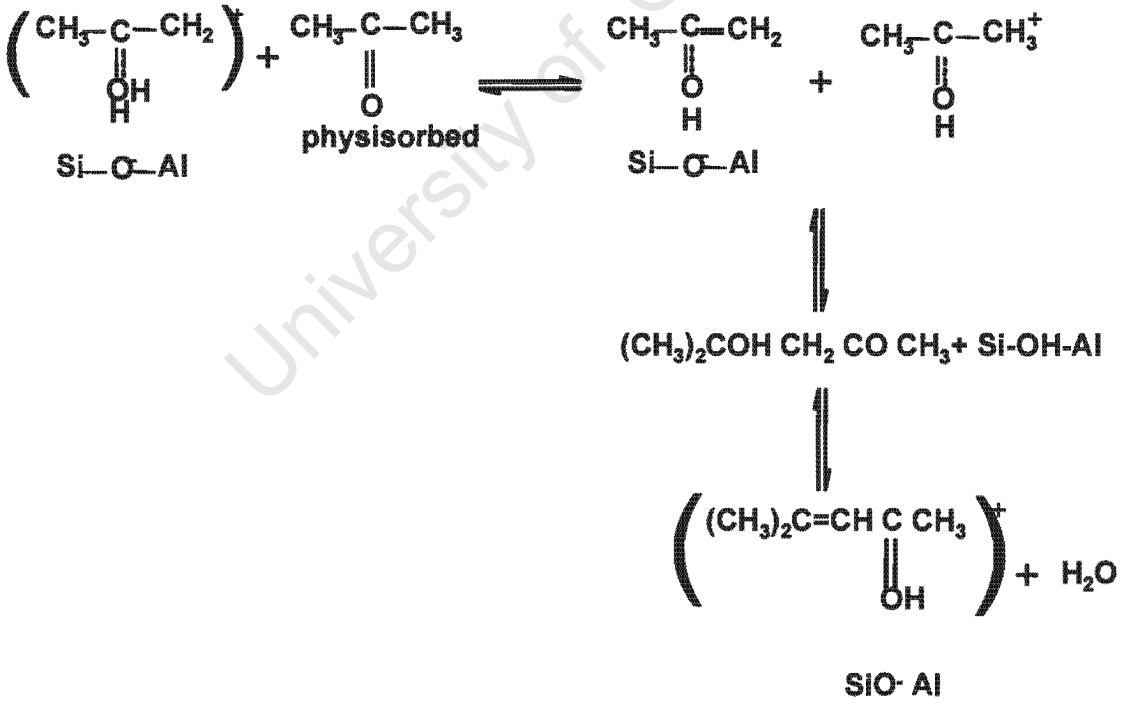
Fourier Transform infra-red studies used for the activation of acetone on HZSM-5 (Si/Al: 19), Na-ZSM-5 and dehydroxylated HZSM-5 revealed that mesityl oxide more readily forms on HZSM-5 (Brønsted acid sites) than on Na-ZSM-5 (Lewis acid sites) and dehydroxylated ZSM-5 (Kubelkova et al., 1991).



Scheme 5 **Acetone interaction with alumina entities of zeolites (Kubelkova et al., 1991)**

Kubelkova et. al (1991) extensively investigated the adsorption of ketones on zeolite surfaces using *FT*-IR spectroscopy and suggested the formation of an enolate on alumina entities shown above on scheme 5.

The pKa of protonated molecule of acetone was equal to -3.7 and the pKa of bridging hydroxyls of a zeolite was less than –8, and thus physisorbed acetone accepted a proton from methyl group of a protonated species as shown in scheme 6.



Scheme 6 **Acetone/Brønsted acid complex formation (Kubelkova et al., 1991)**

The enol form of acetone was formed by physisorbed acetone accepting a hydrogen atom from methyl group of a protonated species, and it reacts with the physisorbed acetone molecule to form diacetone alcohol, which is dehydrated to adsorbed mesityl oxide at room temperature (Kubelkova et al., 1991). Scheme 6 above also shows the formation of mesityl oxide and proton exchange in the acetone/Brønsted acid complex with zeolite silanol groups. The adsorption of ketones on silanol groups, which are present on the external surface, impurities or defects of all zeolites, proceeds after the adsorption on stronger sites like Na^+ and Al Lewis sites. Furthermore, the acetone condensation is said to be bimolecular reaction, it proceeds by acetone activated on a Lewis site (non-framework alumina) and acetone adsorbed on bridging OH zeolites. The Lewis sites were reported to be as active as Brøsted sites in the investigation by Fripiat and Panov, 1998.

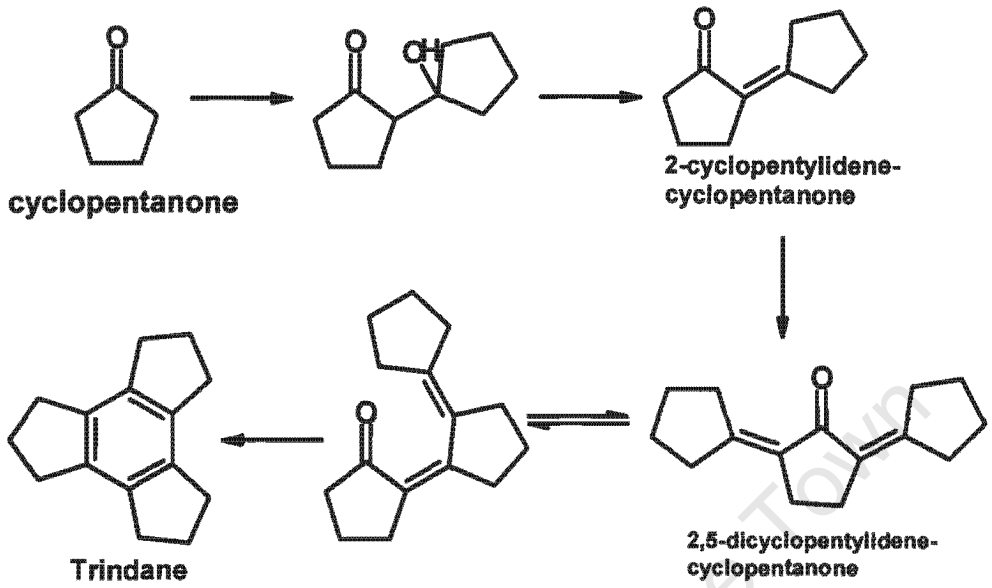
Coverage effects (between acetone and zeolite active site) can decrease the temperatures necessary for the bimolecular reaction and change the initial products and may also affect the mobility of the adsorbed species (Sepa et al., 1995). The thermally activated site exchange between acetone and active sites leading to condensation products of acetone and can also occur at low surface coverages, even below one molecule per Brønsted site. It was found that the lower the surface coverage, the higher the temperature required for a given rate of formation of condensations products.

1.4.2 Self-Aldol Condensation of Cyclohexanone and Cyclopentanone

The self-condensation of cyclic ketones was proven to be exothermic in nature by Efimova et al. (1989). Furthermore, Haw et al. (1994) observed that aldol condensation reaction over acidic zeolites like HZSM-5 and HY, and also at higher temperatures, resulted in cracking of primary aldol products. By using ^{13}C-NMR, the reactive complexes between the ketones and Brønsted acid sites of the zeolites were implicated as the precursors to aldol condensations at lower temperatures. The strength of the complex formation was reflected in the extent of proton transfer to the ketone and it was mapped into significant ^{13}C-NMR isotropical chemical shift.

The shape selective effect of zeolites was shown by the formation of trindane which only formed from the condensation of cylopentanone over large pore zeolite HX and not over

medium pore HZSM-5 (Haw et al., 1994). The reaction scheme of cylopentanone condensation is in scheme 7 below.

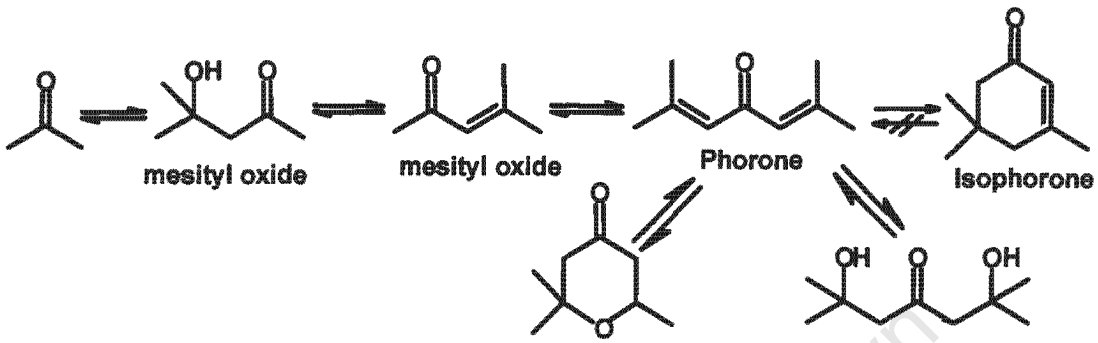


Scheme 7 Schematic presentation of the formation of trindane in the self-condensation of cyclopentanone (Haw et. al, 1994)

An important aspect about aldol condensation reaction is that it is versatile, it can be utilised in many synthetic routes. For example, in the self-condensation of cyclohexanone in the presence of acetic acid and a cation exchanged resin the formaton of 2-(1-cyclohexyl acetate)-cylohexanone was noted. Although it is generally accepted that esters are formed from a reaction of acid and an alcohol, in the investigation by Saha and Streat, (1998), it is assumed that a protonated enone undergoes conjugate addition by the oxygen atom of the hydroxyl group of acetic acid to form esters. Decreasing the 2-(1-cyclohexenyl)-cyclohexanone to acetic acid mole ratio from 1:1 to 1:4 increased the conversion of 2-(1-cyclohexenyl)-cyclohexanone from 52 to 78%. This implied that esterification with acetic acid was an equilibrium-limited reversible reaction (Saha and Streat, 1998).

1.4.3 Base Catalysed Aldol condensation Reactions

In a basic medium, one molecule of the reactant is converted into a nucleophile by forming its enolate. Reichle (1980) used a pulse micro-reactor for the aldol condensation of acetone over basic $MgO-Al_2O_3$ catalyst. Only phorone and isophorone were found to form from the reaction of acetone with mesityl oxide (See Scheme 8).

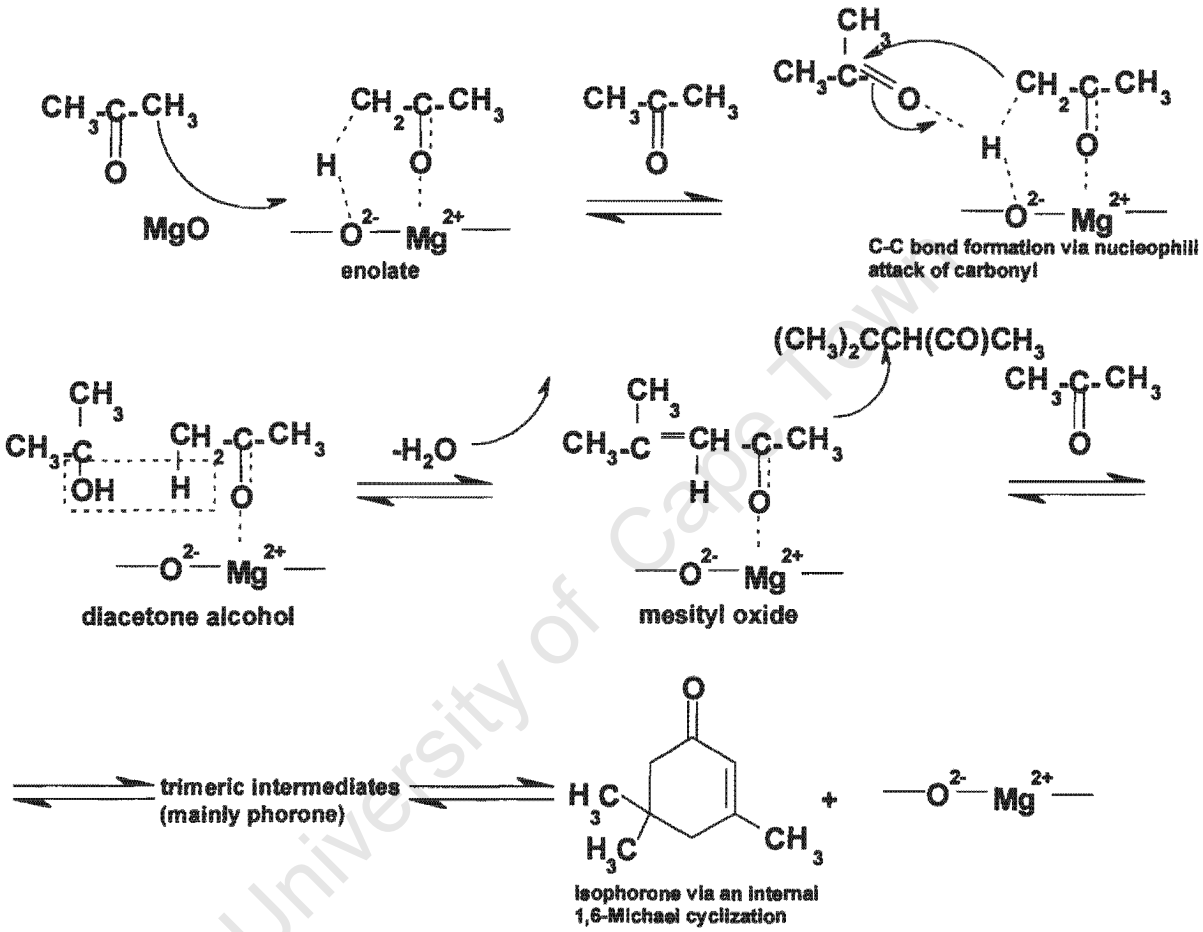


Scheme 8 Acetone self condensation to terminal isophorone (Reichle 1980)

A "promoted MgO" catalyst that was precipitated with sodium aluminate and doped with lithium or zinc nitrate was reported by Di-Cosimo (1998) and Reichle (1980). They studied the deactivation of this catalyst on gas phase self-condensation of acetone. The role of these promoters, whether to aid in catalyst strength or enhance activity was not mentioned. The blockage of basic sites of MgO-based catalysts was due to heavy oligomeric compounds from aldol condensation of non-cyclic trimers with acetone. The key intermediate species in coke formation was phorone, which remained adsorbed on catalyst surface. Both Reichle (1980) and Di-Cosimo made a similar observation that isophorone was a terminal product in the self-condensation reaction of acetone. Phorone is formed by the deprotonation of mesityl oxide in α-position to the carbonyl function and further condensation with another molecule of acetone. The catalytic probe reactions on basic sites generally involve the initial abstraction of a proton from a molecule and the formation of adsorbed carbanions. The reaction scheme 9 of acetone condensation on basic MgO catalyst as derived by Iglesia et al. (1997) is depicted below.

Iglesia et al. (1997) established a relation that the stability of the surface enolate species formed in α-hydrogen abstraction steps make it likely that reaction rates will depend

primarily on the basicity of the metal oxide. This reaction is thought to probe a balance between the basicity of the oxygen anions and the ability of the balancing cation to accommodate the products of the proton abstraction steps.



Scheme 9 **Acetone condensation over MgO catalyst (Iglesia et. al., 1997)**

1.4.4 Mixed and Cross-Aldol Condensation of Ketones and Aldehydes

The aldol condensation between two different carbonyl compounds (cross-aldol condensation) has four or more possible primary products depending on reaction conditions. A high selectivity towards a single product can be obtained if one reactant has no α-hydrogens such as in formaldehyde and benzaldehyde. Other factors that influence the formation of a single product include first mixing reactant with the catalyst and adding the other reactant with no α-hydrogens slowly into the mixture.

The example of shape selectivity in aldol condensation reaction between benzaldehyde and cyclic ketones (cyclohexanone, cyclopentanone, cyclooctanone, 3-methyl-cyclohexanone) over ion exchanged zeolites like LiZSM-5, CsZSM-5, MgZSM-5 and BaZSM-5 was studied by Posner and Augustine (1995). The size of the zeolite cages, the cation and the ring size of the substrate were found to influence the selectivity towards a mono-subtituted product. The cation was important in creating a basic site in the zeolite. These basic active sites are created if the cation has large enough ionic radius that can provide charge separation between itself and the $(AlO_4)^-$ species of zeolite framework. These extra framework cations in zeolites were shown to enhance product formation in the mixed aldol condensation reactions.

The crossed aldol condensation between acetone and benzaldehyde was investigated between 60^0C and 150^0C over Nafion-H and Amberlite IR-120. A 28% yield was obtained for 4-phenyl-3-buten-2-one (benzilidene-acetone) after 24 hours. The equilibrium limitation was circumvented by the simultaneous hydrogenation of mesityl oxide with hydrogen and Pd/C catalyst at 50 p.s.i to give 4-phenyl-2-butanone (Pittman and Liang, 1980).

Reactions between acetone and various aldehydes over diamino-functionalised mesoporous materials at 50^0C were investigated by Choudary et al. (1999). After three-hours, the reaction between acetone and benzaldehyde gave 79% conversion of benzaldehyde and 52% yield of aldol product. Reproducible results were obtained with a regenerated catalyst that indicated that no deactivation of the catalyst occurred.

1.5 Adsorption of Organic Compounds on Zeolites

The adsorption of molecules from the liquid phase involves the saturation of adsorbate molecules on the adsorbent material like zeolite. Non-ideal concepts like adsorbate-adsorbate interactions and surface heterogeneity are important in this type of adsorption. Chemisorption, which is the first step in surface catalysis, occurs when a molecule or an atom is brought in contact with a surface, where it may combine with the surface through the formation of a chemical bond. Physisorption, on the other hand, is the association of molecules with the surface in a physical process that resembles simple condensation. This process is characterised by weak interaction forces called van der Waals forces.

Adsorption is the term used to describe the process whereby a molecule (an adsorbate) forms a bond to the surface (an adsorbent). There is little knowledge on the interplay that creates the environment in which the adsorbed molecule finds itself on zeolites. Although the fundamental microscopic processes in zeolites are frequently speculated by analogy with solutions, the two processes are different.

There are different ways in which adsorption of organic molecules in zeolites is measured, these may include gas phase adsorption using gas chromatography and liquid (batch) method where concentration of molecules is also analysed by GC. Recently a method involving a modified high-pressure liquid chromatography (HPLC) by connecting a column packed with molecular sieves like a zeolite was developed by Baron et al (1998). The packed column is saturated with a solvent carrier from the HPLC pump to the detector. The sample is injected through the injector port and the detector measures the difference in retention time between the sample and the solvent.

The method uses the following model to determine the value of adsorption coefficient, which is defined as $K = q/C$;

where q : adsorbed concentration (mol/m^3)

C : liquid phase concentration (mol/m^3),

The equilibrium constant can be determined from the retention time in the column

$$\mu = \frac{L}{V_f}\left(\varepsilon + (1-\varepsilon)K\right) \qquad (1)$$

Where, μ : retention time (s)

L : column length (m)

V_f : superficial velocity (m/s)

ε : bed porosity (-)

K : adsorption coefficient (q)

Using this method, Baron et. al (1998) were able to determine the partition coefficients (*K* values) of acetone and 2-hexanone as 11.4 and 5.22 respectively on n-octane as mobile phase on Na-USY at room temperature. The effect of polarity is important in understanding the adsorption of different compounds. Figure 6 below illustrates the effect of polarity of components using retention times and n-octane as mobile phase.

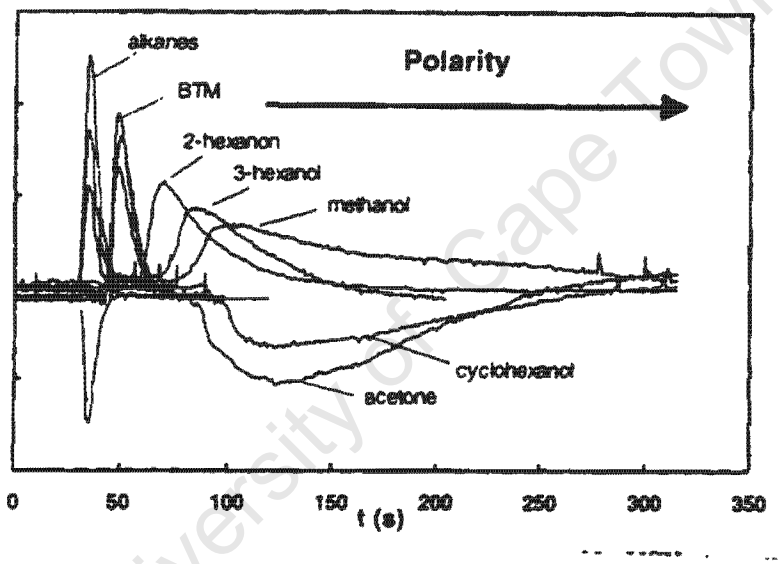


Figure 6 **Typical chromatography showing polarity of adsorbed compounds (Baron et al., 1998)**

The partition coefficients of more polar components were found to increase in the order as follows; 2-hexanone < 3-hexanol < methanol < acetone < cyclohexanol, but the partition coefficients of the branched alkanes were nearly the same as those of linear isomers (Baron et al., 1998).

1.6 Objectives of Research

The overall objective of this project is to investigate substitution of traditional homogeneous catalysts with heterogeneous catalysts (zeolites) for the aldol condensation reactions of acetone, cyclohexanone and benzaldehyde. Acetone and cylohexanone are the simplest carbonyl compounds and they are the common models for studying the reactions of carbonyl compounds on acidic zeolites. The α,β-unsaturated ketones generated in these investigation may have some applications of their own.

The investigation would be carried out with special attention to the effects of zeolites on the activation of self and mixed aldol condensations involving acetone and cylcohexanone and their product distribution or selectivity. The following was a focus of the investigations:

a) To determine the effects of size and shape selectivity properties of several zeolite on liquid phase, acid catalysed aldol condensation of ketones as a function of substrate size, and zeolite pore size.

b) To study the effects of reaction conditions such as temperature, molar ratio's, and reaction time.

c) To investigate the effects of adsorption complexes of different ketone substrates on zeolites and correlate with the catalytic activity and/or initial reaction rates of ketones

Chapter 2

Experimental

2. Experimental

2. 1 Materials and Methods

2.1.1 Reagents and Catalysts

All reagents, acetone (+99%), cyclohexanone (+99%), benzaldehyde (99%), toluene (99%), 3-hexanone (+99%), 3-pentanone (+99%) and 1,3,5-triisopropyl benzene (+99%) were obtained from Sigma Aldrich.
Tracer compounds, cyclohexanone, 3-hexanone and 3-pentanone and acetone used in adsorption measurements were of analytical grade (+99%) obtained from ACROS Chemicals.

The three commercial catalysts used in this work were HZSM-5 with variable Si/Al ratio's of 13, 22, 45 and SiO_2/Al_2O_3 of 300, H-Beta (Si/Al: 8) and H-USY (Si/Al: 14). All ZSM-5 and H-Beta zeolites were obtained from Sud-Chemie, Germany. H-USY was obtained from Akzo Noble, Germany. The types of catalysts were chosen because of their different pore sizes/geometry and acidity.

2.1.1.1 Catalysts

2.1.1.1.1 Characterisation

The following techniques were used to characterise the catalysts mentioned above.

Morphology and crystallinity : X-ray diffraction (XRD)

Surface Area : N_2 BET

2.1.1.1.2 X-Ray Diffraction

For sample preparation in XRD, particle size should be fairly uniform and small, preferably less than 10μ. Grinding for the reduction of particle size is normally performed under acetone to prevent strain. Samples must be thick enough to ensure that the beam does not pass through. A holder is used to load the samples with areas sufficient enough so that the beam irradiates only the sample. The XRD powder patterns of catalyst samples were obtained with a Philips diffractometer equipped with Cu-K_α radiation lamp. The instrumental settings used are listed in Table 2;

Table 2 – XRD Parameters (Copper Tube was used)

Voltage	**40kV**
Current	**25mA**
Range	**6^0 2θ to 50^0 2θ**
Scanning Speed	**0.1^0/sec**

The powder samples were loaded into a 1mm deep perspex holder and the sample surface was orientated by applying pressure with a glass slide.

2.1.1.1.3 N_2 BET

The surface areas of zeolite samples were estimated from the results of adsorption experiments using nitrogen as the adsorbate. Experiments were carried out using a Carlo-Erba Sorptometer. All zeolite samples were previously calcined at 500^0C for 16 hours.

2.1.1.1.4 Calcination Program of Faujasite and MFI/ZSM-5 zeolites

HZSM-5, H-Beta and H-USY were calcined in air using the following program: 0 to 100^{0}C at 4^{0}C / minute, from 100 to 200^{0}C at 3^{0}C/minute and at 10^{0}C/minute to 550^{0}C and maintained for 16 hours.

2.1.1.2 Experimental Apparatus and General Equipment

2.1.1.2.1 Experimental Apparatus

The autoclave used for all the reaction work up is shown in figure 7. The autoclave was manufactured from stainless steel and the seal was constructed from a teflon sheet. The interior dimensions are 1.7cm (diameter) x 5.5cm (height) giving a volume of 12.5cm^3. A small magnetic stirring bar was used for stirring. A pressure gauge, sample valve, gas inlet valve and K-type thermocouple were all fitted tightly through the stainless steel clamp into the vessel. An autoclave was equipped with a PID-temperature controller and a 220-Volt heater, which heated the heating block.

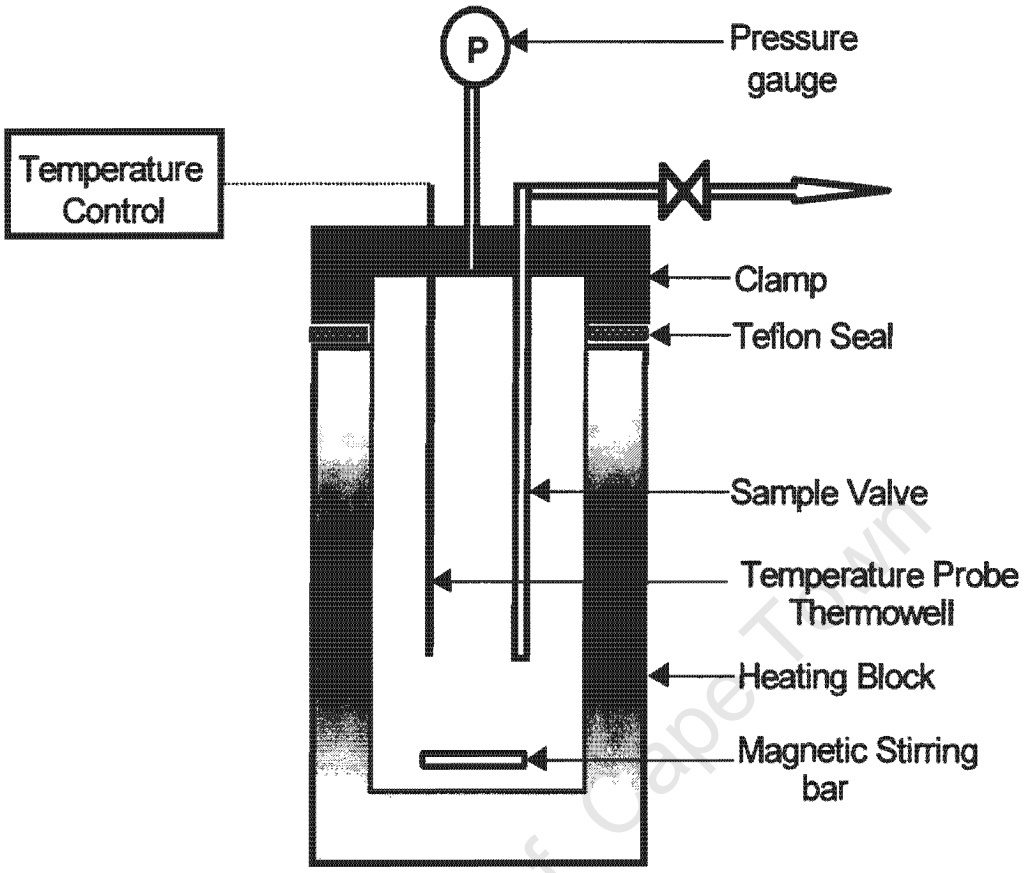


Figure 7 **Schematic representation of autoclave used in all aldol condensation reactions**

2.1.1.2.2 Gas Chromatography Equipment

A Carlo Erba 4200 gas chromatography instrument fitted with a 50-meter long OV1 column was used in all analysis of the samples mixtures. The capillary column had 0.25-mm inside diameter and coated with 0.25-μm thick dimethyl-polysiloxane. A temperature program used for all samples is shown in the table 3 below:

Table 3 Temperature program for GC analysis

Initial oven temperature	80^0C maintained for 3 minutes
Heating rate	10^0C/min
Final oven temperature	250^0C maintained for 10 minutes
Injector temperature	250^0C
Detector temperature	260^0C

2.1.1.2.3 HPLC Equipment used in Adsorption Studies

Liquid chromatography technique consisted of a standard Hewlett Packard HPLC 1100 series system with refractometer (HP 1047A), thermostatic oven and connection to the computer through the interface system. The three stainless steel columns used were 0.05m long and 4.6mm in diameter and packed with ZSM-5, H-Beta and H-USY. For each experimental measurement, each column was connected to the injector and detector with 1/4in. stainless steel tubing. The stainless steel tubing used to connect an injector and detector allowed us to increase the pressure from 10 to 45 bars by increasing the adsorbate flow rates from 0.3 to 3 ml/min. Acetone, cyclohexanone, methanol and a mixture of 1:1 acetone/cyclohexanone were used as carrier solvents. A 1:1 acetone/cyclohexanone was investigated to determine how strongly either ketone is adsorbed systematically because they are in the same ratio and also were injected simultaneously.

A schematic representation of the equipment used is represented in figure 8 below.

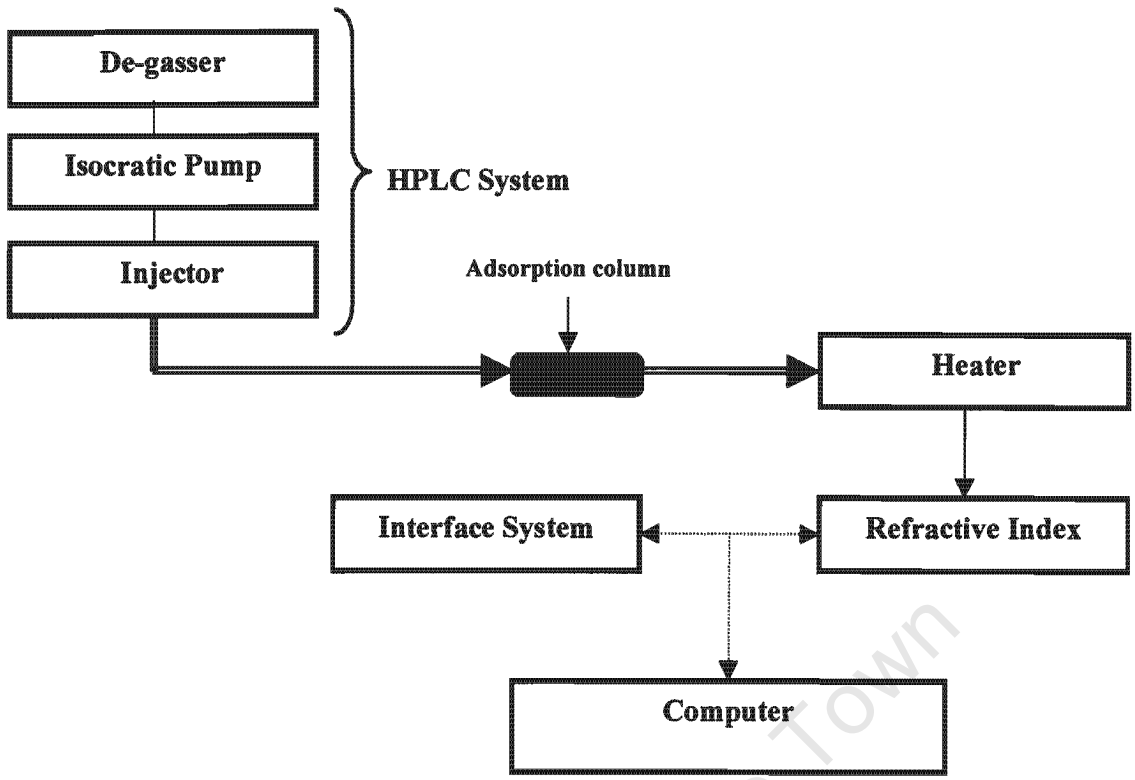


Figure 8 **Schematic representation of liquid chromatography adsorption system**

2.2 Catalytic Reactions of Ketones

Prior to each experiment, the autoclave was thoroughly cleaned and rinsed with acetone. In all cases 6ml of reaction mixture was charged to the autoclave. The autoclave was sealed and magnetic stirrer started. The temperature was set at 100^0C, 140^0C and 170^0C for each experiment and monitored by means of a thermocouple inserted in the reaction vessel. It took 5 to 15 minutes to reach the set point temperature and depending on the reaction conditions, pressures of 1 to 10bars were reached. The reaction mixtures were held for 1, 5, 10, and 24-hour period for each reaction temperature.

2.2.1 General Procedure for Aldol Condensations of Ketones

Catalytic reactions of ketones were performed in the vessel mentioned above. In each experiment a sample (6ml) of analytical grade reagent, and a portion of catalyst (HZSM-5, H-Beta or H-USY, 0.5g) were charged into an autoclave. In the case of mixed aldol condensation reactions, ratios of acetone and cyclohexanone were varied from 1:1, 1:3 and 3:1. The sample mixture was purged with nitrogen gas before heating to the reaction temperature (100 or 140 or 170^{0}C). Reactions were allowed to run for periods ranging from 1hour to 24 hours, after which the reaction vessel was cooled to room temperature and a sample withdrawn using a syringe for analysis by GC.

The crossed aldol condensation reactions of acetone and benzaldehyde were performed in a 600ml-batch reactor (Parr Instruments) using acetone (30g), benzaldehyde (60g) toluene (1g) and catalyst (2.5g). Nitrogen was used to purge the mixture before heating to 150^{0}C for periods ranging from 1hour to 24 hours. After the reaction time, the reaction vessel was cooled a representative sample withdrawn and analysed by GC after filtering out the catalyst.

A list of all the aldol condensation reactions performed between acetone, cyclohexanone, benzaldehyde over HZSM-5, H-Beta and H-USY zeolites and different reaction time is given in Appendix III.

2.3 Liquid Phase Adsorption Studies of Ketones on Zeolites

Adsorption of various reagents was investigated to determine the relative activities of various adsorbates (acetone and cyclohexanone) in over different zeolites. Preliminary batch experiments on zeolites NaY and HZSM-5 (SiO_2/Al_2O_3) and liquid chromatography experiments using HPLC on HZSM-5 (Si/Al: 45), H-Beta and H-USY zeolites were performed.

2.3.1 Procedure

Adsorption measurements were carried out by the liquid chromatography method developed by Baron et al. (1998) using equipment described in section 2.1.1.2.3. The dead time or dead volume was measured with no packed column connected at different flow rates using 1,3,5-triisopropyl benzene as a tracer (reference) compound. The dead time was subtracted from retention time of tracer compounds. A small pulse (5µl) of pure tracer compounds of cyclohexanone, 3-hexanone and 3-pentanone and acetone were injected into the mobile phase through an auto-injector. The mobile phase was pumped through the column filled with adsorbent crystals by isocratic pump. Flow rates were varied from 0.3 to 3ml/min. The inlet pressure of the system was constantly monitored during the experiment. All adsorption measurements were collected at 25^0C. Temperature was elevated to 50 and 75^0C to check the effect of temperature on adsorption. The three columns prepared were regenerated in a vacuum oven at 160^0C and 336mbar for 24 hours.

Chapter 3

Results and Discussions

3 Results and Discussions

The following results and discussions are presented to answer the objectives mentioned earlier for the present investigation; they include catalyst characterization of zeolites used, self-condensations of acetone and cyclohexanone, crossed and mixed aldol condensation of acetone with benzaldehyde and also cyclohexanone. The last section deals with adsorption of ketones on zeolite catalysts.

3.1 Catalyst Characterization

Full characterization of zeolites is important in order to establish the identity of the catalysts and provide a basis for comparison with the zeolites after reaction. It was important to check the mechanical integrity of the catalyst, in this case through comparison of their x-ray fingerprint before and after the reaction.

3.1.1 X-Ray Diffraction

Below in figure 9 and 10 are the XRD data of HZSM-5 zeolites, no significant change in the crystallinity of the catalysts was observed. Also, XRD's of zeolite samples after different reaction times and temperature indicated no characteristic change on the zeolites. This indicated that the catalyst remained stable during the reaction. The same observation was made from the XRD data reported in Appendix V.

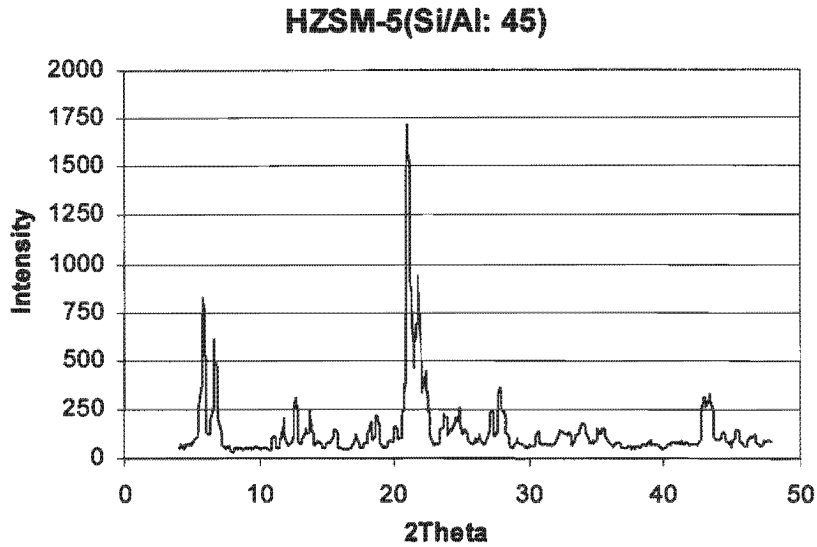


Figure 9 Diffractogram of HZSM-5 (Si/Al: 45) before reaction

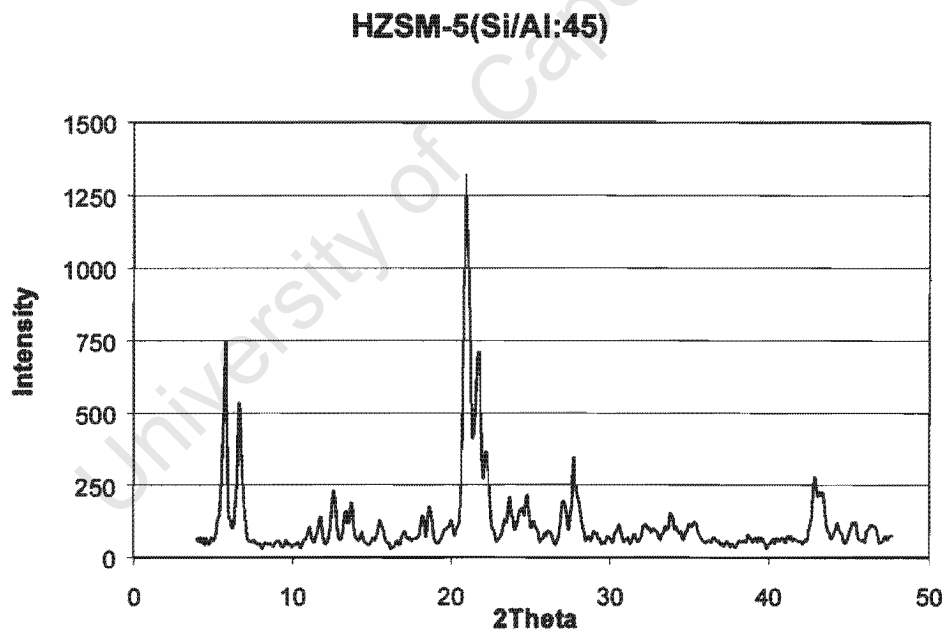


Figure 10 Diffractogram of HZSM-5 (Si/Al: 45) after the mixed aldol condensation of acetone and cylohexanone reaction

3.1.2 BET Measurements

The physical properties of HZSM-5, H-USY and H-Beta were determined through BET measurements. The surface areas, pore volumes and crystal sizes shown in table 4 below are in agreement with results published by Bhattacharya et al. (1995).

Table 4. BET Surface Areas of H-ZSM-5, H-Beta and H-USY Zeolites

Catalyst	Surface Area (m^2/g)	Micropore Volume (ml/g)	Crystal Size (μm)
HZSM-5 (Si/Al: 22)	442	-	-
HZSM-5 (Si/Al: 45)	425	0.102	0.4
H-USY (Si/Al: 14)	609	0.25	0.4 - 0.5
H-Beta (Si/Al: 8)	558	0.17	3 - 4

The micropore volume and crystal size of HZSM-5 (Si/Al: 22) was not measured. This catalyst was not extensively studied compared to the HZSM-5 (Si/Al: 45).

The trend observed in measurements shown in table 4 suggests that increasing Si/Al of zeolite increases its micropore volume. A clearly documented effect on changing Si/Al of zeolites by Gates (1991) indicated that zeolites with low Si/Al have high acid site concentration but high ratios have high crystal framework stability. Zeolites with high H^+ concentrations are hydrophilic, with strong affinity for polar molecules whereas zeolites with low H^+ concentrations are hydrophobic.

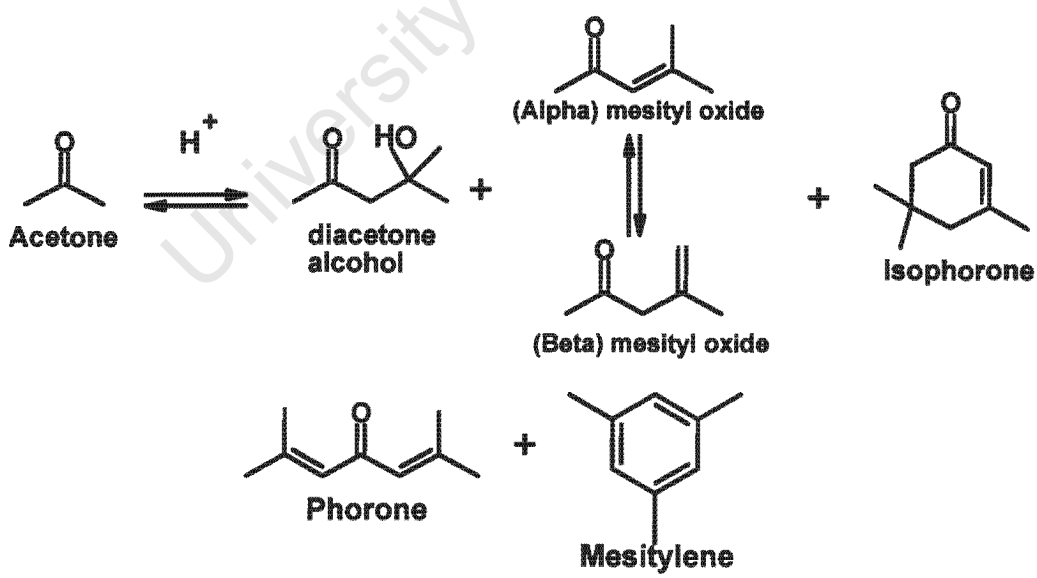
3.2 Self-condensations of Acetone and Cyclohexanone

The first phase of the work involved investigation of the self-condensation reactions of acetone and cyclohexanone. These reactions are of interest in themselves, but will be competing reactions in the mixed-aldol reactions. The activity of the catalysts and product selectivity is therefore important as a basis for studying the mixed-aldol reactions.
Reactions were carried out using the zeolites, HZSM-5, H-Beta, and H-USY over a temperature range 100°C to 170°C and conversions and selectivities monitored with time.

In the following sections, 3.2.1 and 3.2.2, the self-condensation results of acetone and cyclohexanone are presented and these investigations were important to establish the extent of these reactions over a solid catalyst. The investigations were carried out as outlined in section 2.2.1.

3.2.1 Self-condensation of Acetone

Scheme 10 below shows the range of products that can form in the self-condensation of acetone.



Scheme 10 **Reaction scheme showing the products obtained in the aldol condensation of acetone**

Results shown in figures 11 and figure 12 represent acetone conversions and product distributions with time over three different zeolites, HZSM-5 (Si/Al: 45), H-USY and H-Beta respectively. The overall conversion for each experiment was calculated as the combination of yields of all the products obtained. Acetone conversion over HZSM-5 and H-USY increased with increase in reaction time whereas an apparent decrease in conversion was observed over H-Beta. The observed brown colour of zeolite Beta after longer reaction times (5 to 24 hours) indicated coke formation that accounts for the decrease in detectable products. Thus, the overall acetone conversion for each zeolite did not exceed 4%.

For the purpose of simplifying the analysis of results, mesityl oxide was reported as the combination of its α and β forms. The occurrence of α and β forms of mesityl oxide was in the ratio of 8, whereas Paulis et al. (1999) obtained a ratio of 4. For all three catalysts, mesityl oxide was the major product (combined selectivity of 95%) and phorone, mesitylene and isophorone (shown on scheme 10) were obtained at lower selectivity.

Mesitylene is the most abundant of these by-products showing a significant increase over H-Beta and H-USY with time, with selectivities of 20% after 24 hours with a corresponding decrease in mesityl oxide. Phorone was also detected over these zeolites with time, but was not observed over HZSM-5, while isophorone was not detected over all the zeolites tested.

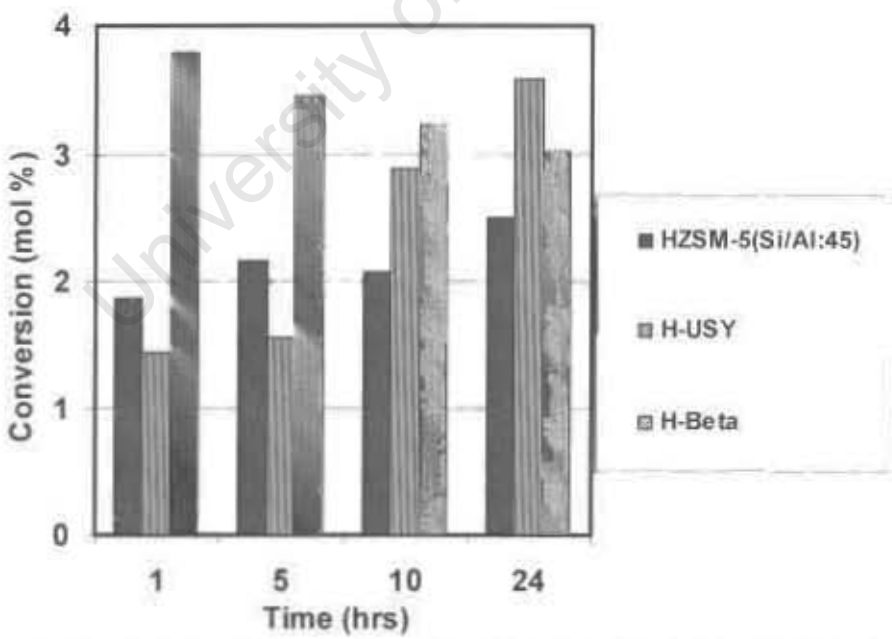


Figure 11 **Acetone conversion over different zeolites against time at 170°C**

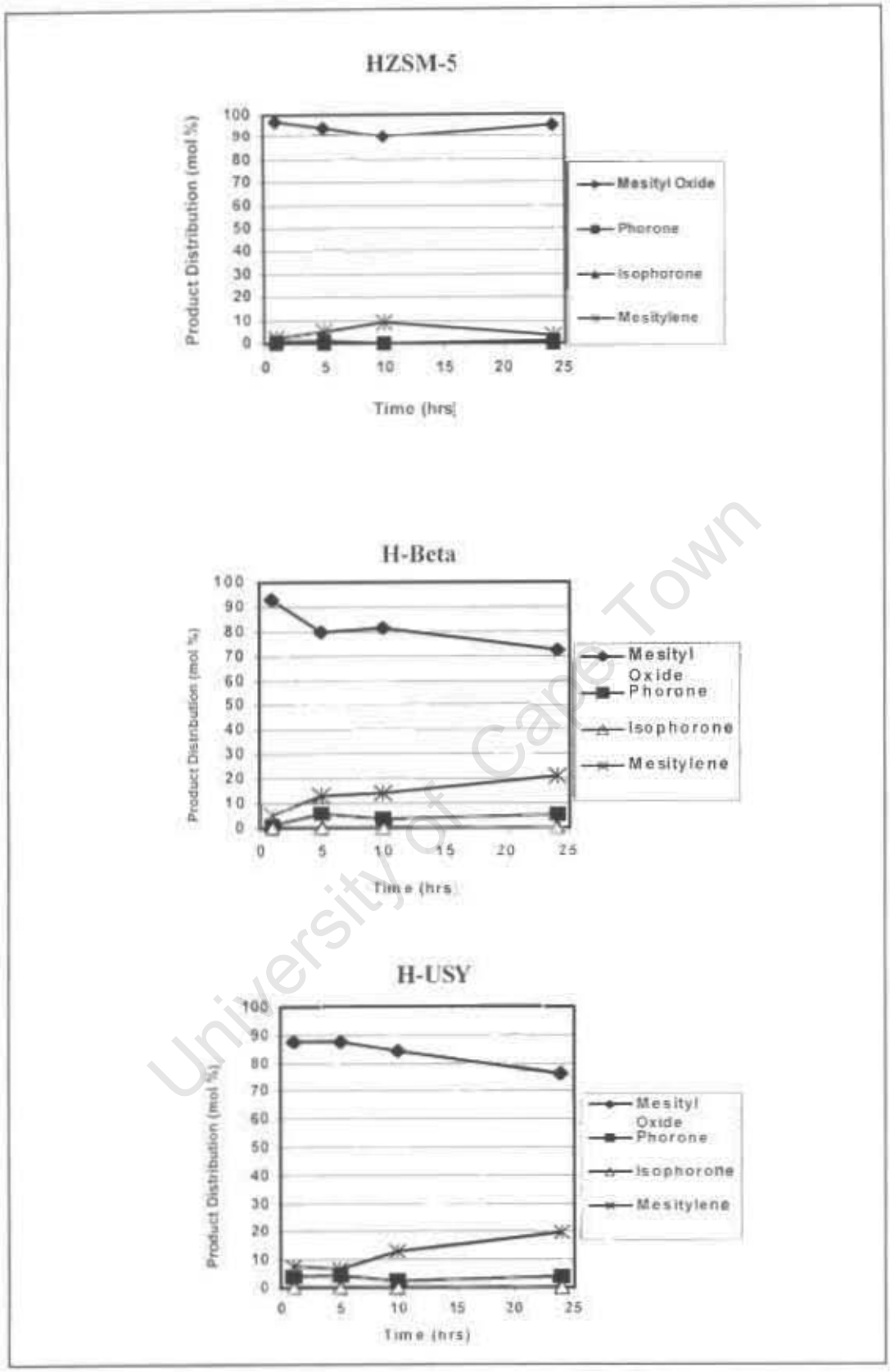


Figure 12 **Product distribution of acetone self-condensation over three zeolites**

It is important to compare product selectivity of different catalysts at similar conversions. Conversions obtained after 24 hours are all in the range of 3 +/-0.5 mol % and as such the corresponding selectivities were used for the comparison of three zeolites.

Initially, the mesityl oxide selectivity was high over all catalysts, but dropped significantly to less than 80% after 24 hours over H-Beta and H-USY zeolites, whereas the decrease over HZSM-5 was less marked, final selectivity in the range of 90 – 94%.

Shape selective effects were evident over higher micro-pore volume of H-Beta and H-USY with higher selectivies of mesitylene and phorone compared to HZSM-5. These zeolites seem to be more susceptible to coke formation, as deduced after a brown colour of catalysts was observed at longer reaction times. HZSM-5 is known be resistant to coke formation primarily due to its narrow pores that impose steric constraints on transition states in reactions (Bhattacharya and Sivasanker, 1995), and that may have prevented the formation of mesitylene. The apparent decline in acetone conversion with time over H-Beta is probably due to accumulation of coke (high molecular weight products) in the zeolite pores which are not detected in the gas chromatography analysis of product mixtures in solution.

Temperature Effect

Since the highest selectivity towards mesityl oxide was obtained over HZSM-5 (Si/Al: 45), it was decided to further investigate the effect of temperature on selectivity over this zeolite. The investigation was carried out using the same procedure as outlined in the experimental section. Figure 13 below shows acetone conversion at different temperatures, while figure 14 illustrates the product distribution at 170°C. At lower temperatures mesityl oxide was the only product formed.

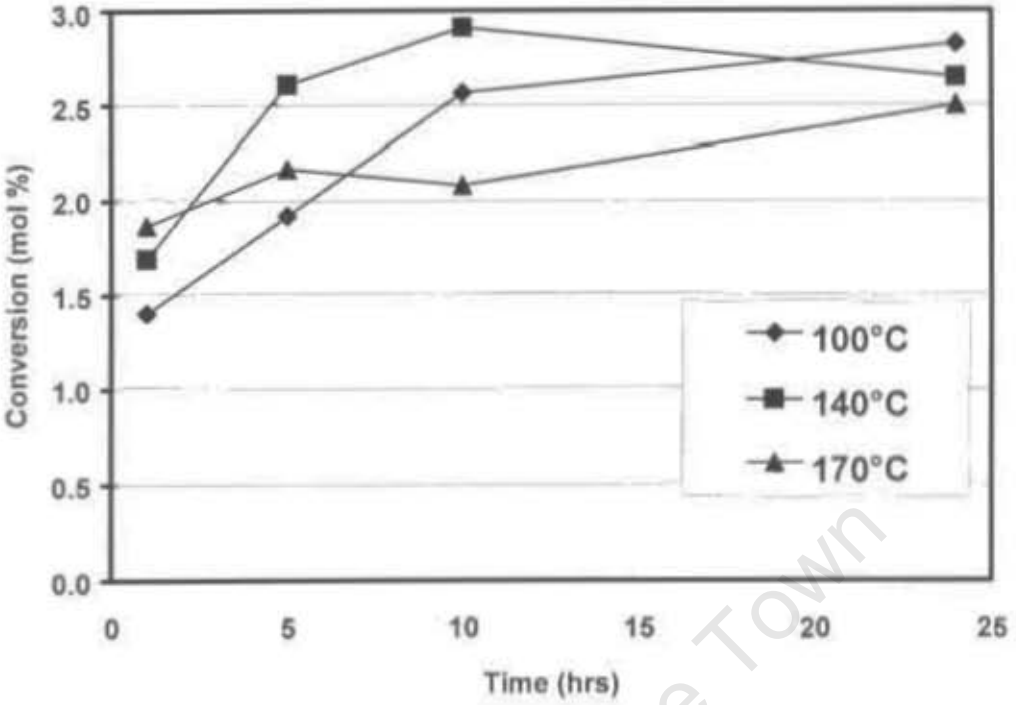


Figure 13 Acetone conversion over HZSM-5 (Si/Al: 45) against time at different reaction temperatures

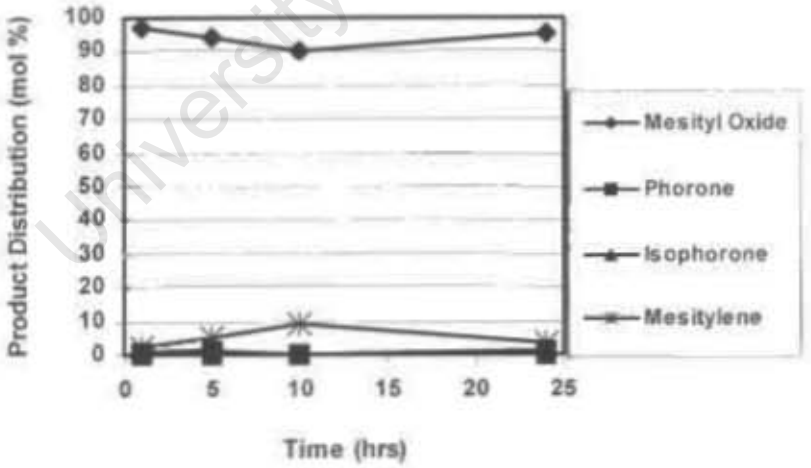


Figure 14. Product distribution of acetone self-condensation over HZSM-5 at 170°C

An increase in temperature does not have a significant influence on rate of conversion to mesityl oxide but does decrease the selectivity. After 24 hours at 170°C the yield was slightly lower than results at 100°C and 140°C.

The high selectivity (98%) towards mesityl oxide obtained at lower temperature suggests that temperature effects and steric constraints of the micro-pores combine to eliminate formation of bulkier products.

Acetone Self-Condensation using H_2SO_4

To put the zeolite-catalysed reactions in perspective, the self-condensation of acetone using H_2SO_4 was investigated. Reactions were carried out under identical conditions with the procedure used for zeolites. A 0.15g of concentrated H_2SO_4 was used in a 6ml of solvent and reaction were at different times.

Figures 15 and 16 below shows conversion and product distribution respectively. The acetone conversions are slightly lower than the results obtained over HZSM-5.

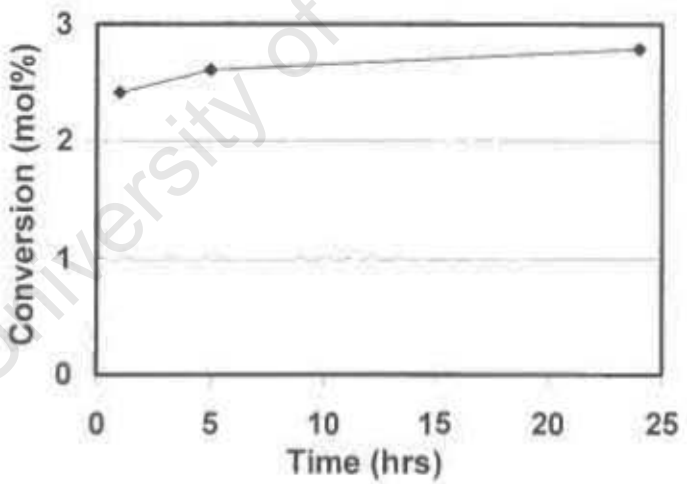


Figure 15. Acetone conversion over H_2SO_4 at 140°C

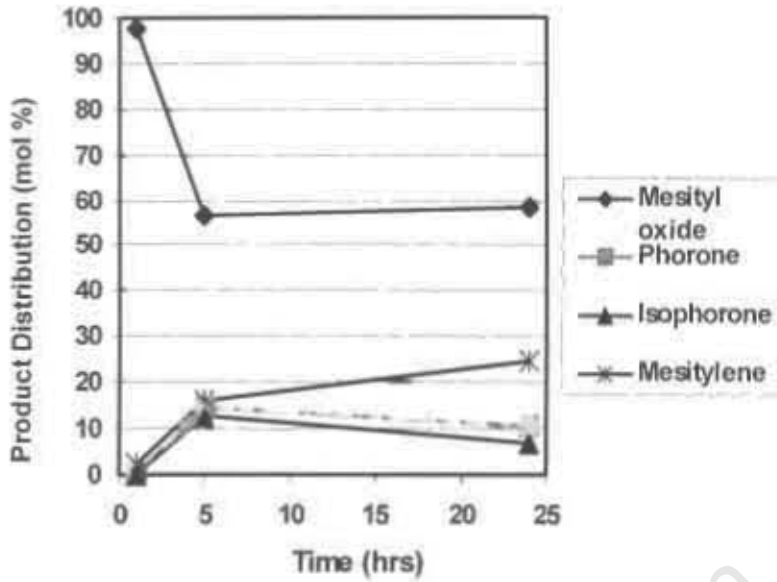


Figure 16. Product distribution from acetone self-condensation over H_2SO_4

Mesityl oxide was initially the dominant product, but other products, notably mesitylene, increased with time. After each reaction time a brown colour was observed in the sample mixture that indicated coke formation, presumably related to the formation of bulkier products like mesitylene.

The initial high selectivity using H_2SO_4 for mesityl oxide that decreased rapidly with time with corresponding increase in formation of phorone, isophorone and mesitylene is similar to the results obtained with H-Beta and H-USY although over these catalysts there was slightly lower selectivity towards mestylene, isophorone and phorone.

3.2.1.1 Discussions

It is important to indicate that acetone conversion at all reaction conditions reported above acetone conversion was less than 4%. This observation suggest that between 100°C to 170°C, the thermodynamic equilibrium of this reaction is limited to less than 4% of acetone conversion.

Although most of aldol condensations of ketones (acetone, cyclohexanone) investigations reported in literature were carried out in gaseous phase, the present investigation was carried out in a liquid phase. Previous studies on zeolite catalysed aldol condensation of acetone

followed its conversion to di-acetone alcohol via Brønsted acid site of zeolite to mesityl oxide where this was achieved through the use of in-situ NMR (Fripiat, 1998; Haw et al., 1998; Reichle, 1980).

The approximately 20% drop in mesityl oxide selectivity over H-Beta and H-USY compared to 2% drop with time over HZSM-5 could be ascribed to shape selectivity induced by the ten-membering of the HZSM-5 zeolite.

The yields of about 4% of mesityl oxide obtained over zeolites, which were lower than the 19% obtained by Pittman and Liang (1980), (see table 5) can be ascribed to differences in reaction temperature and different catalysts used. However, Pittman and Liang did not indicate the product selectivity results, whereas in the present study using zeolites a high selectivity (97%) towards mesityl oxide was observed.

Raising temperature from 100°C to 170°C does not significantly increase the conversion of acetone. Although the secondary product, mesitylene, emerged at higher reaction temperature, 170°C, and longer reaction times, this product was suppressed at lower temperatures and almost 100% selectivity towards mesityl oxide was obtained. The opposite was observed in the case of cyclohexanone (figure 20) which was clearly temperature sensitive. All acetone condensation reactions were performed at temperatures higher than its boiling point (56°C) whereas cyclohexanone showed highest conversions above its boiling point, 155°C. Temperatures higher than 170°C and also high acidity of zeolites, can determine the nature of secondary reactions in the aldol condensation reactions (Jacobs et al., 1985). At higher temperatures, (over 300°C) the gas phase self-condensation of acetone yielded a mixture of isobutene and acetic acid (Di Cosimo et al., 1998), obtained by cracking of di-acetone alcohol.

Bell and Gold (1983) also showed that higher temperatures (302°C) and longer reaction times favoured for the formation of mesitylene, the ^{13}C-NMR technique being used to identify products.

The work by Bosacek et. al (1990 and 1991) and Sepa et. al (1995) demonstrated that the control of both the temperature and surface coverage was critical factor for understanding the reactivity of species interacting with Bronsted acidic sites of the zeolites.

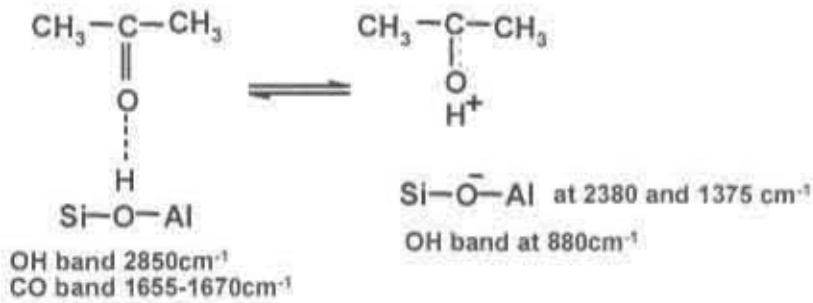
Table 5 below indicates that lower temperatures have no significant influence on the yield of mesityl oxide when acidic resins are used as catalysts.

Table 5 Mesityl oxide yields over different catalysts (**Pittman and Liang, 1980**)

		Yield of mesityl oxide , %	
Temperature (^{0}C)	**Time (hours)**	**Nafion-H**	**Amberlite IR-120**
60^{0}C	**1**	10.5	4.6
	6	18.1	10.8
	12	19.0	16.4
	24	19.7	19.8
100^{0}C	**1**	10.7	5.5
	6	18.4	14.0
	12	19.3	18.8
	24	19.8	19.8
140^{0}C	**1**	10.9	9.7
	6	18.7	18.2
	12	18.7	18.3
	24	18.8	18.3

The extent of acidity of zeolite, influenced by its Si/Al ratio was noticeable in this investigation. Initially, higher activity in H-Beta (Si/Al: 8) is an indication of its larger acid sites. The same observation cannot be made in the case of HZSM-5 (Si/Al: 45) and H-USY (Si/Al: 14) where the latter did not as higher activity, initially, as expected because of lower Si/Al ratio. However, its activity increased at longer reaction times compared to other two zeolites. Haw et. al (1994) and Kubelkova and Bosacek (1990) suggested that the extent of acidity in zeolites was important as it influenced proton transfer from the zeolite Bronsted sites to the ketones in the adsorption complex. This affects the probability that it will condense with a second ketone molecule. Kubelkova et al. (1991) also established through the use of Fourier transform infrared spectroscopy that for acetone adsorbed in HZSM-5, the protonated form of acetone was probably in equilibrium with acetone H-bonded to the bridging hydroxyls. The studies by Haw and Kubelkova are similar in that the self-condensation of acetone is a bimolecular reaction between an acetone adsorption complex and

a free acetone molecule. Scheme 4 (also represented in the introduction section 1.2.1) below illustrate their observations.



Scheme 4 **Complex formed between acetone and Brønsted acidic stes of zeolite (Bosacek and Kubelka, 1991)**

The initial selectivity towards mesityl oxide over sulphuric acid was comparable to the zeolite results, but it dropped sharply to 55% with time and this was primarily due to secondary reactions towards mesitylene, phorone and isophorone predominating.

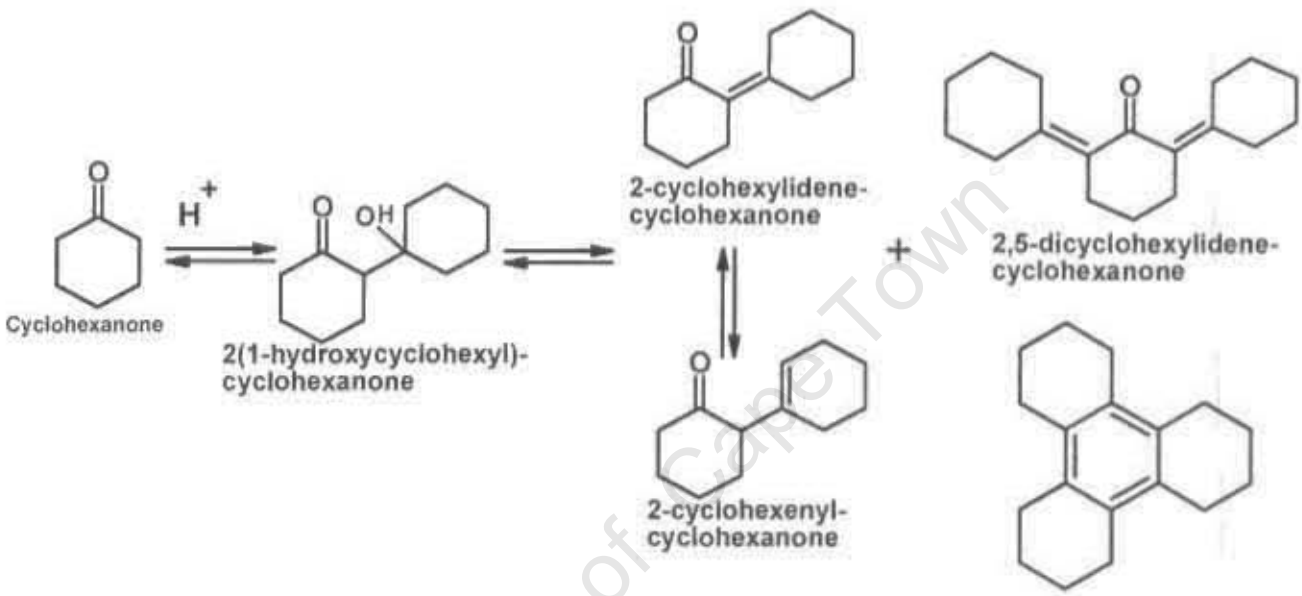
A clear indication emerged that liquid phase zeolite catalysed were better in terms of selectivity, and this may be ascribed to shape selective effects induced by zeolites as stated before.

At similar acetone conversions, zeolites are superior to sulphuric acid in that higher selectivity was achieved towards mesityl oxide compared to sulphuric acid and comparable conversions.

3.2.2 Self-Condensation of Cyclohexanone

In this investigation, the effect of zeolites with different pore sizes, temperature and reaction time were investigated in aldol condensation of cylcohexanone. The autogeneous pressures in this investigation were much lower than in the acetone self-condensation.

Scheme 11 below shows typical products formed in the self-condensation of cyclohexanone.



Scheme 11 Reaction scheme showing products of self-condensation of cyclohexanone

In the first set of experiments, various zeolites were screened as catalysts for the self-condensation of cyclohexanone. The effect of zeolite pore size was investigated over medium (HZSM-5) and large pore zeolites (H-Beta and H-USY).

Figure 17 and 18 below show the conversion and yield of 2-cyclohexylidene-cyclohexanone respectively. The highest cyclohexanone conversion was obtained over zeolite H-USY and the lowest over HZSM-5 and conversion was still increasing after 24 hours over all the zeolites. The intermediate product, 2-(1-hydroxycyclohexyl)-cyclohexanone could not be detected due to rapid dehydration to other products in acidic medium. The major product, 2-

cyclohexylidene-cyclohexanone, obtained from dehydration of 2-(1-hydroxycyclohexyl)-cyclohexanone was observed in combination with its isomeric product, 2-cyclohexenyl-cyclohexanone. The yield of 2-cyclohexenyl-cyclohexanone in figure 18 is reported as a combination of its α and β isomeric products.

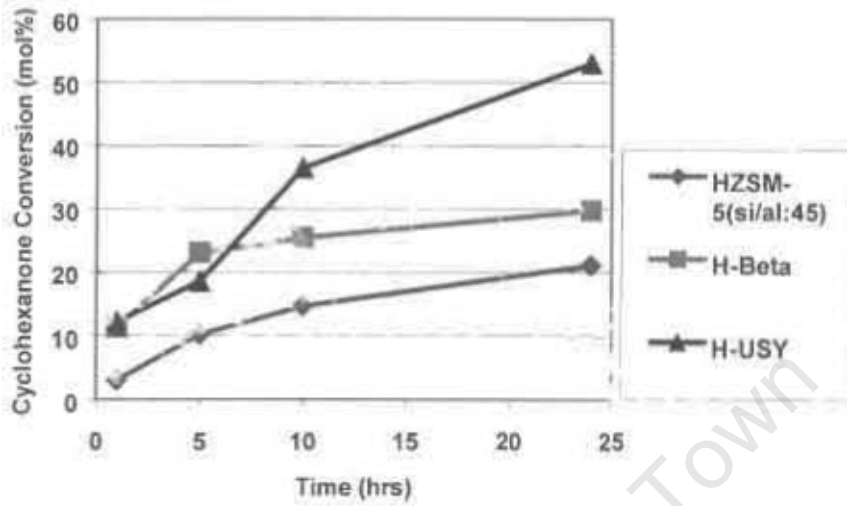


Figure 17 **Cyclohexanone conversion over different zeolites against reaction time at 170^{0}C**

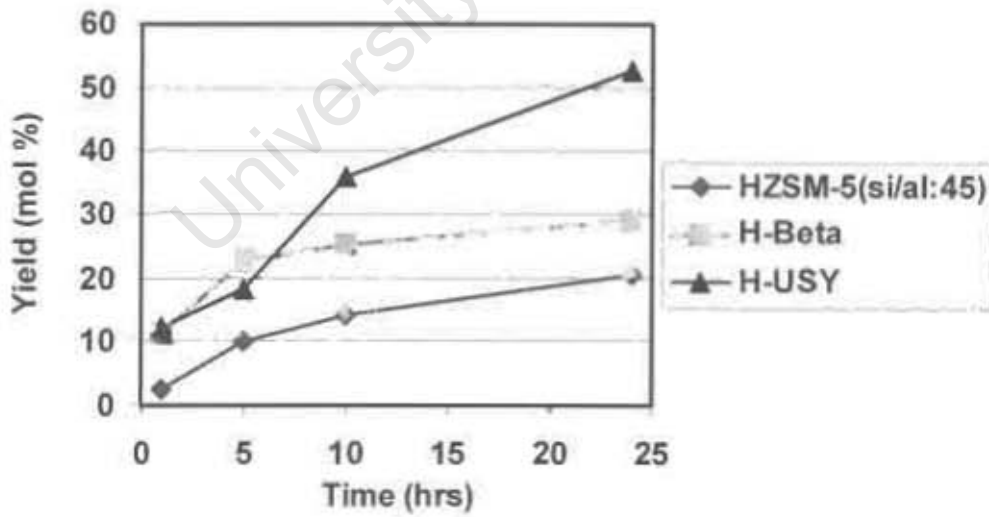


Figure 18 **Percent yield of 2-cyclohexylidene-cyclohexanone over three zeolites at 170^{0}C**

The main product detected was 2-cyclohexenyl-cyclohexanone and it is clear from above figures 17 and 18 that its selectivity was over 98% because both conversion and yield are similar. A high yield of 2-cyclohexylidene-cyclohexanone at 52% was obtained over zeolite H-USY and the lowest yield over zeolite HZSM-5 (Si/Al: 45) with yield of 20% of the same product after 24 hours.

The effect of zeolite pore size on selectivity was evident with the highest yield 2-cyclohexylidene-cyclohexanone over a large pore zeolite H-USY and the lowest yield over medium pore HZSM-5. The yield of 2,5-dicyclohexanone-cyclohexylidene (that is not shown in the result) was less than 1% over H-USY and H-Beta zeolites each and was not detected over HZSM-5.

Effect of Acidity in HZSM-5

A trimeric product, 2,5-dicylohexylidene-cyclohexanone was not formed over HZSM-5 compared to small amounts detected over H-Beta and H-USY. This influenced our decision to investigate the reaction further only over HZSM-5 and to limit the number of products formed.

In figure 19, the effect of acidity was investigated using HZSM-5 zeolites with different silicon / aluminum ratios. The HZSM-5 (Si/Al: 13) zeolite was inactive and gave low yields (less than 1%) towards 2-cyclohexylidene-cyclohexanone. Both the HZSM-5 (Si/Al: 22) and HZSM-5 (Si/Al: 45) gave 9% yield each of the main product.

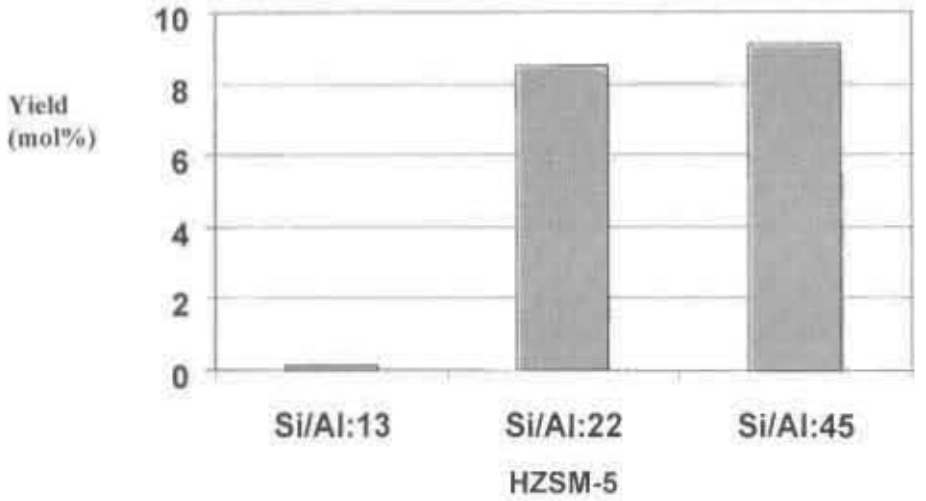


Figure 19 **Yield of 2-cyclohexylidene-cyclohexanone over ZSM-5 (different Si/Al) after 5 hours at 170^{0}C**

Effect of Temperature

The results of the effects of temperature on the self-condensation of cyclohexanone are shown in figure 20. This reaction is clearly temperature sensitive, with the highest yield of 12% and 19% obtained at 140^{0}C and 170^{0}C respectively. At 100^{0}C the yield of the same product was restricted to less than 3%. Figure 20 indicate the expected increase in reaction rate with increasing temperature.

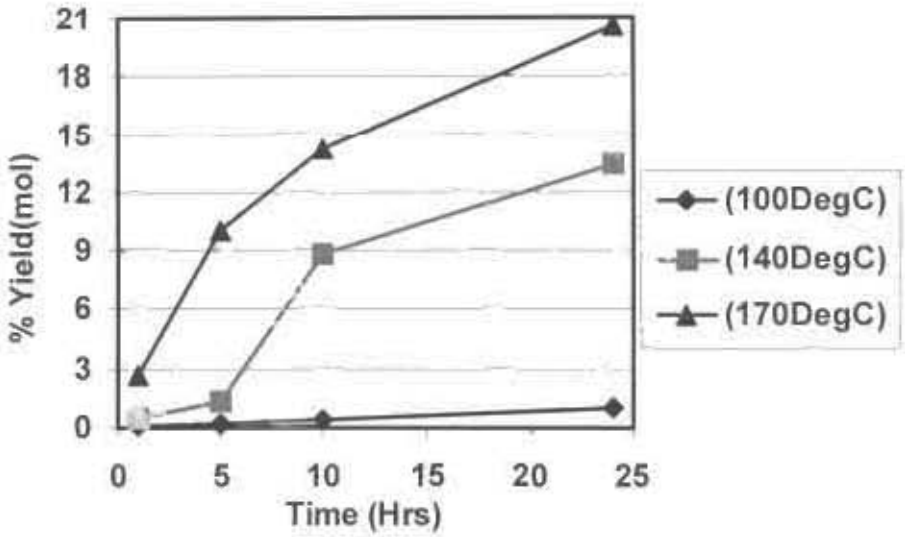


Figure 20 **Yield of 2-cyclohexylidene-cyclohexanone over HZSM-5 (Si/Al: 45) at different reaction temperatures**

Cyclohexanone Condensation over H_2SO_4

This investigation was carried out using a procedure outlined in section 2.2.1. A 0.14g of concentrated H_2SO_4 was substituted for zeolites and experiments were allowed to run for periods ranging from 1hour to 24 hours.

The results are shown in figures 21 and 22. Cyclohexanone conversion increased sharply initially and decreased slightly after 5 hours of reaction. A slight decrease in cyclohexanone conversion would suggest an error in measurements as conversion cannot decrease, can only increase or stay constant. A maximum conversion of 22% correlates well with the results obtained over zeolites. A more bulky product, 2,5-dicyclohexylidene-cyclohexanone was formed over H_2SO_4 compared to zeolite reactions where 2-cyclohexylidene-cyclohexanone was the predominant product.

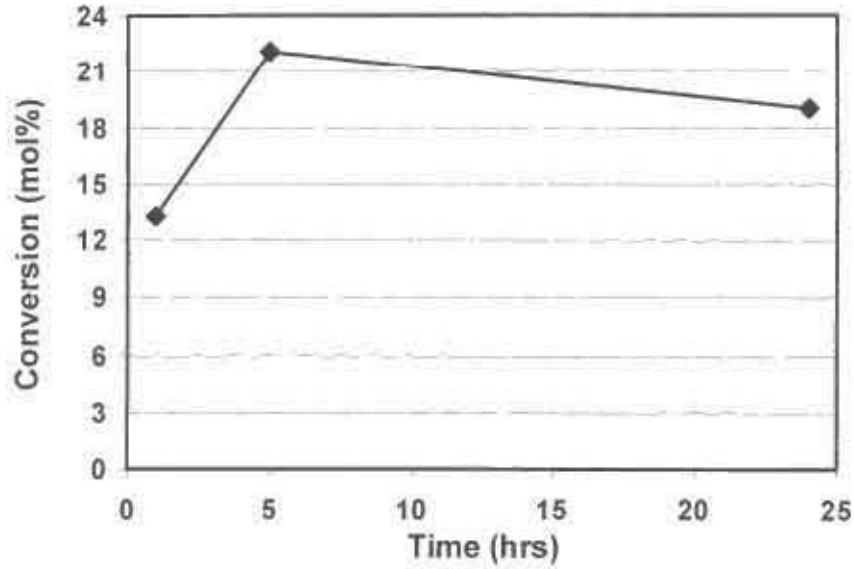


Figure 21 Cyclohexanone conversion over H_2SO_4 at 140^0C

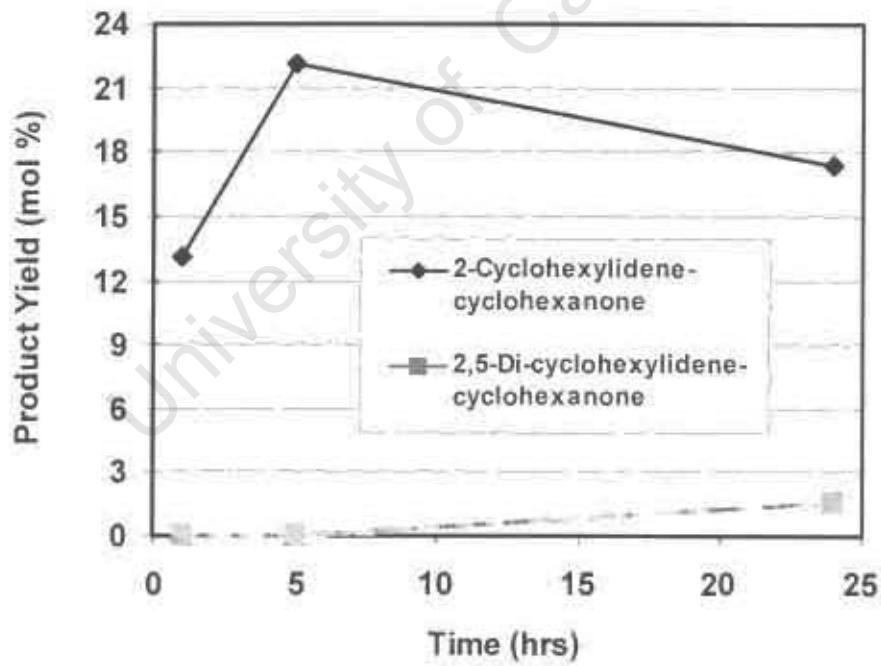


Figure 22 Yield for cyclohexanone self-condensation over H_2SO_4 at 140^0C

3.2.2.1 Discussions

The effect of different acidity of HZSM-5, H-USY and H-Beta on figure 18 was not evident as the yield did not follow the degree of acidity, based on Si/Al of the catalyst which decreases in the following order; H-Beta > H-USY > HZSM-5. This result indicate that the effect of zeolite acidity is not important in determining the selectivity of 2-cyclohexylidene-cyclohexanone but the shape selective effect of zeolites does play a role. A different observation was seen on figure 19. Low Si/Al ratio in molecular sieves are associated with larger number of acid sites in zeolites. HZSM-5 (Si/Al: 13) was inactive in the cyclohexanone condensation reaction.

Haw and co-workers (1994) reported that acidity of zeolite HZSM-5 is sufficiently strong that the secondary reactions are important even at modest temperatures. This behavior was not seen in the present investigation.

The product distribution is clearly influenced by the shape selective effects of zeolites with different pore geometries. Shape selectivity imposed by three zeolites was manifested by low yields of 2-cyclohexylidene-cyclohexanone over HZSM-5 followed by H-Beta and then H-USY. Small amount of less than 1% over H-Beta and H-USY of 2,5-dicyclohexylidene-cyclohexanone seems to be due to steric effects of these zeolites as the same products was not detected over medium pore HZSM-5.

The present investigation reported liquid phase condensation of cyclohexanone over zeolitic materials, while in the literature the same investigation was mainly performed in the gas phase. The intermediate product, 2(1-hydroxycyclohexyl)-cyclohexanone was not identified in the present work probably due to its rapid dehydration to the main product, but it was identified in the work by Efimova and coworkers (1989).

Unlike the self-condensation of acetone, the rate of cylohexanone condensation increased at elevated temperatures and longer reaction time as indicated by high yields of 2-cyclohexylidene-cyclohexanone. Reactions of cyclic ketones are said to be more exothermic in nature and this may explain the high reaction rate of cyclohexanone acetone (Efimova, 1989).

An investigation of H_2SO_4 as catalyst on cyclohexanone condensation revealed similar behavior of this catalyst with those of zeolite. The disadvantage in using sulphuric acid or large pore is the higher tendency for coke formation mainly due to 2,5-dicyclohexylidene-cyclohexanone.

Cyclohexanone has a high boiling point compared to acetone, and as such its partial pressures at high temperatures, 170^{0}C, was low compared to acetone.

The effect of pressure on the self-condensation of cyclohexanone in this investigation could not be determined as the reaction was performed at autogeneous pressure. Matsumoto and Acheson (1991) reported formation of all the products shown in scheme 11 at pressures greater than 2GPa. Table 6 shows the autogeneous pressures of acetone and cyclohexanone at different temperatures

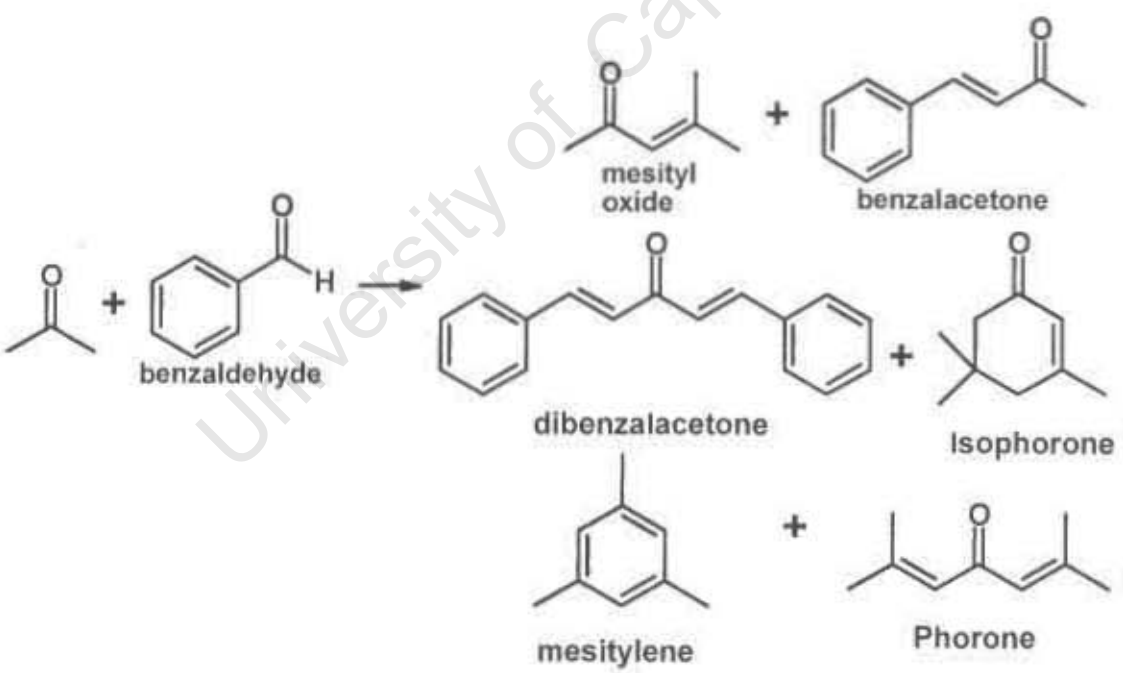
Table 6 Autogeneous pressures at different reaction temperatures obtained in the present study of acetone and cyclohexanone self-condensations reactions

Temperature (^{0}C)	Acetone (Boiling Point = 56^{0}C)	Cyclohexanone (Boiling Point = 155^{0}C))
	Pressure (bars)	Pressure (bars)
100	3	< 1
140	8	< 1
170	14	1

3.3 Cross-Condensation between Acetone and Benzaldehyde

Reactions between a ketone and an aldehyde are important since a limited number of products can be obtained especially when the aldehyde does not have hydrogens α- to the carbonyl and therefore it cannot condense with itself. Examples of such aldehydes include formaldehyde and benzaldehyde.

The zeolite-catalysed reaction between acetone and benzaldehyde was investigated to check whether the restricted pore geometry and unique acidic properties enhanced its product selectivity. It was of interest to know, for example, whether crossed aldol condensations took place in preference to self-condensation of acetone and whether the formation of benzal-acetone maximised and other by-products were minimised. Benzal-acetone is of particular interest because it may have industrial applications (Pittman and Liang, 1980). HZSM-5 was chosen for this investigation primarily for its resistance to coke formation and to limit the formation of bulky products like dibenzalacetone. Some possible products of this reaction are shown in scheme 12.



Scheme 12 **Schematic representation of the reaction between acetone and benzaldehyde**

The results obtained, shown in figures 23 and 24, represent the reactant conversion and product distribution with time respectively. The data was based on a gas chromatographic determination of concentration of reactants and products in the reaction mixture, using detector response factors described in Appendix I.

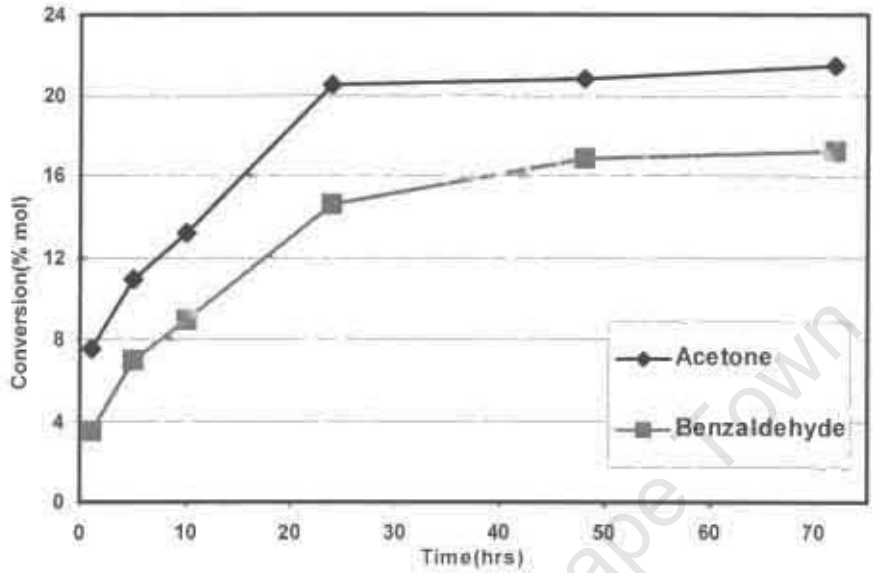


Figure 23 **Conversion of acetone and benzaldehyde (1:1 mole ratio) over HZSM-5 (Si/Al: 45) at 150^{0}C with time.**

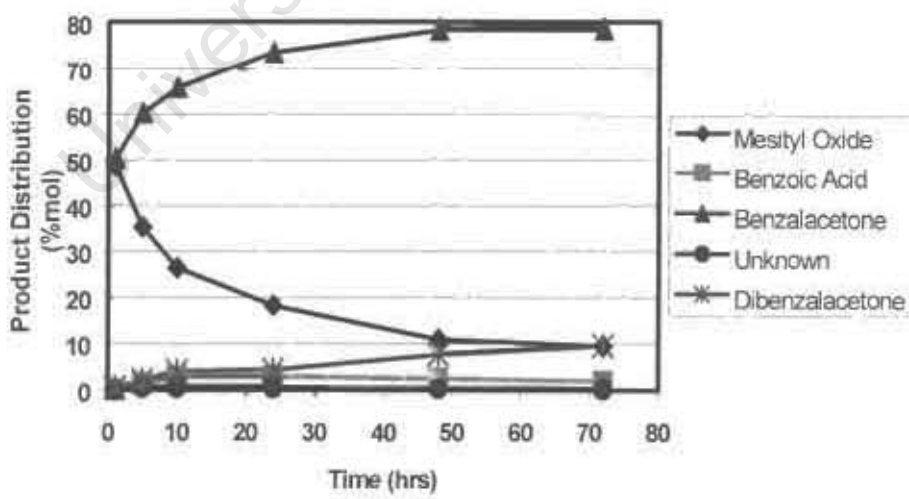


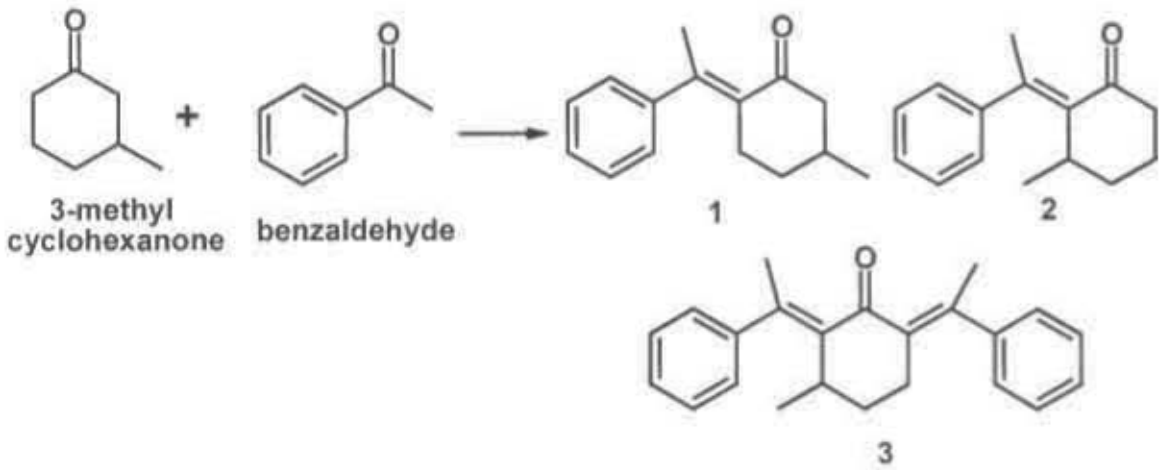
Figure 25 **Product distribution for the acetone/benzaldehyde (1:1 mole ratio) condensation over HZSM-5 (Si/Al: 45) at 150^{0}C with time**

The overall conversion of acetone was higher than of benzaldehyde, reflecting the involvement of acetone in both self- and crossed-condensations. The yield of benzalacetone was found to range from 4% to 17% based on acetone consumption. This is significantly low compared to the 23% to 28% (after 1 and 24 hours respectively) over Nafion-H reported by Pittman and Liang (1980). However, these authors did not report on product selectivities.

Initially, both mesityl oxide and benzalacetone were formed in equal proportions (50%), but thereafter mesityl oxide decreased rapidly to a selectivity of 10% and benzalacetone increased to a selectivity of 79% after 72 hours. The significant drop in mesityl oxide may be due to its involvement in the formation of other products. The other products, benzoic acid, di-benzalacetone and other unknown products were restricted to less than 10%. Of these, only dibenzalacetone increased with time from less than 1% after 1 hour to 10% after 72 hours. It was noted that neither isophorone nor mesitylene and further products of self-condensation of acetone were detected in this reaction.

3.3.1 Discussions

The high selectivity towards benzalacetone compared to dibenzalacetone is likely due to shape selective of HZSM-5. However, dibenzalacetone was the major competing product to benzalacetone, and as mentioned may have formed by some interaction with other products. It has been shown by Augustine and Posner (1995) that a choice of zeolite influences selectivity depending on reactant ring size and size of zeolite cage. Indeed due to sterical hindrance aspects products **2** and **3** would be limited due to α-positioned on the methyl Using ZSM-5, Mordenite, Faujasite 'X' and Linde A zeolites, only a 6-benzylidene (**1**) product was formed from a reaction between 3-methyl-cyclohexanone with benzaldehyde shown in scheme 13. No 2-benzylidene (**2**) product or di-substituted (**3**) product was obtained over all zeolites used.

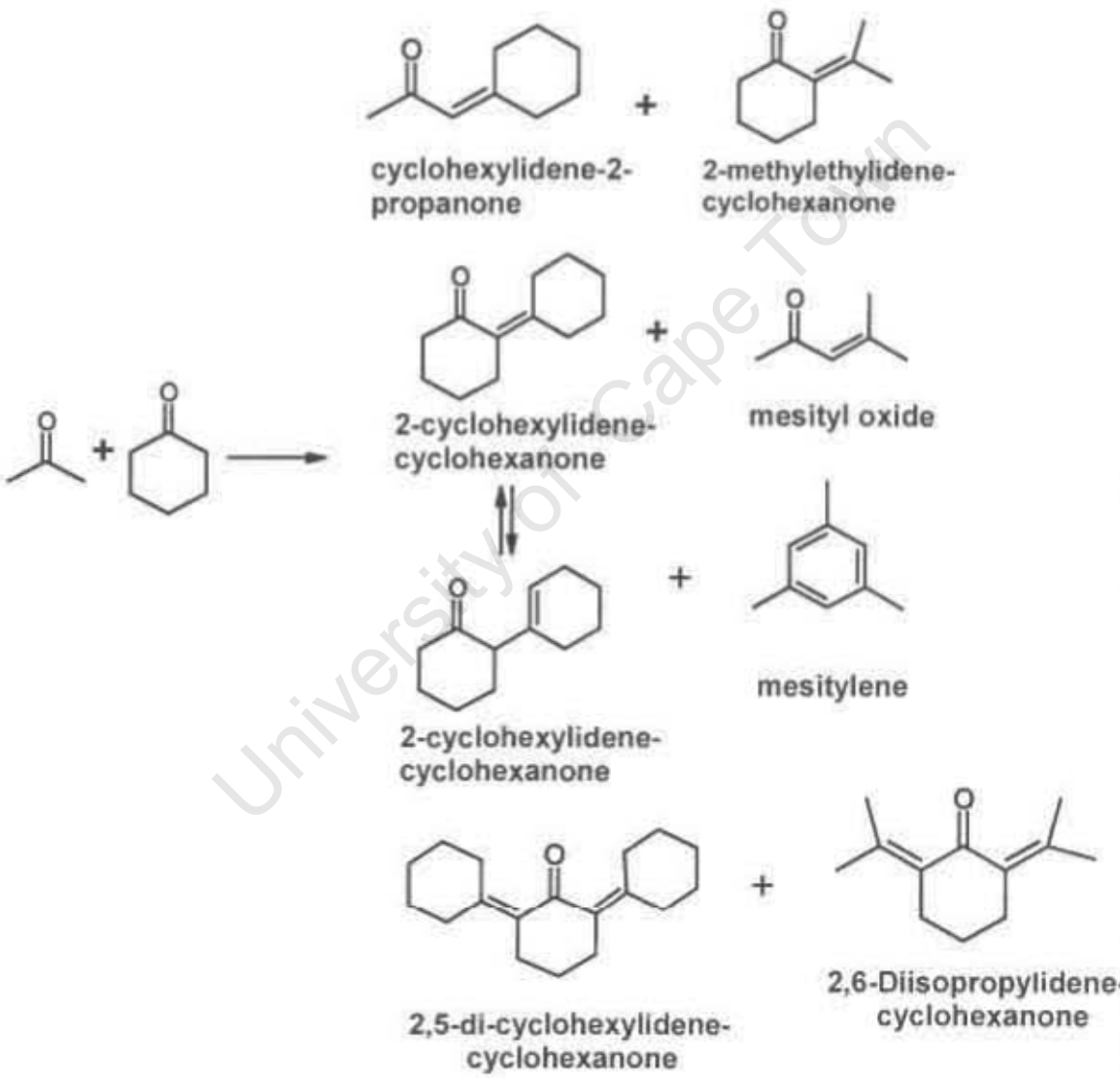


Scheme 13 Reaction between 3-methyl-cyclohexanone and benzaldehyde (Augustine and Posner, 1995).

Pittman and Liang (1980) described the aldol condensation between acetone and benzaldehyde as normally hindered by equilibrium limitation. In the present investigation, similar behaviour was observed as conversion for acetone and benzaldehyde was limited to 22% and 17% respectively, and benzalacetone selectivity was restricted to 79%. This behaviour was observed at longer reaction times, between 48 and 72 hours.

3.4 Mixed Aldol Condensation of Acetone and Cyclohexanone

The aim of the following investigation was to determine the product selectivity for mixed aldol product between acetone and cyclohexanone over zeolites of different pore sizes.
Scheme 14 below shows possible products of mixed aldol condensation of acetone and cyclohexanone. The products such as mesityl oxide and 2-cyclohexylidene-cyclohexanone, from self-condensations of acetone and cyclohexanone respectively, are obtained together with their mixed aldol condensation products.



Scheme 14 Reaction scheme of mixed aldol condensation of acetone and cyclohexanone

3.4.1 The Effect of Zeolite Pore Size

Figures 25 and 26 show acetone and cyclohexanone conversions and product distributions respectively in a mixed aldol condensation of acetone and cyclohexanone. The acetone and cyclohexanone conversions obtained over HZSM-5 (Si/Al: 45) were the highest compared to other zeolites. Cyclohexanone conversion was overall higher than acetone conversion over all zeolites used and the same observation was noted in sections 3.2.1 and 3.2.2 of the self-condensation of acetone and cyclohexanone respectively.

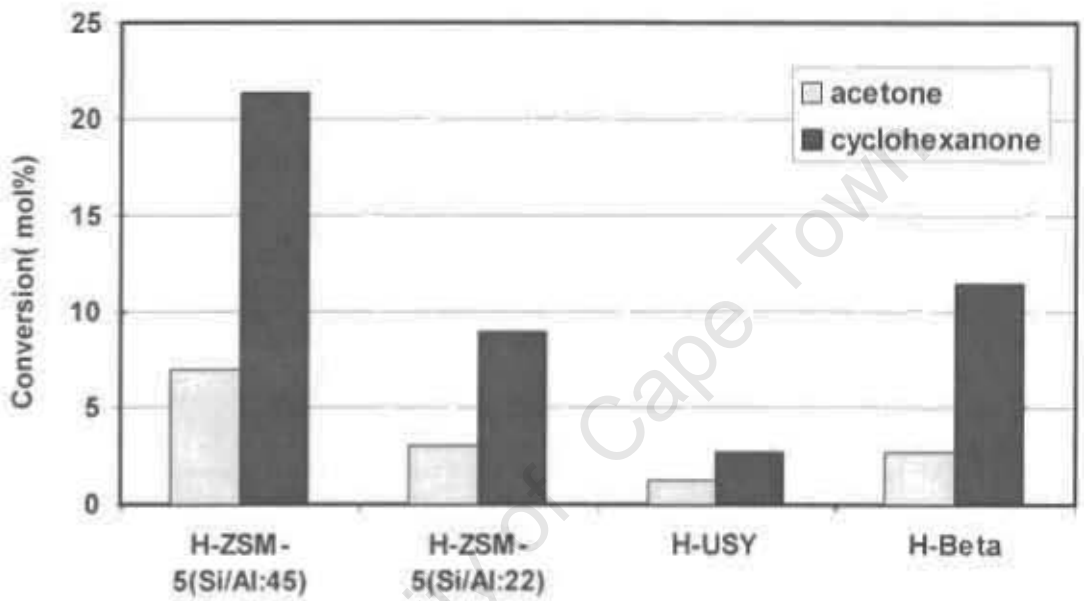


Figure 25 **Percent conversions mixed aldol condensation of acetone and cyclohexanone (3:1mol/mol) over different zeolites at 170^{0}C after 5hours of reaction**

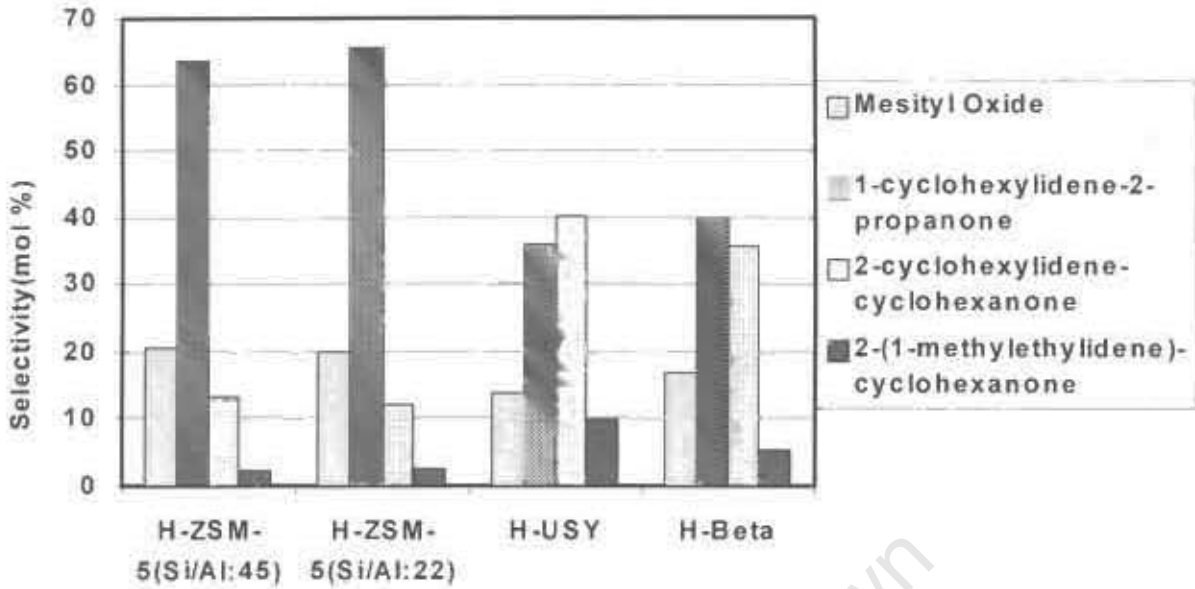


Figure 26 **Product distribution in the mixed aldol condensation of acetone and cyclohexanone (3:1mol/mol) over different zeolites at 170^{0}C after 5hours**

The selectivity of all products obtained over the two HZSM-5 zeolites (with Si/Al: 45 and Si/Al: 22) were similar, and those obtained over H-USY and H-Beta also followed similar trend. A mixed aldol product, 1-cyclohexylidene-2-propanone was obtained at significantly high selectivity (65%) over HZSM-5 zeolites whereas over large pore zeolites significantly lower selectivity (39%) was obtained.

On H-USY and H-Beta higher selectivity towards a bulky product, 2-cyclohexylidene-cyclohexanone was obtained (40% and 35% respectively) whereas over HZSM-5 zeolites 12% selectivity was obtained towards this product. Mesityl oxide was slightly higher over HZSM-5 zeolites.

High conversion of acetone and cyclohexanone over HZSM-5 zeolite and high selectivity towards a mixed product, cyclohexylidene-2-propanone influenced the decision to investigate other aspects of this reaction in terms of reactant ratios and reaction time.

3.4.2 Effect of Acetone / Cyclohexanone ratio

On the basis of the results shown in section 3.4.1, where HZSM-5 (Si/Al: 45) was the most active zeolite, further investigation was carried out on this zeolite to study reaction conditions which optimise selectivity towards the mixed aldol product, 1-cyclohexylidene-2-propanone.

The results shown in figure 27 represent conversions of acetone and cyclohexanone in the mixed aldol condensations over HZSM-5. At all mole ratios the conversion of cyclohexanone was higher than acetone conversion. The cyclohexanone conversion was highest at 3:1 mole ratio (acetone/cyclohexanone) where cyclohexanone reached a 40% conversion and acetone only 10% after 48 hours of reaction time. At acetone/cyclohexanone ratio of 1:3, acetone conversion levelled off after 10 hours of reaction time whereas cyclohexanone conversion was still increasing after 24 hours.

At equi-molar ratios, the conversion reached an equilibrium after 24 hours of reaction time whereas at 3:1 and 1:3 (acetone/cyclohexanone) mole ratio both acetone and cyclohexanone conversions were still increasing.

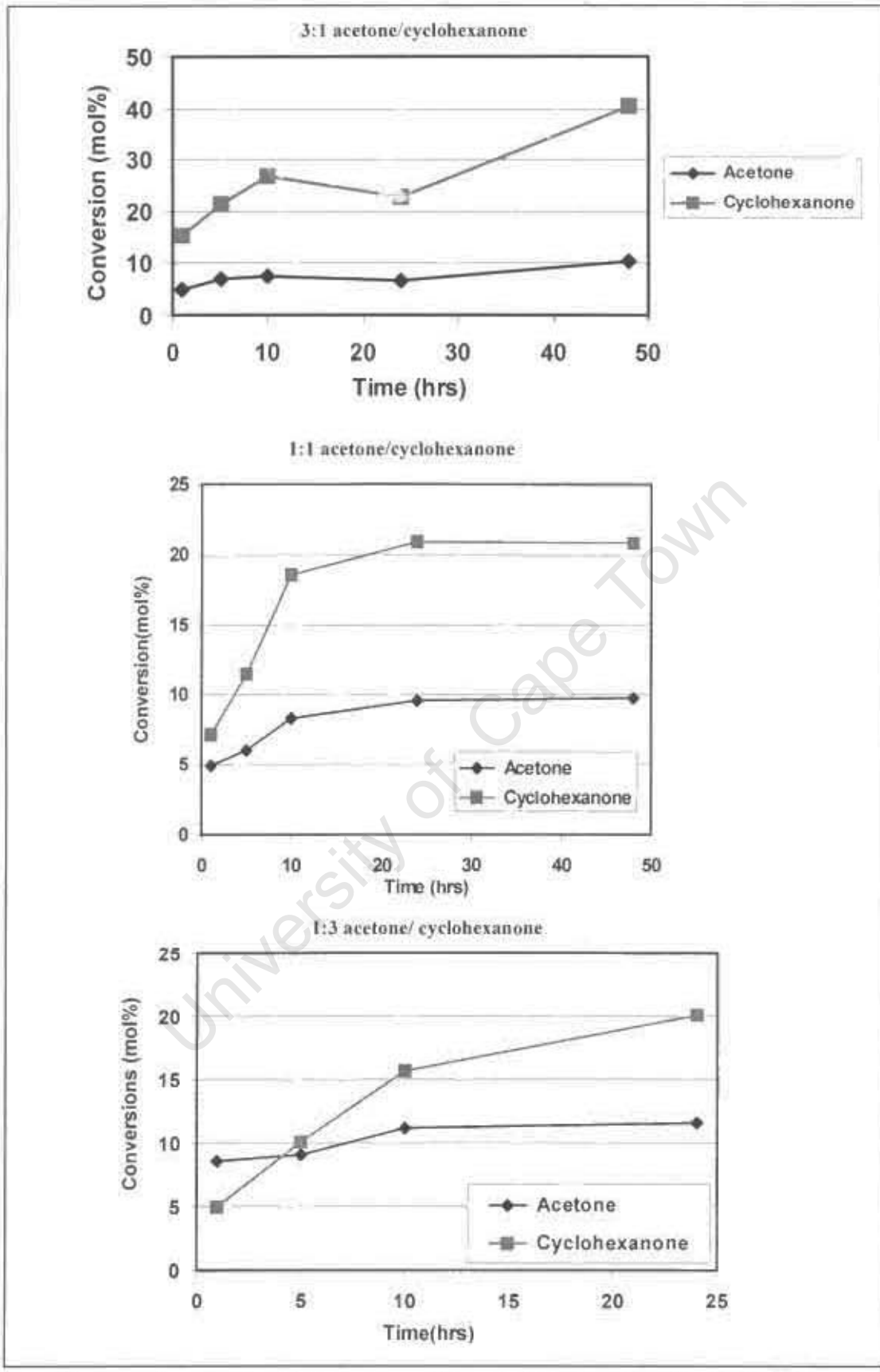


Figure 27 Acetone and cyclohexanone at three different mole ratios at 170^{0}C

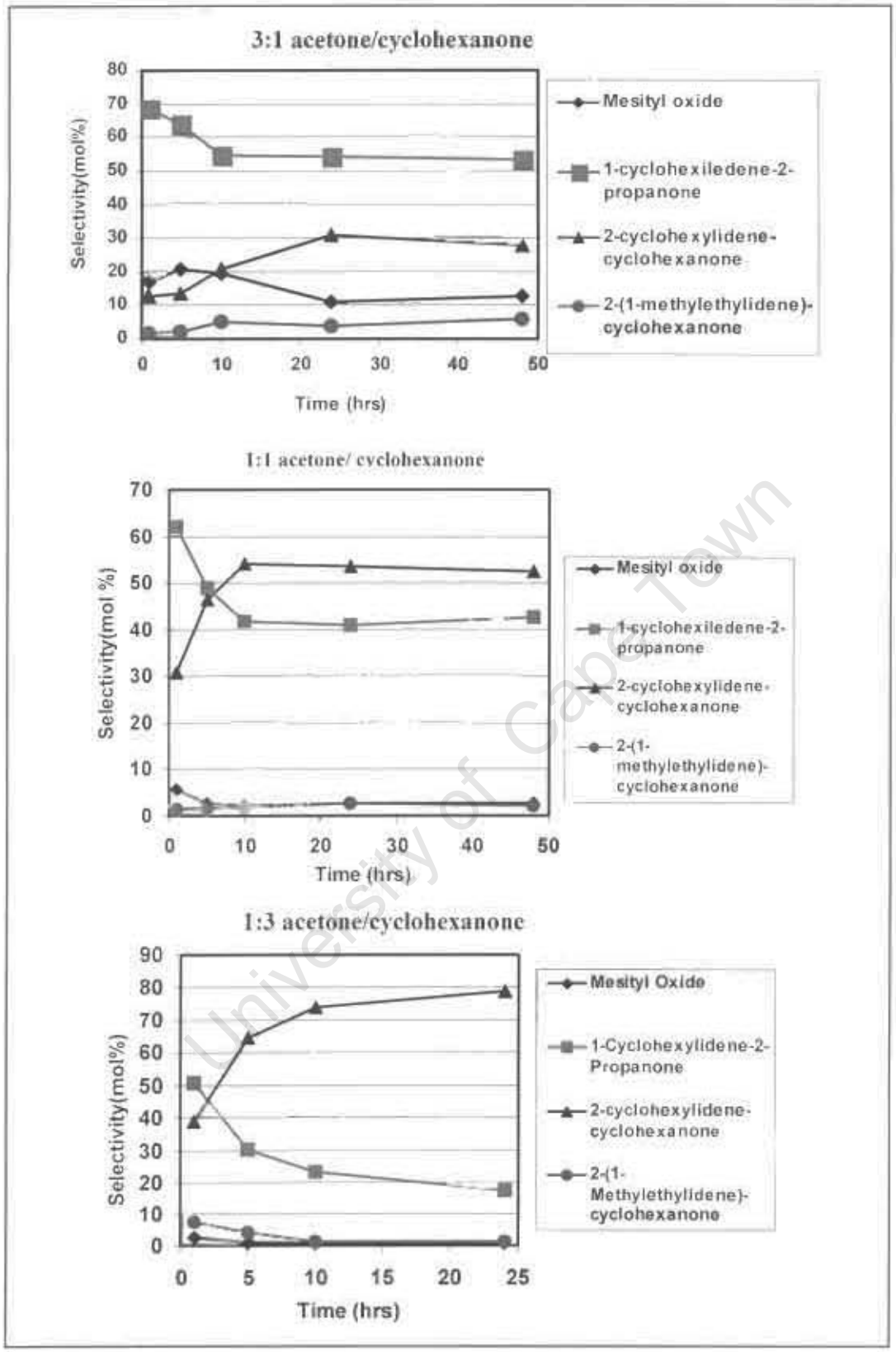


Figure 28 **Product distribution of the mixed aldol condensation of acetone and cyclohexanone at different mole ratios over HZSM-5 (Si/Al: 45) at 170^{0}C**

Figure 28 shows the product selectivity over HZSM-5 (Si/A: 45) for the mixed aldol condensation of acetone and cyclohexanone at different mole ratios. At longer reaction times, the self-condensation product, 2-cyclohexylidene-cyclohexanone was favoured at 1:1 and 1:3 acetone/cyclohexanone mole ratios. Other products like mesityl oxide and 2-(1-methylethylidene)-cyclohexanone remained significantly low at these ratios. At 3:1 (acetone/cyclohexanone) selectivity towards 1-cyclohexylidene-2-propanone was higher at 55%, while selectivity towards the self-condensation product of cyclohexanone, 2-cylclohexylidene-cyclohexanone dropped to less than 30%.

Initially, at all ratios there was significantly high selectivity towards 1-cyclohexylidene-2-propanone, which decreased with reaction time. Selectivity towards this product was highest at highest dilution of cyclohexanone (highest acetone / cyclohexanone).

The other mixed aldol product, 2-(1-methylethylidene)-cyclohexanone, increased slightly with time and also mesityl oxide started with high selectivity at 1:1 and 3:1 mole ratios compared to 3:1 ratio.

The best selectivity towards a single product, 1-cyclohexylidene-2-propanone, was obtained at a 3:1 ratio of (acetone/cyclohexanone).

3.4.3 Discussions

In the mixed aldol condensation of acetone and cyclohexanone the two main products were 1-cyclohexylidene-2-propanone and product of self-condensation of cyclohexanone, 2-cyclohexylidene-cyclohexanone. It is also noted from all the results presented in figure 28 that both mesityl oxide and 1-cyclohexylidene-2-propanone were decreasing and 2-cyclohexylidene-cyclohexanone was increasing with time.

The molar ratio and the reaction time have influence on the product distribution of the mixed aldol condensation of acetone and cylcohexanone. In all results cyclohexanone conversion was higher than of acetone consistent with earlier observations that cyclohexanone was more reactive than acetone.

The higher reactivity of cyclohexanone was probably due to high adsorption on zeolite active sites these supported by its self-condensation and mixed aldol condensation with acetone. Contrary to this observation, the adsorption measurements it was found that acetone and cyclohexanone were equally adsorption on the same zeolite materials.

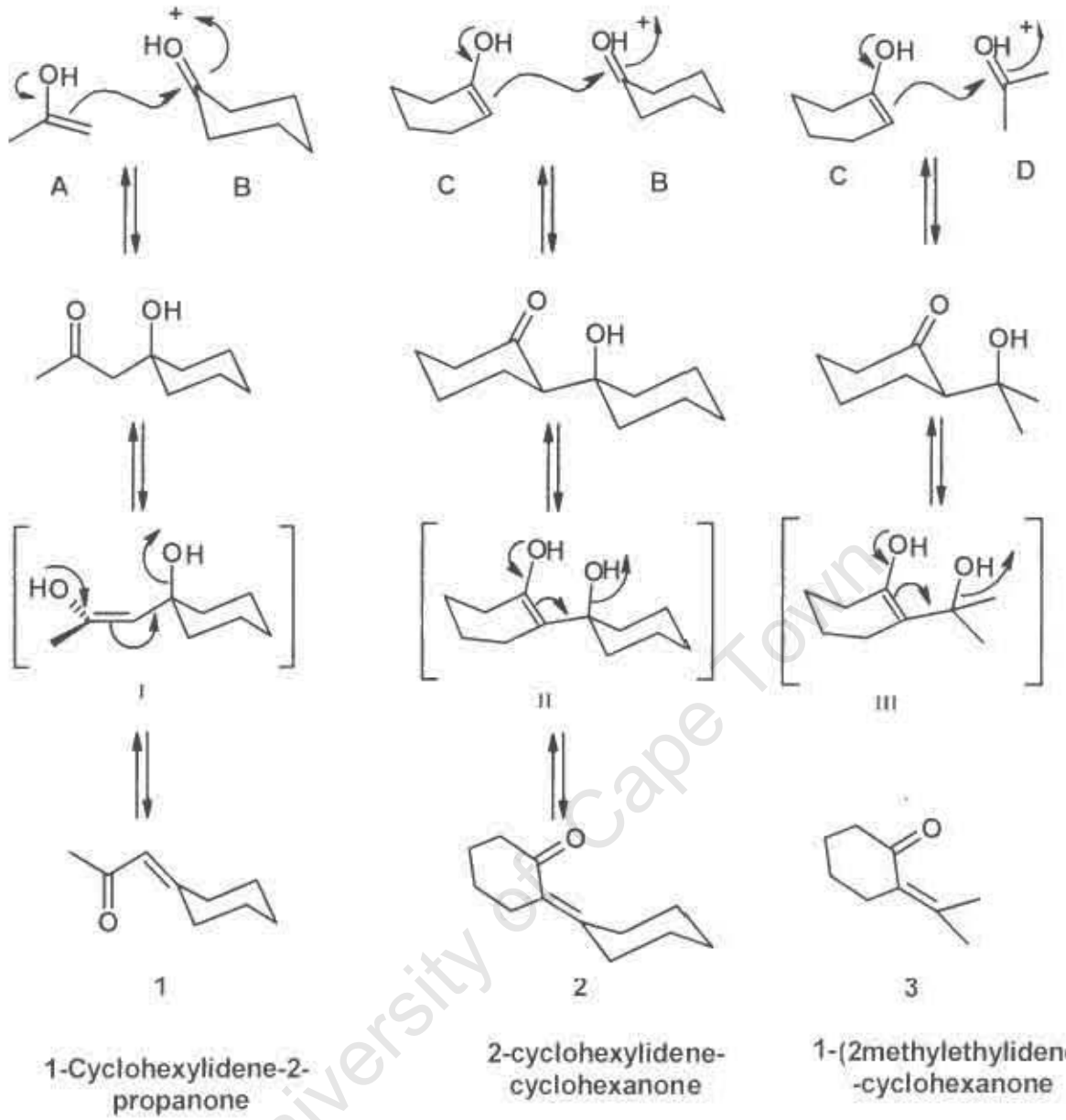
Somewhat surprisingly, the activity of H-ZSM5 is highest of the three catalysts in the mixed aldol reactions. Earlier results on self-condensation reactions over H-ZSM5, H-Beta and H-USY showed that conversions of cyclohexanone were higher over the latter catalysts while conversions of acetone were ~4% over all catalysts. This suggest that in H-USY and H-Beta acetone may dominate in the competition for active sites but then fail to react further. This could either be due to acetone being more readily adsorbed, or may be due to a higher rate of diffusion through pores which is related to its smaller molecular dimensions. However, in separate experiments (discussed in section 3.5) it was established that there is no significant difference between the rate of adsorption of acetone and cyclohexanone on these catalysts, so that this factor appears not to be significant.

When the reactant ratios were varied in a set of experiments using H-ZSM5, the key observations that (a) there is high selectivity for one of the two possible mixed-aldol condensation products (1-cyclohexylidene-2-propanone), (b) this product is preferentially formed in the early stages of the reaction, but drops off with time, (c) the overall selectivity towards this product is highest at highest dilution of cyclohexanone, and (d) the self-condensation of cyclohexanone is the most significant competing reaction.

These observations can be rationalised by considering steric constraints imposed by the pore geometries of the zeolites (shape selective effects) and steric and stereoeletronic aspects of the reactants, reaction transition states and products. Scheme 15 shows a summary of the competing reactions, including the key intermediates expected. The dominant products in the reactions over H-ZSM5 involve interaction of the reactive intermediates **B, C** and **D**, and the occurrence of the cyclohexyl unit in all of products is consistent with the observation that cyclohexanone is more reactive than acetone by virtue of its more basic oxygen and more readily enolizable carbonyl group. The high initial rate of formation of 1-cyclohexylidene-propanone establishes this as the kinetic product and by implication having the lowest energy demand in the transition state.

Scheme 16 gives a comparison of the mechanistic steps in the reactions involving intermediates **B, C** and **D**. Each reaction produces a hydroxyketone which is dehydrated under acid catalysis via intermediates such as **I, II** and **III**. Products **2** and **3** are relatively highly strained structures, incorporating adjacent sp^2 centres in a six membered ring. The intermediates **II** and **III** leading to these are of higher energy than intermediates **I** leading to product **1**, as they have tetra-substituted alkanes which are also constrained by the ring. These considerations together with the fact that product **1** is the least bulky of the products help to explain the observed preference for 1-cyclohexylidene-2-propanone in the reactions over H-ZSM5. The high selectivity for this product when an excess of acetone is present is consistent with a high rate of protonation of cyclohexanone combing with a high concentration in the pores.

The above argument explains the high selectivity towards one of the two possible mixed aldol condensation products. Product **1** is favoured over product **3** due to shape selectivity operating at both the transition state and product level of the reaction, and that **1** is favoured energetically. However, by this argument the self-condensation product **2** should be even less favoured than **3** since it is more sterically demanding. The fact that **2** is present in significant proportions at all ratios of acetone/cyclohexanone is further confirmation of the inherent high reactivity of cyclohexanone.



Scheme 15 Proposed mechanism of the mixed aldol condensation between acetone and cyclohexanone.

3.5 Adsorption Measurements of Ketones on Zeolites

3.5.1 Liquid Adsorption Measurements of Ketones

Adsorption measurements of ketone substrates on zeolites were performed to determine how strongly each of the substrates was adsorbed on the catalyst. The measurements were carried out to investigate whether adsorption effects might explain the activity of different ketones over zeolites. All liquid adsorption measurements were performed as described in section 2.3.1.

The adsorption characteristics of different ketone substrates onto zeolite catalysts (HSZM-5, H-Beta and H-USY) were determined using a technique described by Baron et. al (1998). The adsorption coefficient (K) was calculated from the model shown in section 1.3 in the introduction. It was used to determine how strongly the component was adsorbed with respect to carrier compound. A high value of K indicated that the component was adsorbed more strongly than the solvent whereas if the value was unity (equal to 1), that would indicate that both the components were adsorbing equally.

All the adsorption results of linear and cyclic ketones are presented in Tables 7, 8, 9 below.

Table 7: Partition coefficients in acetone carrier solvent

Compound	HZSM-5 (Si/Al:45)	H-Beta	H-USY
cyclohexanone	0.9	2	0.7
cyclopentanone	0.8	1	0.7
3-hexanone	0.8	0.9	0.6
3-pentanone	0.8	0.8	0.6

Table 8: Partition coefficients in cyclohexanone carrier solvent

Compound	HZSM-5 (Si/Al:45)	H-Beta	H-USY
cyclopentanone	0.4	0.5	0.5
3-hexanone	0.9	0.4	0.5
3-pentanone	0.9	0.5	0.5
acetone	1	0.7	1

Table 9: Partition coefficients in methanol carrier solvent

Compound	HZSM-5 (Si/Al:45)	H-Beta	H-USY
cyclohexanone	1	0.3	0.5
cyclopentanone	0.9	0.4	0.5
3-hexanone	2	0.4	0.5
3-pentanone	1	0.4	0.4
acetone	1	0.3	0.4

In Table 6, acetone was used a carrier and all the partition coefficients on HZSM-5 (Si/A: 45) were less than one. Adsorption coefficient (K) less than one imply that the ketones were adsorbed less strongly than the solvent. The same observation was obtained on H-USY. On H-Beta, there was higher K values for the cyclic ketones than linear ketones although this was not significant.

Another difference was observed in Table 8 where methanol was used as a carrier and the partition coefficients were higher on HZSM-5 than on both H-Beta and H-USY columns. Higher K values were obtained for 3-hexanone and 3-pentanone than for other compounds. An increasing partition coefficient (K) with increasing ketone molecular weight (3-pentanone → 3-hexanone) was observed in H-ZSM-5. No such behaviour was present in the larger pore zeolites H-Beta and H-USY.

In Table 7, with cyclohexanone used as a carrier, adsorption coefficient of acetone was slightly higher than other compounds on HZSM-5 and HUSY columns. On H-Beta, all compounds had relatively similar *K* values which indicated that all selected ketone components adsorbed similarly in different catalyst materials.

High partition coefficient values of *n*-alkanes, acetone, 2-hexanone and branched alkanes with *n*-octane as carrier on NaY, Na-USY, and ZSM-5 at room temperature were determined by Baron et al. (1998). Higher *K* values were obtained on ZSM-5 (Si/Al: 13), ZSM-5 Si/Al: 137) and Na-USY in his work than the values obtained in these work. The difference in carrier solvent strongly influences the adsorption of different compounds.

Table 10 below shows the results obtained by Reichle (1980) who used pulse reactor technique to determine how strongly various compounds were adsorbed onto the (LiMgAl(OH)) catalyst surface and the solvent used was not mentioned. Mesitylene was found to be nominally inert due to the extent of its retention time whereas isophorone was strongly adsorbed indicated by high retention time and a broad peak.

Table 10: Retention times Adsorption Studies reported by Reichle (1980)

Compound injected	Maximum Peak(minutes)	10% peak width(minutes)	Remarks
mesitylene	9.3	4.2	Sharp peak
Mesityl oxide	9.0	8.0	Medium broad peak
isophorone	23.3	25	Broad peak
acetone	5.9	34	Very broad peak
Water	7.0	34	Very broad peak

In Appendix VI, the corresponding chromatograms of the results presented above showed similar adsorption behaviour over H-USY and H-ZSM-5 columns than over H-Beta column.

These chromatograms revealed that retention times of acetone and cyclohexanone were similar.

Due to similar adsorption behaviour of acetone and cyclohexanone on zeolites using liquid chromatography method, it was not possible to correlate the results with the reaction work results. In order to see a clear difference in adsorption behaviour of different solutes, bigger differences in partition coefficients would be expected. This behaviour was not observed in the present investigation, as such adsorption behaviour of acetone and cyclohexanone on zeolite does not probably have effect on their reactivity on these materials.

Chapter 4

Conclusions

4 Conclusions

4.1 Characterisation Results

The crystallinity of all zeolites from XRD results before and after the reaction investigations confirmed that all zeolites were stable after the reaction work-up.

4.2 Self-Condensations of Acetone and Cyclohexanone

Self-condensation reactions of ketones are influenced by factors like shape selective effects of zeolites, temperature and residence time. Ten-member rings zeolite (HZSM-5) is best for acetone self-condensation compared to 12-member rings zeolite (H-USY and H-Beta).
Although high selectivity was obtained on all zeolites for cyclohexanone self-condensation, the best yields were obtained over H-USY.
Unlike acetone self-condensation reaction, self-condensation of cyclohexanone was strongly influenced by increase in temperature.

4.3 Cross-Aldol and Mixed aldol Condensations Reactions

High selectivity towards a single product was achieved through acetone and benzaldehyde reaction. This was attributed to the nature of reaction and the shape selective effects of HZSM-5.
The influence of shape selectivity of HZSM-5 was evident towards a mixed aldol condensation product, 1-cyclohexylidene-2-propanone compared to other zeolites. A 3:1 (cyclohexanone/acetone) ratio was the best condition for the optimum selectivity towards 1-cyclohexylidene-2-propanone.
A more subtle mechanistic effects related to differential rates of enolization versus carbonyl oxygen protonation in each ketone seems to explain differences in their conversions and thus in influenced product distributions observed in the mixed aldol condensation.

4.4 Adsorption Studies

Liquid adsorption of acetone and cyclohexanone revealed no preferential adsorption on all the zeolites investigated.

The results of liquid phase adsorption measurements of ketones (acetone and cyclohexanone) revealed similar adsorption behavior on different zeolite materials and no correlation to results of the reaction work could be drawn. The product selectivity in the acid catalysed aldol condensation reaction was obviously not controlled by adsorption phenomena, as similar adsorption properties were obtained for the different ketone substrates. In order to explain the observed catalyst activity and selectivity, other factors such as intrinsic kinetics and sterical effects may explain the behavior.

4.5 Recommendations and Future Work

The main product obtained in this work, 1-cyclohexylidene-2-propanone does not have known industrial applications but it could be beneficial in the some mechanistic insights.

Separation of the liquid product from zeolite material after the reaction was simple. This meant that the zeolite could be regenerated to their active form to be used again.

The reactor set-up was simplified such that each separate experiment could be performed concurrently. The weakness in the present batch reactor set-up was no control in pressure. Again, due small reactor no sampling could be done during the run.

The weakness in the present study that the effect of surface active sites could not be separated from the ones in the zeolite pores, as this is important for shape selectivity.

To solve this problem, further work would involve the eliminating surface active sites of zeolites and this would eliminate its effects on these reactions. A decrease in overall reactant conversions would occur but selectivity will be improved, as mostly active sites in the pores would be involved.

In order to follow the mechanism towards main products observed, other methods like FT-IR, NMR could used to determine the interaction between reactant species and zeolites active sites.

References

References

Augustine, R. L., Posner, L. S. Shape Selective Liquid Phase Aldol Reactions Using Alkali Modified Zeolites. Catalysis of Organic Reactions. Scaros and Prunier, Editors. Marcel Dekker Inc. New York, 1995, 531-534.

Augustine, R. L., Heterogeneous Catalysis for the Synthetic Chemist. Marcel Dekker Inc. New York, p. 97 -100. 1996.

Baron, G. V., Denayer J. F., Bouyermaouen, A. Adsorption of Alkanes and Organic Molecules in Liquid Phase and in the Dense Vapor Phase: Influence of Polarity, Zeolite Topology and External Fluid Density and Pressure. Industrial Engineering Chemistry Research., **37**, 3691-3698, 1998.

Bell, V., Gold, H. Carbon-13 Nuclear Magnetic Resonance Studies of the Aldol Condensation Products of Acetone on an Activated Alumina Catalyst. Journal of Catalysis, **79**, 286-290, 1983.

Bhattacharya, D. and Sivasanker, S. A Comparison of Aromatization Activities of the Medium Pore Zeolites ZSM-5, ZSM-22, and EU-1. Journal of Catalysis, **153**, 353-355, 1995.

Bosacek, V., Kubelkova L. Interactions of Acetone with Skeletal Hydroxyls of Zeolites. Zeolites, **10**, 64 - 65, 1990.

Choudary B. M., Kantam, M. L., Sreekanth, P., Tuel, A. Figueras, F., Bandopadhyay, Y. Knoevenagel and Aldol Condensation Catalyzed by a New Diamino-functionalised Mesoporous Material, Journal of Molecular Catalysis A:Chemical, **142**, 361-365, 1998.

Corma, A., Garcia, H. Organic Reactions Catalyzed over Solid Acids, Catalysis Today, **38**, 257 - 308, 1997.

Di-Cosimo, I. J., Apesteguia, C. R. Study of the Catalyst Deactivation in the Base-Catalysed Oligomerization of Acetone, Journal of Molecular Catalysis A: Chemical, **130**, 177-185, 1998.

Efimova, G. A., Shutova, I. V., Shapiro, Y. E., Turov, B. S., Makarov, V. M., Efimov, V. A. Autocondensation of Cyclohexanone. Journal of Organic Chemistry (USSR - English Translation) EN, 25, 6. 1., 1081-1084, 1989.

Gates, C. G., 'Catalytic Chemistry'. John Wiley & Sons Inc. 1991

Fripiat, J. J., Panov, A.G., Acetone Condensation Reaction on Acid Catalysts. Journal of Catalysis, **178**, 188-197, 1998.

Flego, C., Perego, C. Acetone Condensation as a Model Reaction for the for the Catalytic Behavior of Acidic Molecular Sieves: A UV-Visible Study. Applied Catalysis A: General 192, 317 – 329, 2000.

Hagan, G. P., US Patent 4433174 (1984)

Haw, J. F., Munson, E. J., Xu, T. Towards a Systematic Chemistry of Organic Reactions in Zeolites: In Situ NMR Studies of Ketones. Journal of American Chemical Society, **116**, 1962-1972, 1994.

Haw, J. F., Xu, T, Goguen, P. W., Skloss, T. W., Song, W., Wang, Z. In Situ NMR Investigations of Heterogeneous Catalysis with Samples Prepared under Standard Reaction Conditions. Angewante Chemie. Int. Ed., 7, **37**, 948-949, 1998.

Hine, J. 'Physical Organic Chemistry', McGraw-Hill Book Company, 1956.

Hofmann, H., Niu, F. Activity and Deactivation Behavior of Various Zeolite Catalysts, Applied Catalysis A: General, **128**, 107-118, 1995.

Iglesia E, Barton, D. G., Biscardi, J. A., Gines, M. J. L., Soled, S. L. Bifunctional Pathways in Catalysis by Solid Acids and Bases. Catalysis Today, **38**, 339-360, 1997.

Ingold, C.K. Structure and Mechanism in Organic Chemistry, 2nd Edition, Cornell University Press, 1969.

Jacobs, P. A., Martens, J. A., Vervecken, M., Servotte, Y., Wydoodt, M. Zeolite Induced Selectivity in the Conversion of the Lower Aliphatic Carboxylic Acids. Chemical Reactions in Organic and Inorganic Constrained Systems. R. Setton (editor), 95 - 114, Reidel Publishing Company, 1986.

Jones, R. A. Y. Physical and Mechanistic Organic Chemistry, 2nd Edition, Cambridge University Press. Cambridge, 1987.

Kubelkova, L., Cejka J., Novakova, J. Surface Reactivity of ZSM-5 zeolites in Interaction with Ketones at Ambient Temperature (a FT-i.r. Study). Zeolites, **11**, 48-53, 1991.

Langhendries, G., De Vos, D. E., Baron, G. V., Jacobs, P. A. Quantitative Sorption Experiments on Ti-Zeolites and Relation with α-Olefin Oxidation by H_2O_2, Journal of Catalysis, **186**, 1999.

Leofanti, G., Tozzola, G., Padovan, M., Petrini, G., Bordiga, S., Zecchina, A. Catalyst Characterizations: Applications. Catalysts Today, **34**, 329 - 352, 1997.

Levenspiel, O. 'Chemical Reaction Engineering' 2nd edition, John Wiley & Sons, 1972.

Margheri G., Rosi, L., Salvini, A., Bianchi, M., Frediani, P. Oligomerization of Aldehydes Catalysed by Cobalt Carbonyl Complex. Journal of Molecular Catalysis A: Chemical, **132**, 189-201, 1998.

Martin-Luengo M. A., Yates, M. Review: Zeolitic Materials as Catalysts for Organic Synthesis. Journal of Material Science, **30**, 4483 - 4491, 1995.

Matsumoto, K., Acheson, R.M. (Editors). Organic Synthesis at High Pressures. John Wiley & Sons, New York, 1991.

Morrison, T. R., Boyd, N. R. 'Organic Chemistry', 4th edition, New York University Publishers, 1983.

Newman, M. S. (Editor). Steric Effects in Organic Chemistry. John Wiley & Sons, Inc. 1956.

Niu, F., Hofmann, H. Activity and Deactivation Behavior of Various Zeolite Catalysts. Applied Catalysis A: General, **128,** 107 -118, 1995.

Norman, R., Coxon, J. M. 'Principles Of Organic Synthesis', 3rd edtion, Blackie Academic & Professional, 1993.

Paulis, M., Martin, M., Soria, D. B., Diaz, A., Odriozola, J. A., Montez, M. Preparation and Characterization of Niobium Oxide for the Catalytic Aldol Condensation of Acetone, Applied Catalysis A: General, **180**, 411-420, 1999.

Pittman, C.U., LiangY. F., Sequential Catalytic Condensation-Hydrogenation of Ketones. Journal of Organic Chemistry, **45**, 5048-5052, 1980.

Reichle, W. T. Pulse Microreactor Examination of the Vapor Phase Aldol Condensation of Acetone. Journal of Catalysis, **63**, 295 - 306, 1980.

Ruthven, M. D., Ching, C. B., A Liquid Phase Chromatography Study of Sorption and Diffusion of Glucose and Fructose in NaX KX Zeolites Crystals, Zeolites, **8**, 68-73, 1988.

Ruthven, M. D., Narayan, S., Awum, F. Measurement of Intracrystalline Diffusion in NaX Zeolites by Liquid Chromatography. Ind. Eng. Chem. Res., **27**, 1510-1515, 1988.

Saha, B., Streat, M. Cation Exchange Resin-catalysed Esterification of Acetic Acid with 2-(1-cyclohexenyl)cyclohexanone. Catalysis Letters, **51**, 121-127, 1998.

Sepa, J., Gorte, L. R., White, D., Kassab, E, Evleth, E. M., Jessri, H., Allavena, M. Carbonyl ^{13}C Shielding Tensors and Heats of Adsorption of Acetone Adsorbed in Silicalite and the 1:1 Stoichiometric Complex in H-ZSM-5. Journal of Physical Chemistry, **100**, 18515-18523, 1996.

Sepa, J., Gorte, L. R., Biaglow, A. I., White, D. A ^{13}C NMR Study of the Condensation Chemistry of Acetone and Acetaldehyde Adsorbed at the Bronsted Acid Sites in H-ZSM-5. Journal of Catalysis, **151**, 373 - 384, 1995.

Tencer, Y. Michman, M., Goldenfeld, I. Catalysis by Cobalt Compounds of Aldol and Retro-Aldol Reactions. Journal of Organometallic Chemistry, **412**, 203 - 214, 1991.

Tichit, D., Naciri Bennani, M., Figueras, F., Tessier, R., Kervennal, J. Aldol Condensation of Acetone over Layered Double Hydroxides of the Meixnerite Type, Applied Clay Science, **13**, 401 – 415, 1998.

van Bekkum, H., Kunkeler, P.J., Moeskops, D. Zeolite Beta: characterization and passivation of the external surface acidity. Microporous Materials, **11**, 313-323, 1997.

van Bekkum, H., Flanigen, E. M., Jansen J. C. (editors). Studies in Surface Science and Catalysis: Introduction to Zeolite Science and Practice, vol. 58, Elsevier Science Publishing Co., New York, p531-570, 1991

Weitkamp, J., Knözinger, H., and Ertl G. (Editors). Handbook of Heterogeneous Catalysis. Volume 2, 1997, VCH Verlagsgesellschaft mbH, Germany.

Appendices

APPENDIX I

Calculation of Response Factors

The response factors for each compound was determined using a group contribution method.

The method assumes the following contribution for each group. It is defined by the following expression;

$$RF = \frac{\text{no. of C} - \text{atoms in compound}}{\text{Sum of contribution of each group}}$$

Listed below is the contribution for each group.

Group	Contribution
CH_3 -	1.0
CH_2 -	1.0
CHO	0
CH	1.0
C=O	0
COH	0.55
C-O-	0.55

Using the above contributions, the response factors were calculated as follows

Acetone	C_3H_6O
Cyclohexanone	C_5H_8O
Cyclopentanone	$C_6H_{10}O$
Benzaldehyde	C_6H_7O
Toluene	C_7H_8

Toluene was used as an internal standard and all the balances were relative to the moles of toluene

All response factors were calculated using internal standard method as follows;

$$RF = \frac{Area_{(internal\ standard)}}{Area_{(componet1)}} x \frac{n_{(component\ 1)}}{n_{(internal\ standard)}}$$

$$Yield = \frac{mmoles\ of\ product\ (n_1)}{total\ mmoles\ of\ reactant}$$

$$Conersion = \sum Yield$$

$$Selectivity = \frac{Yield}{Conversion}$$

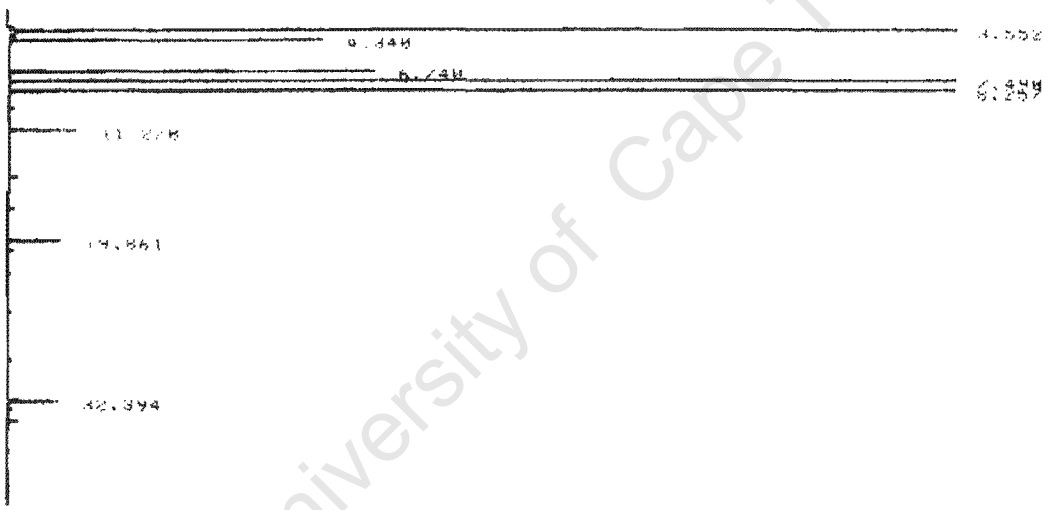
$$Product\ Selectivity = \frac{mmoles\ of\ product\ (n_1)}{total\ mmoles\ of\ all\ products}$$

Appendix II GC Temperature Programs and Chromatograms

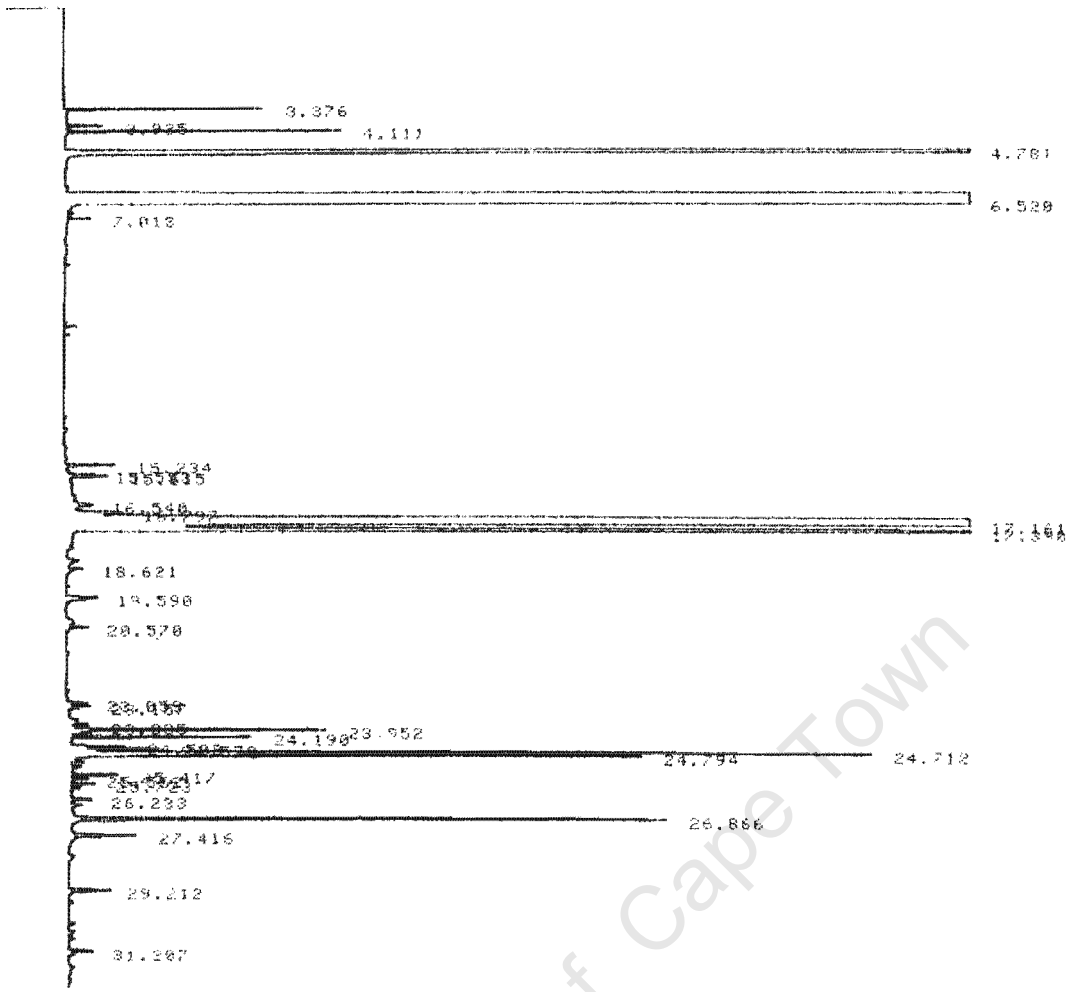
A: Temperature Programs

One GC program was used for the analysis of the reaction products from the aldol condensation reactions.

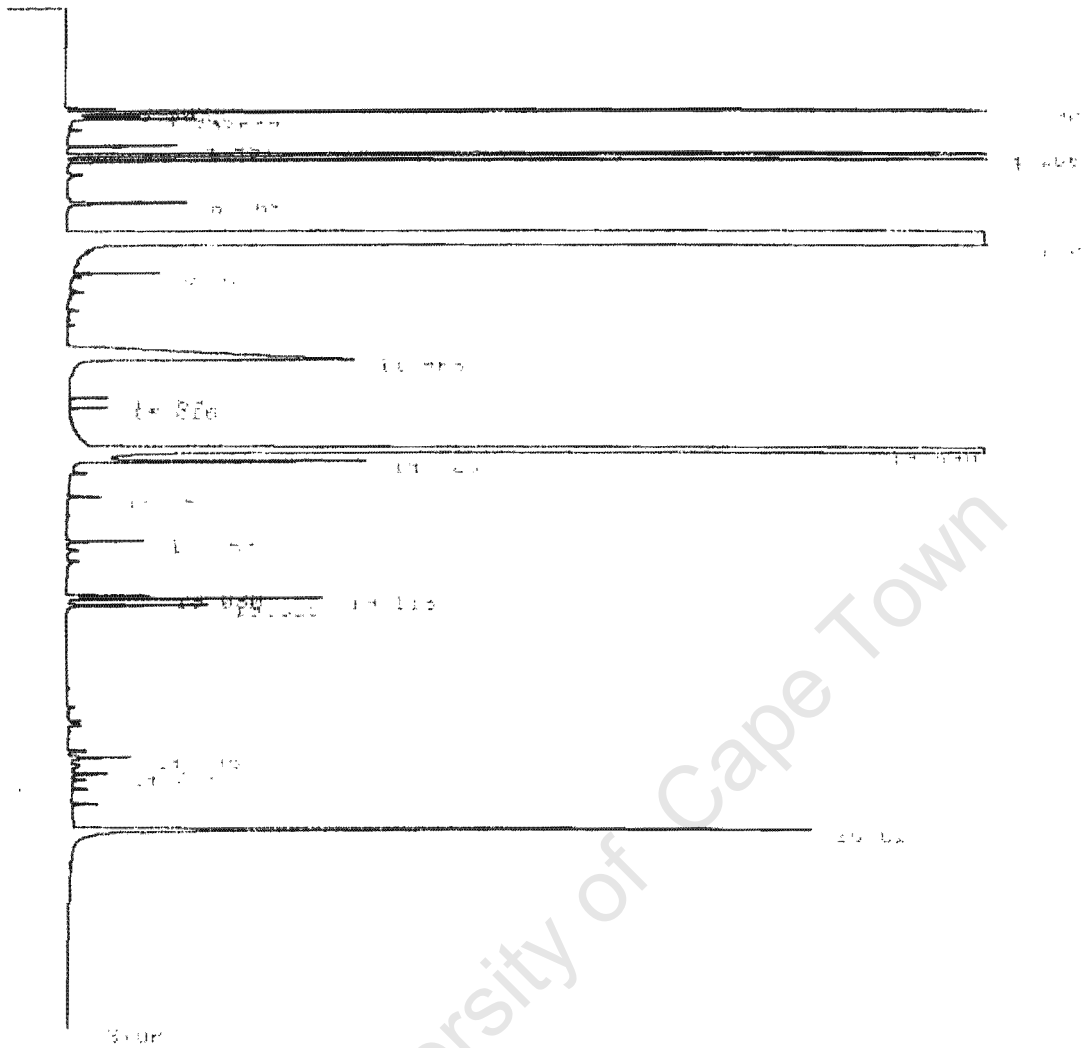
Self-condensation of acetone



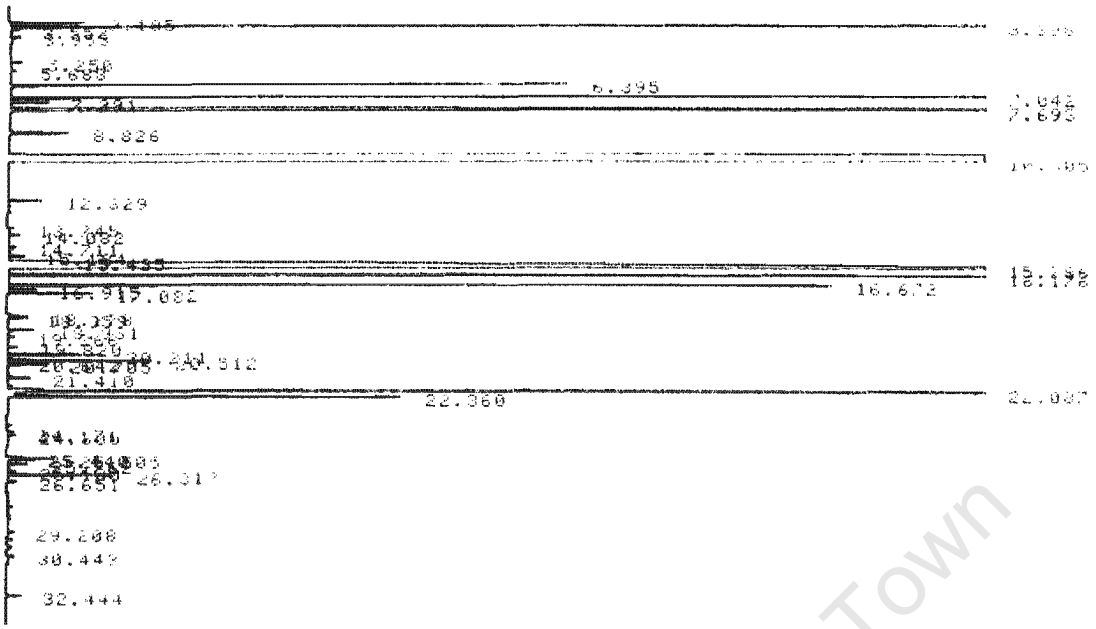
Self-condensation of cyclohexanone



Cross-condensation of Acetone + Benzaldehyde



Mixed aldol condensation of acetone and cyclohexanone



APPENDIX III

List of all Aldol Condensation Experiments

Experiment #	Volume of Acetone (ml)	Vol. of Cyclohehexanone (ml)	Vol. of Benzaldehyde (ml)	Catalyst (0.15g)	Temperature (^{0} C)	Time (Hrs)
1	6	0	0	HZSM-5(Si/A:45)	170^{0}C	1,5,10,24
2	6	0	0	H-Beta	170^{0}C	1,5,10,24
3	6	0	0	H-USY	170^{0}C	1,5,10,24
4	6	0	0	HZSM-5(Si/A:45)	100^{0}C	1,5,10,24
5	6	0	0	HZSM-5(Si/A:45)	140^{0}C	1,5,10,24
6	0	6	0	HZSM-5(Si/A:45)	170^{0}C	1,5,10,24
7	0	6	0	H-Beta	170^{0}C	1,5,10,24
8	0	6	0	H-USY	170^{0}C	1,5,10,24
9	0	6	0	H-ZSM-5(Si/Al:13)	170^{0}C	5
10	0	6	0	H-ZSM-5(Si/Al:22)	170^{0}C	5
11	0	6	0	H-ZSM-5(Si/Al:45)	170^{0}C	5
12	0	6	0	H-ZSM-5(Si/Al:45)	100^{0}C	1,5,10,24
13	0	6	0	H-ZSM-5(Si/Al:45)	140^{0}C	1,5,10,24
14	0	6	0	H-ZSM-5(Si/Al:45)	170^{0}C	1,5,10,24
15	2.5	3.5	0	H-ZSM-5(Si/Al:45)	170^{0}C	1,5,10,24,48
16	1.2	4.6	0	H-ZSM-5(Si/Al:45)	170^{0}C	1,5,10,24
17	4.3	1.8	0	H-ZSM-5(Si/Al:45)	170^{0}C	1,5,10,24,48
18	4.3	1.8	0	H-ZSM-5(Si/Al:22)	170^{0}C	5
19	4.3	1.8	0	H-USY	170^{0}C	5
20	4.3	1.8	0	H-Beta	170^{0}C	5
21	40	58	0	H-ZSM-5 (Si/Al:22)	150^{0}C	1,5,10,24,48, 72
22	40	58	0	H-ZSM-5 (Si/Al:22)	150^{0}C	1,5,10,24,48, 72
23	40	0	58	H-ZSM-5 (Si/Al: 45)	150^{0}C	1,5,10,24,48
24	6	0	0	H_2SO_4	140^{0}C	1,5,10,24

APPENDIX IV-A Self-Condensation of Acetone (Various Zeolites)

Reaction Mixture	HZSM-5(Si/Al:45), 170degC				H-Beta,170degC				H-USY, 170degC			
Volume (ml)	6	6	6	6	6	6	6	6	6	6	6	6
Acetone (g)	4.8	4.7	4.7	4.8	4.7	4.7	4.7	4.8	4.7	4.7	4.8	4.7
Toluene (g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Acetone (ml)	6.0	6.0	6.0	6.1	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Toluene (ml)	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.3
Acetone (mmol)	81.9	81.6	81.2	82.8	81.6	81.4	81.2	81.9	81.0	81.2	81.9	81.2
Toluene (mmol)	2.2	2.2	2.3	2.2	2.4	2.2	2.2	2.3	2.2	2.2	2.3	2.6
Quantity	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g	0.15g
Reaction Time(hrs)	1	5	10	24	1	5	10	24	1	5	10	24
Area's												
Acetone	84.4	86.6	86.6	81.4	83.8	76.4	77.7	80.0	87.4	83.0	83.4	79.0
Toluene	9.9	8.1	8.2	10.2	7.5	8.1	9.2	8.1	8.6	10.7	8.4	9.4
b-MO	0.5	0.5	0.4	0.8	0.7	0.7	0.7	0.6	0.4	0.4	0.6	0.7
a-MO	4.3	3.9	3.5	5.9	5.8	5.2	5.8	3.9	2.5	3.5	4.7	5.1
Phorone	0.0	0.1	0.0	0.1	0.1	0.7	0.4	0.5	0.2	0.3	0.2	0.5
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.2	0.4	0.7	0.4	0.6	1.8	2.0	2.4	0.5	0.5	1.4	2.6
1-(2-butenyl)-2,3-dimethyl-benzene	0.0	0.0	0.0	0.0	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1
mmoles												
Acetone	64.7	81.7	84.0	60.4	93.5	72.2	64.1	79.2	77.2	59.2	79.1	76.4
Toluene	2.2	2.2	2.3	2.2	2.4	2.2	2.2	2.3	2.2	2.2	2.3	2.6
b-MO	0.2	0.2	0.2	0.2	0.3	0.3	0.2	0.2	0.1	0.1	0.2	0.3
a-MO	1.3	1.5	1.4	1.7	2.6	2.0	1.9	1.5	0.9	1.0	1.8	2.0
Phorone	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.1	0.1	0.1
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.0	0.1	0.2	0.1	0.2	0.4	0.4	0.5	0.1	0.1	0.3	0.6
1-(2-butenyl)-2,3-dimethyl-benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Yields / conversion (mol%)												
Conversion (from products and Acet	1.9	2.2	2.1	2.5	3.8	3.4	3.2	3.0	1.4	1.6	2.9	3.6
b-MO	0.2	0.2	0.2	0.3	0.4	0.3	0.3	0.3	0.2	0.1	0.3	0.3
a-MO	1.6	1.8	1.7	2.1	3.1	2.4	2.3	1.9	1.1	1.2	2.2	2.4
Phorone	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.2	0.1	0.1	0.1	0.1
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.0	0.1	0.2	0.1	0.2	0.5	0.5	0.6	0.1	0.1	0.4	0.7
1-(2-butenyl)-2,3-dimethyl-benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Selectivity(mol%)												
b-MO	10.5	10.5	10.1	11.1	10.5	9.5	8.9	9.6	10.7	8.7	9.3	8.6
a-MO	86.8	83.6	80.3	84.0	82.9	70.5	72.6	62.7	77.0	79.0	75.0	67.2
Phorone	0.3	0.9	0.2	1.3	1.2	5.6	3.5	5.1	3.8	4.2	2.4	3.9
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	2.3	4.9	9.3	3.5	5.1	13.5	14.1	21.1	7.6	6.9	12.9	19.5
1-(2-butenyl)-2,3-dimethyl-benzene	0.1	0.1	0.1	0.2	0.3	0.9	1.0	1.4	0.9	1.3	0.4	0.7

Reaction Mixture	HZSM-5(Si/Al:45) - 170				HZSM-5(Si/Al:45) - 140				HZSM-5(Si/Al:45) - 100			
Total Volume (ml)	6	6	6	6	6	6	6	6	6	6	6	6
Acetone (g)	4.8	4.7	4.7	4.8	4.71	4.71	4.71	4.71	4.71	4.71	4.71	4.71
Toluene (g)	0.2	0.2	0.2	0.2	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
Acetone (ml)	6.0	6.0	6.0	6.1	6	6	6	6	6	6	6	6
Toluene (ml)	0.2	0.2	0.2	0.2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Acetone (mmol)	81.9	81.6	81.2	82.8	81.3	81.3	81.3	81.3	81.3	81.3	81.3	81.3
Toluene (mmol)	2.2	2.2	2.3	2.2	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
Quantity	0.15g	0.15g	0.15g	0.15g	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Time(hrs)	1.0	5.0	10.0	24.0	1	5	10	24	1	5	10	24
Area's												
Acetone	84.4	86.6	86.6	81.4	77.4	75.0	76.7	75.3	79.9	77.0	75.8	76.4
Toluene	9.9	8.1	8.2	10.2	18.4	18.6	16.7	18.0	16.5	17.3	17.8	16.7
b-MO	0.5	0.5	0.4	0.8	0.5	0.6	1.7	0.9	0.7	0.7	1.1	0.3
a-MO	4.3	3.9	3.5	5.9	3.4	5.4	4.3	5.0	2.1	3.4	4.5	5.5
Phorone	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.2	0.4	0.7	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
mmoles												
Acetone	64.7	81.7	84.0	60.4	69.2	66.4	75.9	68.9	80.1	73.6	70.3	75.4
Toluene	2.2	2.2	2.3	2.2	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
b-MO	0.2	0.2	0.2	0.2	0.2	0.2	0.7	0.3	0.3	0.3	0.4	0.1
a-MO	1.3	1.5	1.4	1.7	1.2	1.9	1.7	1.8	0.9	1.3	1.7	2.2
Phorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.0	0.1	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Conversion (%)	1.9	2.2	2.1	2.5	1.7	2.6	2.9	2.6	1.4	1.9	2.6	2.8
Yield (mol%)												
b-MO	0.2	0.2	0.2	0.3	0.2	0.2	0.8	0.4	0.3	0.3	0.5	0.1
a-MO	1.6	1.8	1.7	2.1	1.5	2.4	2.1	2.2	1.1	1.6	2.1	2.7
Phorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	0.0	0.1	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Selectivity(%)												
b-MO	10.5	10.5	10.1	11.1	12.4	9.4	28.2	15.3	24.6	17.6	19.6	4.8
a-MO	86.8	83.6	80.3	84.0	87.6	90.6	71.8	84.7	75.4	82.4	80.4	95.2
Phorone	0.3	0.9	0.2	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isophorone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mesitylene	2.3	4.9	9.3	3.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX IV-B Self-Condensation of Cyclohexanone

	HZSM5(Si/Al:45),					HZSM5(Si/Al:45),				HZSM5(Si/Al:45),			
Reaction Mixture	**170Deg C**					**140Deg C**				**100Deg C**			
Volume(ml)	6	6	6	6	6	6	6	6	6	6	6	6	6
Cyclohexanone(g)	5.67	5.71	5.75	5.71	5.72	5.76	5.65	5.71	5.7	5.71	5.78	5.7	5.71
Toluene(g)	0.52	0.52	0.51	0.54	0.52	0.52	0.5	0.72	0.5	0.51	0.51	0.5	0.52
Cyclohexanone(ml)	5.99	6.03	6.07	6.03	6.04	6.08	5.97	6.03	6.02	6.03	6.10	6.02	6.03
Toluene(ml)	0.60	0.60	0.59	0.62	0.60	0.60	0.58	0.83	0.58	0.59	0.59	0.58	0.60
Cyclohexanone(mmol)	57.86	58.27	58.67	58.27	58.37	58.78	57.65	58.27	58.16	58.27	58.98	58.16	58.27
Toluene(mmol)	5.65	5.65	5.54	5.87	5.65	5.65	5.43	7.83	5.43	5.54	5.54	5.43	5.65
Amount Catalyst(g)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Reaction Time (Hrs)	**1**	**5**	**10**	**24**	**48**	**1**	**5**	**10**	**24**	**1**	**5**	**10**	**24**
Area's													
Cyclohexanone	77.5	69.4	62.8	48.6	34.2	83.5	82.7	72.6	72.5	86.1	86.8	85.4	84.17
Toluene	13.5	11.2	10.5	11.2	11	13.3	13.8	13.2	7.83	13.3	12.5	12.66	13.33
2-CC	5.24	16.1	21.9	31.6	40.2	0.88	2.72	12.7	15.8	0.1	0.32	0.664	1.97
2-CCi	0.51	2.23	2.95	4.4	5.64	0.21	0.47	0.97	1.86	0.03	0.13	0.212	0.242
2,5-Di-CC	0.55	0.33	0.6	0.92	3.52	0	0.03	0.06	0.15	0.03	0.02	0.082	0
	0.73	0.2	0.61	0.66	1.48	0	0	0.02	0.07	0.02	0.03	0.076	0
Mmoles													
Cyclohexanone	45.5	48.9	46.4	35.6	24.6	49.7	45.4	60.2	70.4	50.3	53.8	51.33	49.97
Toluene	5.65	5.65	5.54	5.87	5.65	5.65	5.43	7.83	5.43	5.54	5.54	5.43	5.65
2-CC	1.40	5.14	7.36	10.52	13.17	0.24	0.68	4.77	6.99	0.03	0.09	0.18	0.53
2-CCi	0.14	0.71	0.99	1.47	1.85	0.06	0.12	0.36	0.82	0.01	0.04	0.06	0.07
2,5-Di-CC	0.09	0.07	0.13	0.20	0.75	0.00	0.00	0.01	0.04	0.01	0.00	0.01	0.00
Aromatic	0.13	0.04	0.13	0.14	0.31	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00
Conversion(%)	3.04	10.24	14.67	21.15	27.54	0.50	1.39	8.85	13.53	0.07	0.23	0.46	1.02
% Yields													
2-CC	2.42	8.82	12.54	18.05	22.56	0.41	1.18	8.19	12.01	0.04	0.15	0.31	0.91
2-CCi	0.24	1.23	1.69	2.52	3.16	0.10	0.20	0.63	1.41	0.01	0.06	0.10	0.11
2,5-Di-CC	0.16	0.12	0.22	0.34	1.28	0.00	0.01	0.02	0.07	0.01	0.01	0.02	0.00
Aromatic	0.22	0.07	0.22	0.24	0.54	0.00	0.00	0.01	0.03	0.01	0.01	0.02	0.00
% Selectvity													
2-CC	79.65	86.19	85.48	85.36	81.94	80.44	84.78	92.59	88.78	61.54	66.18	67.88	89.06
2-CCi	7.81	11.98	11.49	11.89	11.48	19.56	14.65	7.06	10.44	15.70	27.86	21.67	10.94
2,5-Di-CC	5.36	1.13	1.50	1.60	4.64	0.00	0.56	0.26	0.53	13.82	2.44	5.42	0.00
Aromatic	7.18	0.71	1.53	1.15	1.94	0.00	0.00	0.09	0.25	8.94	3.52	5.03	0.00

2-CC	2-cyclohexylidene - cyclohexanone
2-CCi	2-cyclohexylidene-cyclohexanone(isomer)
2,5-Di-CC	2,5-dicyclohexylidene-cyclohexanone

APPENDIX IV-C Self-Condensation of Cyclohexanone using Different Zeolites

	HZSM5(Si/Al:45),					H-Beta, 170degC				H-USY, 170degC			
Reaction Mixture	**170Deg C**												
Volume(ml)	6	6	6	6	6	6	6	6	6	6	6	6	6
Cyclohexanone(g)	5.67	5.71	5.75	5.71	5.72	5.69	5.83	5.64	5.67	5.78	5.78	5.71	5.72
Toluene(g)	0.52	0.52	0.51	0.54	0.52	0.51	0.52	0.52	0.52	0.51	0.54	0.51	1.11
Cyclohexanone(ml)	5.99	6.03	6.07	6.03	6.04	6.008	6.16	5.96	5.987	6.103	6.103	6.03	6.04
Toluene(ml)	0.60	0.60	0.59	0.62	0.60	0.588	0.6	0.6	0.6	0.588	0.623	0.588	1.28
Cyclohexanone(mmo	57.86	58.27	58.67	58.27	58.37	58.06	59.5	57.6	57.86	58.98	58.98	58.27	58.37
Toluene(mmol)	5.65	5.65	5.54	5.87	5.65	5.543	5.65	5.65	5.652	5.543	5.87	5.543	12.07
Amount Catalyst(g)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Reaction Time (Hrs)	**1**	**5**	**10**	**24**	**48**	**1**	**5**	**10**	**24**	**1**	**5**	**10**	**24**
Area's													
Cyclohexanone	77.52	69.4	62.79	48.6	34.2	55.93	35.2	45.6	30.62	69.43	57.43	40.48	34.92
Toluene	13.47	11.23	10.51	11.2	11	15.02	13	10.4	11.2	9.87	10.35	8.19	11.65
2-CC	5.24	16.05	21.92	31.6	40.2	25.16	35.3	40.3	52.08	20.08	29.49	48.63	30.97
2-CCi	0.514	2.23	2.945	4.4	5.64	2.605	13.7	1.56	0	0	0	0	15.87
2,5-Di-CC	0.545	0.325	0.595	0.92	3.52	0	0.56	0.11	1.2	0.04	0.262	0.241	0.069
	0.73	0.203	0.605	0.66	1.48	0.162	0.34	0.58	1.25	0.041	0.589	0.689	0.053
Mmoles													
Cyclohexanone	45.54	48.9	46.38	35.6	24.6	28.9	21.4	34.7	21.63	54.59	45.6	38.36	50.63
Toluene	5.65	5.65	5.54	5.87	5.65	5.54	5.65	5.65	5.65	5.54	5.87	5.54	12.07
2-CC	1.40	5.14	7.36	10.52	13.17	5.91	9.78	13.93	16.73	7.18	10.64	20.95	20.41
2-CCi	0.14	0.71	0.99	1.47	1.85	0.61	3.78	0.54	0.00	0.00	0.09	0.00	10.46
2,5-Di-CC	0.09	0.07	0.13	0.20	0.75	0.00	0.10	0.02	0.25	0.01	0.06	0.07	0.03
Aromatic	0.13	0.04	0.13	0.14	0.31	0.02	0.06	0.13	0.26	0.01	0.14	0.19	0.02
Conversion(%)	3.04	10.24	14.67	21.15	27.54	11.27	23.06	25.42	29.79	12.20	18.54	36.39	52.98
% Yields													
2-CC	2.42	8.82	12.54	18.05	22.56	10.18	16.43	24.21	28.91	12.17	18.04	35.95	34.97
2-CCi	0.24	1.23	1.69	2.52	3.16	1.05	6.36	0.94	0.00	0.00	0.16	0.00	17.92
2,5-Di-CC	0.16	0.12	0.22	0.34	1.28	0.00	0.17	0.04	0.43	0.02	0.10	0.12	0.05
Aromatic	0.22	0.07	0.22	0.24	0.54	0.04	0.10	0.23	0.45	0.02	0.23	0.33	0.04
% Selectvity													
2-CC	79.65	86.19	85.48	85.36	81.94	90.28	71.26	95.25	97.05	99.74	97.32	98.78	66.01
2-CCi	7.81	11.98	11.49	11.89	11.48	9.35	27.57	3.69	0.00	0.00	0.86	0.00	33.82
2,5-Di-CC	5.36	1.13	1.50	1.60	4.64	0.00	0.73	0.16	1.45	0.13	0.56	0.32	0.10
Aromatic	7.18	0.71	1.53	1.15	1.94	0.38	0.44	0.89	1.51	0.13	1.26	0.91	0.07

APPENDIX IV-D Cross-Aldol Condensation of Acetone and Benzaldehyde

Reaction Mixture						
Acetone (g)	30	32	31	30	30	30
Toluene (g)	1	1	1	1	1	1
Benzaldehyde(g)	61	59	62	63	61	63
Acetone (ml)	38	41	40	38	39	39
Toluene (ml)	1	1	1	1	1	1
Benzaldehyde(ml)	58	57	59	61	58	60
Acetone (mmol)	513	554	541	518	524	524
Toluene (mmol)	12	11	12	11	11	11
Benzaldehyde(mmol)	571	559	583	595	575	590
Quantity	2.5g	2.5g	2.5g	2.5g	2.5g	2.5g
Time(Hours)	1	6	10	24	48	72

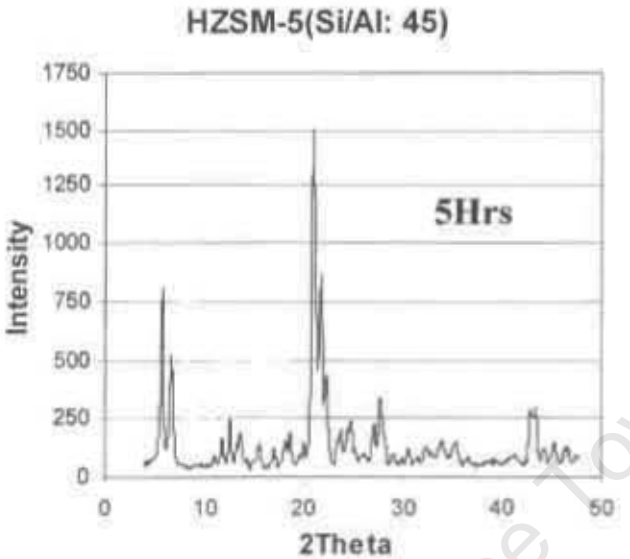
MMOLES						
Acetone	391	393.7	360.6	395.5	253	276.9
b-MO	1.47	1.665	1.45	2.618	0.89	0.799
Toluene	11.6	10.87	11.62	11.01	11	10.96
a-MO	17.3	19.69	17.37	16.84	11	9.948
Benzaldehyde	583	545.4	548.7	621.8	469	400.3
Benzoic Acid	0	0.82	2.045	3.139	2.66	2.051
Benzalacetone	19.5	36.36	46.95	78.41	85.4	88.61
1,3-Diphenyl-2-propen-1-one	0	0.34	0.415	0.532	0.36	0.22
Dibenzalacetone	0.2	1.335	2.888	4.674	8.31	10.87

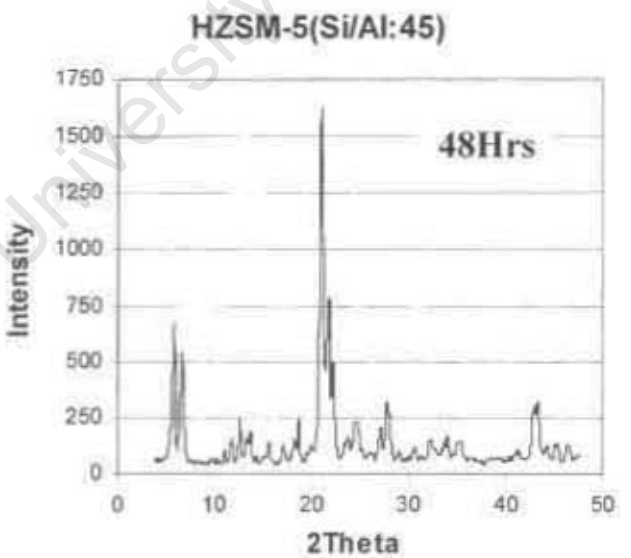
AREA'S						
Acetone	16.7	16.9	15.2	13.9	11.2	13.2
b-MO	0.2	0.2	0.2	0.2	0.1	0.1
Toluene	1.7	1.6	1.7	1.4	1.7	1.8
a-MO	1.9	2.1	1.8	1.5	1.2	1.2
Benzaldehyde	74.9	70.1	69.2	65.6	62.2	57.1
Benzoic Acid		0.1	0.2	0.3	0.3	0.2
Benzalacetone	3.8	7.0	8.9	12.4	17.0	19.0
1,3-Diphenyl-2-propen-1-one		0.1	0.1	0.1	0.1	0.1
Dibenzalacetone	0.1	0.5	1.0	1.3	2.9	4.1
Total Areas	99.2	98.6	98.2	96.6	96.7	96.8

Selectivity based on Acetone (mol%)						
b-MO	3.8	2.8	2.0	2.5	0.8	0.7
a-MO	45.1	32.7	24.4	15.9	10.2	8.8
Benzoic Acid	0.0	1.4	2.9	3.0	2.5	1.8
Benzalacetone	50.6	60.4	66.0	73.8	78.6	78.8
1,3-Diphenyl-2-propen-1-one	0.0	0.6	0.6	0.5	0.3	0.2
Dibenzalacetone	0.5	2.2	4.1	4.4	7.6	9.7

Yields / conversion (mol%)						
Conversion Acetone	7.49	10.9	13.14	20.5	20.8	21.5
Conversion Benzaldehyde	3.44	6.95	8.972	14.6	16.6	17.3

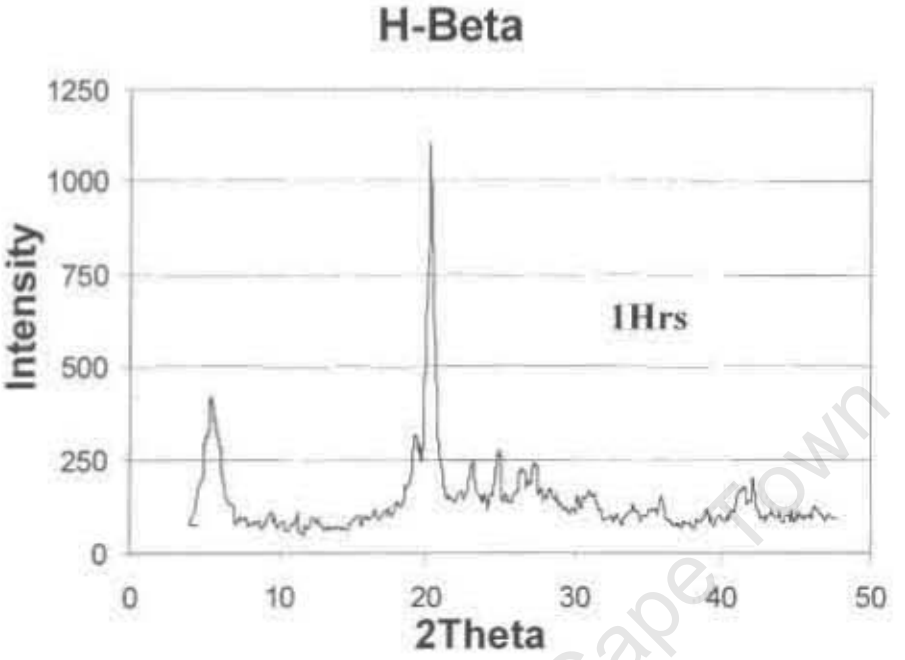
APPENDIX V X-Ray Diffractograms

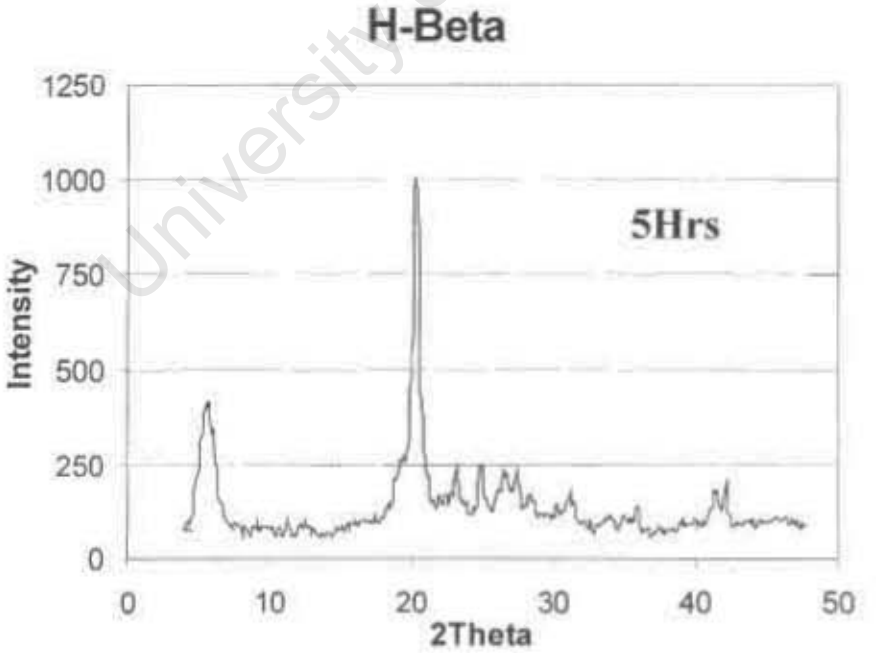




XRD of HZM-5 from the acetone and benzaldehyde reactions after designated reaction times

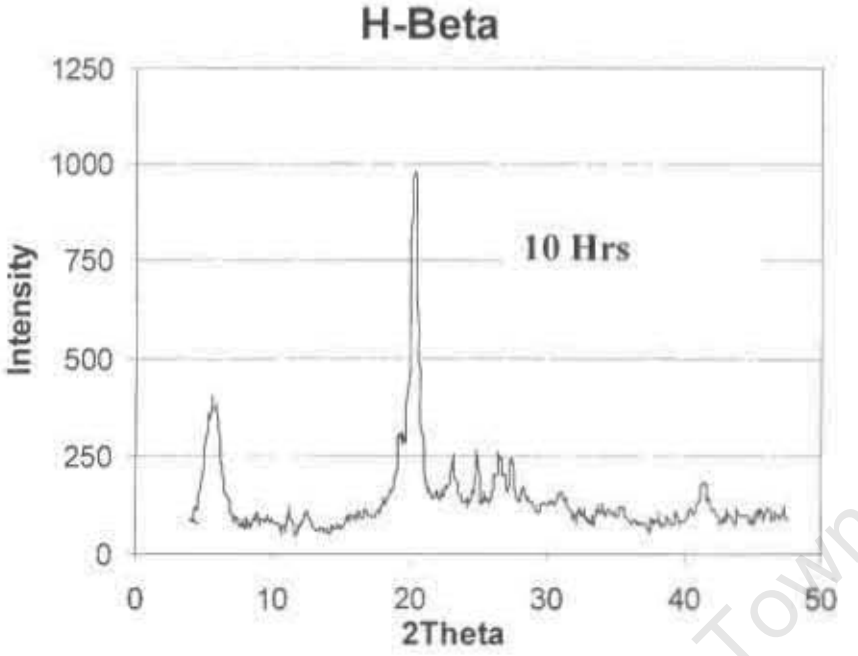
Appendix V (*continued*)

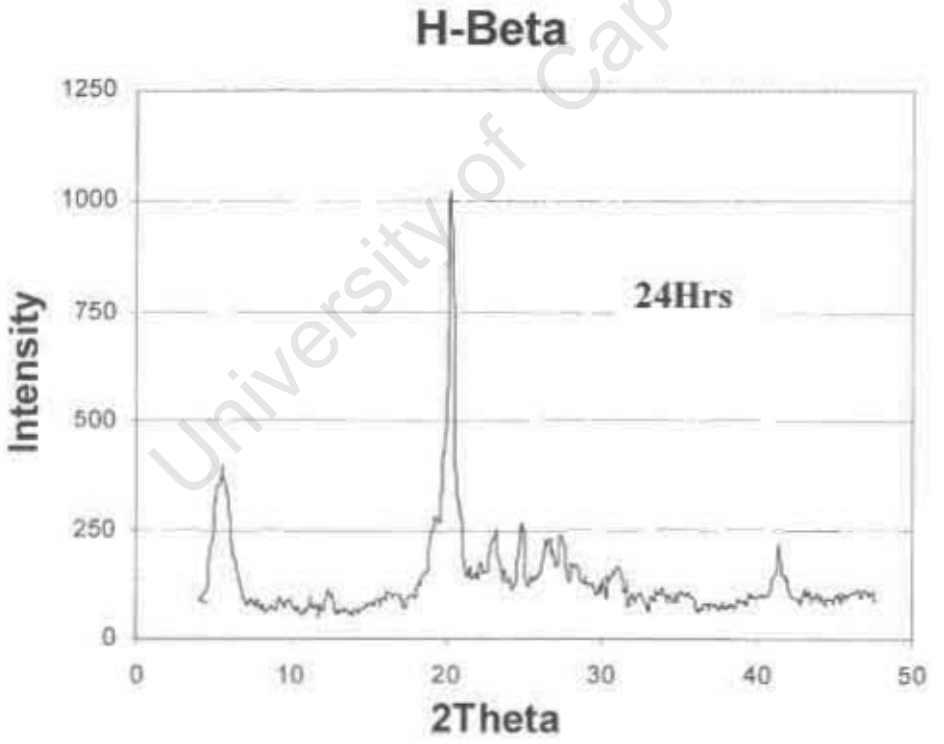




XRD's of H-Beta from the self -condensation reaction of acetone

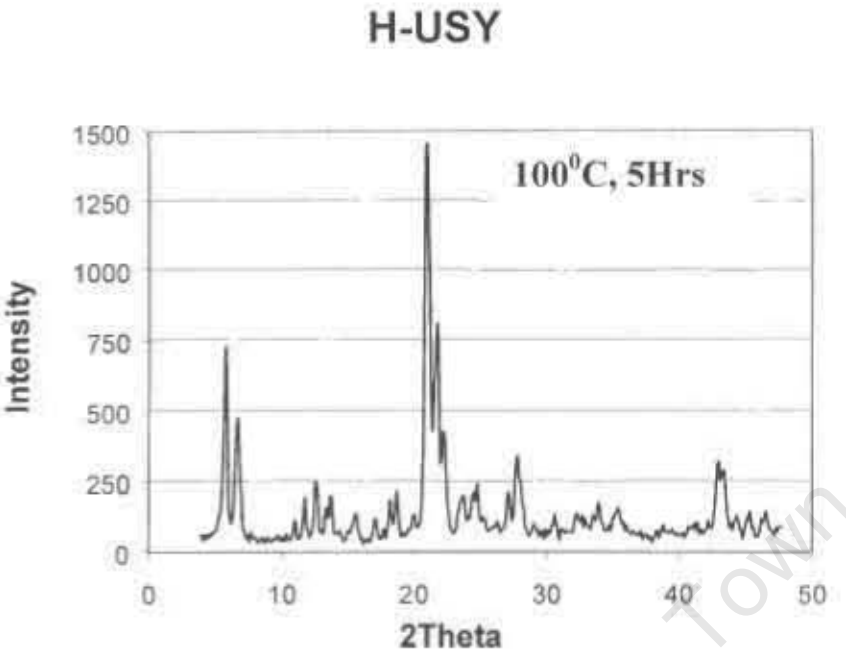
Appendix V ***(continued)***

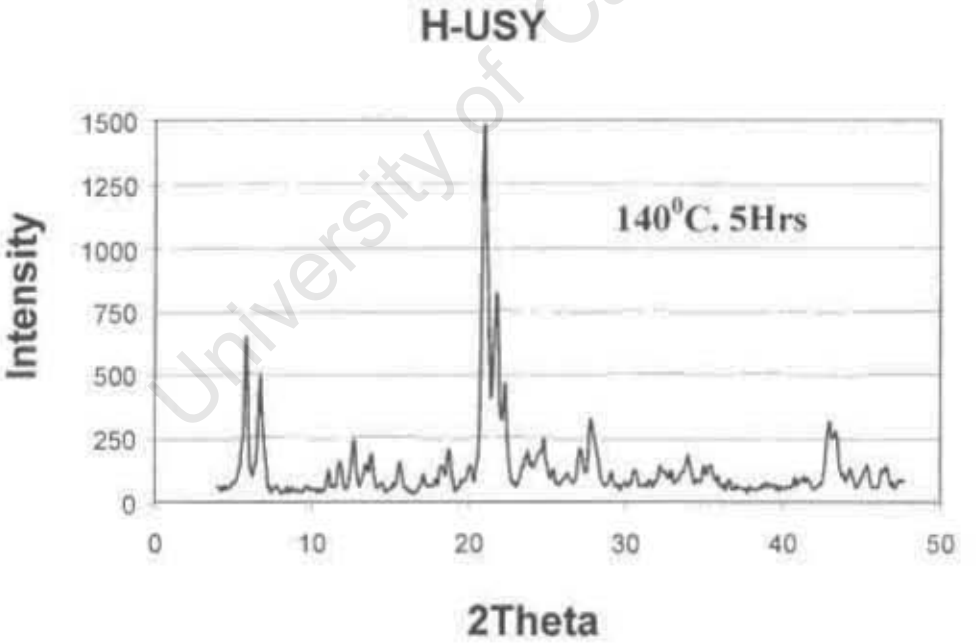




XRD's of H-Beta from the self -condensation reaction of acetone

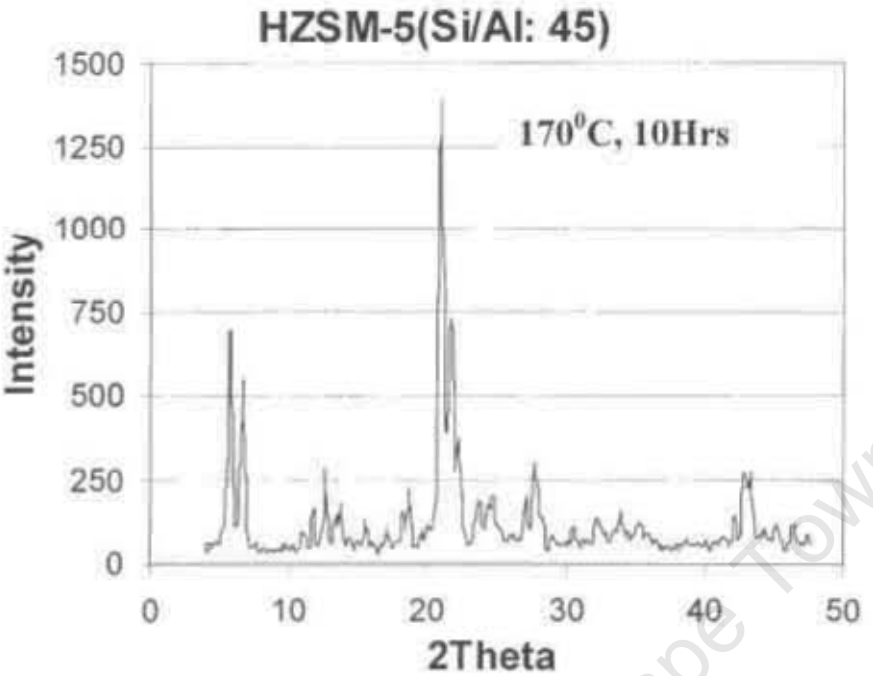
APPENDIX V *(contnued)*

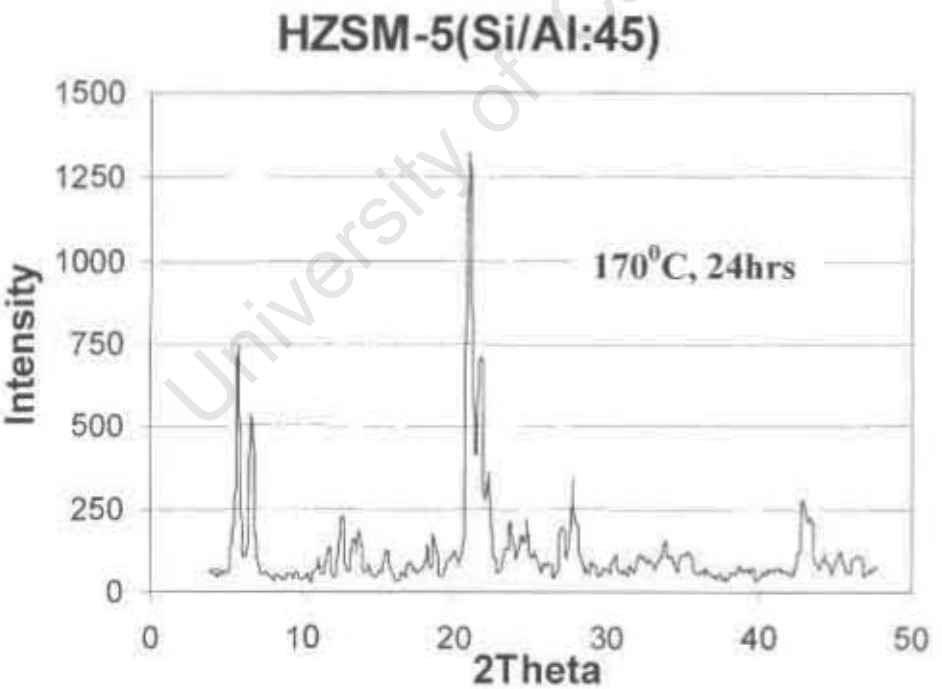




XRD's of H-USY from the self -condensation reaction of cyclohexanone

Appendix V (*continued*)

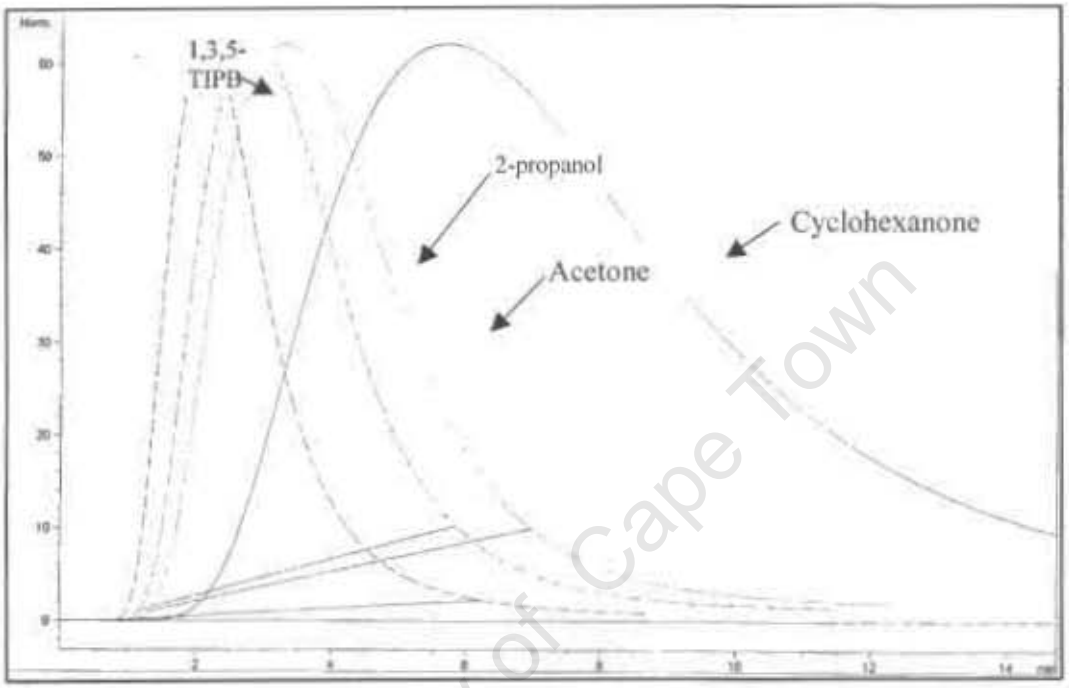




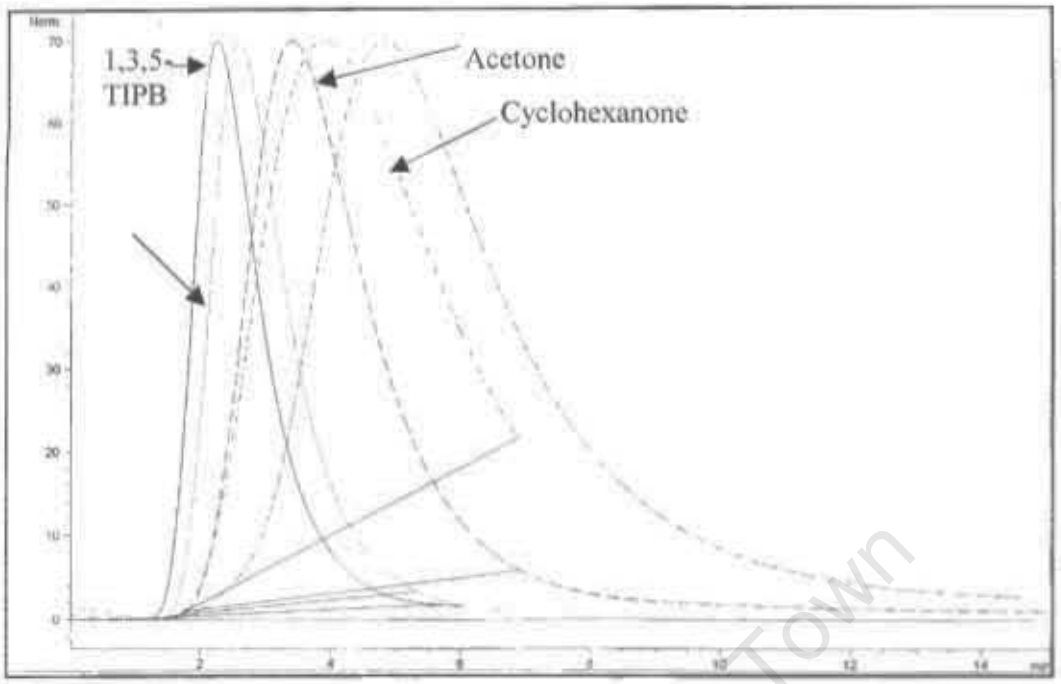
XRD's of HZSM-5 (Si/Al: 45) from the mixed aldol condensation of acetone and cyclohexanone

APPENDIX VI Diffractograms of HPLC Measurements Using Columns of Different Zeolites

H-Beta



HZSM-5 (Si/Al: 45)



H-USY