OLIGOMERIZATION OF PENTENES BY ACID ZEOLITES

by

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ABSTRACT OF THESIS

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Crude oil refining produces numerous light hydrocarbons (alkanes and alkenes). Of these, C_2-C_4 hydrocarbons are commercially important precursors for synthetic rubber, polymers and other chemical products. C_5 hydrocarbons are unwanted by-products; they are not suitable as liquid or gaseous fuels, leading to difficulty regarding storage and handling. The present work is based on an idea to convert C_5 hydrocarbons to fuels via dehydrogenation of C_5 alkanes, oligomerization of C_5 olefins to C_{10} and C_{15} alkenes, and further hydrogenation to fuel-grade medium molecular weight hydrocarbons. We have devised a synthesis strategy to transform the light olefins to more valuable decenes (C_{10} olefins), which can be used as gasoline alternatives. This transformation is termed as the oligomerization of pentene by the catalysts acid-form zeolites. Zeolites are popular catalysts for a variety of heterogeneous catalytic reactions in research as well as in the industry. The oligomerization of pentene was investigated over ZSM-5 (MFI), Beta (BEA*), Mordenite (MOR), Ferrierite (FER) and Faujasite (FAU). The primary aim is to

achieve high activity and selectivity for oligomerization over cracking of pentenes and decenes. The effect of zeolite pretreatment, substrate concentration, reaction temperature on yield and selectivity of decenes was studied. FAU showed a promising high selectivity, so the Si/Al ratio of FAU samples was varied and a Si/Al ratio of 6 showed the greatest yield. Being acid-catalyzed, the products of the reaction are highly branched, implying higher octane ratings and therefore suitability for gasoline blending.

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1.1 C_5 hydrocarbons : By-products of the Petroleum Industry

C_5 hydrocarbons include pentanes (alkanes) and pentenes (olefins); C_5 olefins are predominantly of interest for the purpose of this project.

Pentanes are alkanes with the chemical formula C_5H_{12} (molecular mass 72.15 g/mol). These are highly volatile compounds (boiling point 9 – 36 °C) and because of their non-polarity and lack of functionality, pentanes can only dissolve non-polar and alkyl-rich compounds. Pentenes are olefin molecules with the chemical formula C_5H_{10} (molecular mass 70.14 g/mol). There are six possible isomers of pentenes (figure 1-1) with varying chemical and physical properties, depending on their branching and spatial arrangement [1].

1-pentene (α-olefin) with the C=C double bond between the 1st and 2nd carbon atoms is a flammable, colorless and volatile liquid (boiling point: 30 °C). It is used in the formulation of plasticizers/detergents and as a precursor to production of thiols, amines and ammonium salts. It has also been used as a monomer for manufacture of resins and low-molecular-weight thermoplastic materials.
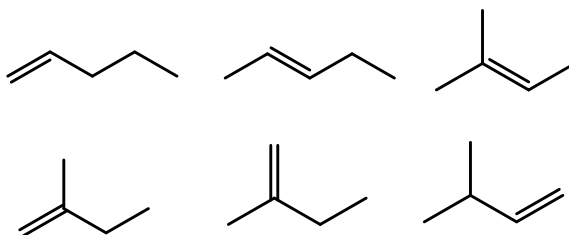
Figure 1-1: Isomers of pentene.

Light alkanes and olefins - pentanes and pentenes - are large impurities of the catalytic cracking process in the petroleum industry. Thermal cracking of naphtha and gas oil yields ethene (C_2) and propene (C_3) as primary products and C_5 hydrocarbons as by-products. Pentanes are highly undesirable of these by-products as they have few direct applications, and are thus, not economically viable compounds. C_5 alkanes (pentanes) can be converted to C_5 alkenes (pentenes) by the process of catalytic dehydrogenation. Presence of C_5 olefins in the gasoline pool can possibly increase the ozone formation potential of the gasoline, as C_5 olefins are 4-7 times more active in forming ozone than corresponding saturated compounds [2]. Ozone forming potential is the reactivity of an individual organic compound to the presence of other precursors (intermediates) for the formation of ozone [3].

Consequently, it is necessary to remove the lighter C_5 hydrocarbons, before further processing can be done. The other option, which is the emphasis of this thesis, is oligomerization to produce commercially important C_{10} olefins (decenes). C_{10} olefins undergo catalytic hydrogenation to form C_{10} alkanes (decanes) which are used as gasoline.

1.2 C_{10} hydrocarbons: Commercially Important Products

C_{10} hydrocarbons commonly include decanes (alkanes) and decenes (olefins); C_{10} olefins are particularly of interest for the purpose of this project. Decanes are long chain, heavy alkanes with molecular formula $C_{10}H_{22}$ (molecular mass 142.28 g/mol). Decenes are long chain olefins with 10 carbon atoms and one double bond between the carbon atoms. The molecular formula for a decene is $C_{10}H_{20}$ (molecular mass 140.27 g/mol).

Isomers of decenes can vary depending on the position and geometry of the double bond and the degree of branching of the molecule. Decenes have a high boiling point in the range of 172 °C, hence are colorless liquid, insoluble in water, at room temperatures.
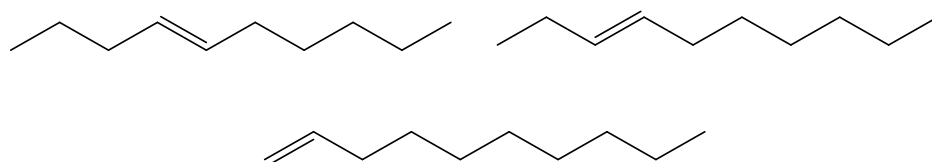
Figure 1-2: Isomers of decenes: 4-decene, 3-decene and 1-decene.

Decenes are vital intermediate precursors in the production of epoxides, amines, synthetic lubricants, alkylated aromatics and synthetic fatty acids. Isomers of decane can be produced by catalytic hydrogenation of decenes, and are commercially very valuable products that can be used as gasoline. They can also be used as hydrocarbon and varnish solvents in paint manufacture industry.

C_{10} olefins are industrially prepared by oligomerization of light olefins such as ethylene by the Ziegler process or by cracking of heavier petrochemical waxes.

1.3   Zeolites

Zeolites (sometimes referred to as molecular sieves) are microporous, crystalline minerals with well-defined structures. A zeolite framework is made up of silicon, aluminum and oxygen. Zeolites are characterized by their silicon to aluminum ratio (Si/Al), which is the ratio of the total number of silicon and aluminum atoms in one

crystal of zeolite. The pores of the zeolites consist of cations, water and other molecules that may be held within the zeolite.

Some zeolites are found in the nature, as minerals and may be mined and processed. Numerous other zeolite structures can be synthesized, and these have wide commercial applications. Zeolites are commonly prepared by heating aqueous solutions of silica and alumina, along with a structure directing agent. Varying the concentration of silica and alumina in the solution changes the final Si/Al ratio of the zeolite produced. The structure directing agent influences the crystallization process and leads to formation of a specific zeolite framework type structure in the final crystal. Some of the common zeolites are ZSM-5, Beta*, Mordenite, Ferrierite and Faujasite. All zeolites are denoted by a three letter code, assigned by the International Zeolite Association (IZA).
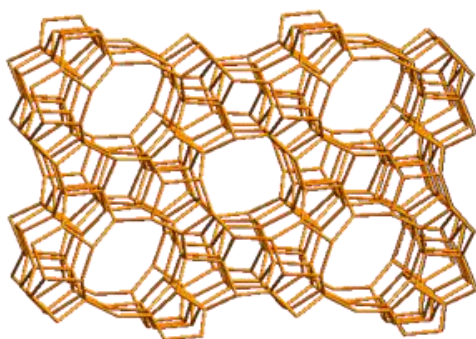
Figure 1-3: MFI (ZSM-5) [4] [5]   **Figure 1-4: BEA* (Beta*) [4] [5]**
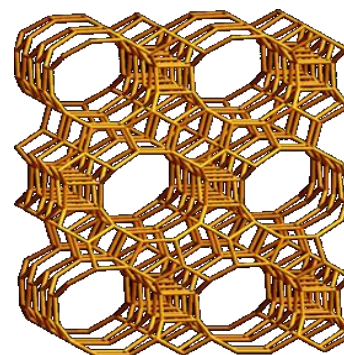
The interconnectivity of pores within zeolite structures consist of two general types: channel type zeolites and window-cage type zeolites. A channel type structure is characterized by an interconnected network of straight or tortuous channels of constant shape and diameter passing through the zeolite. ZSM-5 (MFI), Beta* (BEA*), Mordenite (MOR), and Ferrierite (FER) are examples of channel type zeolites. A unit cell of a

channel type zeolite is made up of interconnected channels of two different member ring channels of either the same or different dimensions or size.
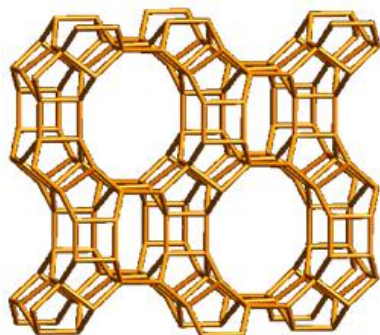
Figure 1-5: MOR (Mordenite) [4] [5]
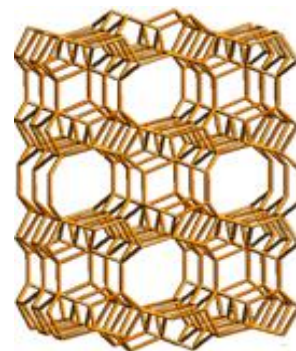
Figure 1-6: FER (Ferrierite) [4] [5]

Window-cage system zeolites are characterized by a series of larger cages connected to one another by smaller windows. These windows that connect the larger cages result in a much larger pore size for this type of system of zeolites as compared to a zeolite of channel type system. Faujasite (FAU) is a popular example of a window-cage system of zeolites.
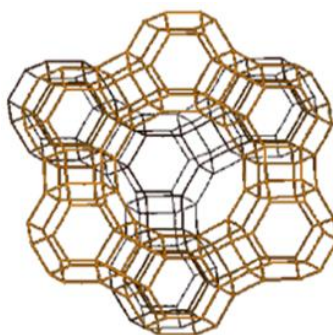
Figure 1-7: FAU (Faujasite) [4] [5]

Table 1-1: Information for structure of zeolites

Zeolite	Pore System	Dimensions of Pore	Zeolite Dimensionality	Maximum Diameter of sphere (A°)	
				Included	Diffused
MFI	Channel System of 10 MR x 10 MR	5.1 x 5.5 A° / 5.3 x 5.6 A°	3 D	6.36	4.46
BEA*	Channel System of 12 MR x 12 MR	6.6 x 6.7 A° / 5.6 x 5.6 A°	3 D	6.68	5.95
MOR	Channel System of 12 MR x 8 MR	7.0 x 6.5 A° / 5.7 x 2.6 A°	1 D	6.7	6.45
FER	Channel System of 10 MR x 8 MR	5.4 x 4.2 A° / 4.8 x 3.5 A°	2 D	6.31	4.89
FAU	Window Cage System of 12 MR	7.4 A°	3 D	11.24	7.35

MR = Membered Ring Channels. Two dimensions of the pore indicate the two directions of channel orientation. Maximum diameter of included sphere indicates the larger channels and that of the diffused sphere indicates the smaller channels connection to the larger ones of the zeolite. [4] [5]

Zeolites can be defined by the framework that is made up of 4-connected network of atoms. This can be imagined in terms of tetrahedra, with a silicon atom in the middle and oxygen atoms at the corners. The tetrahedra structures are linked to one another by their corners to form a variety of possible structures, resulting in different zeolites. If all the tetrahedra contain silicon, the framework is considered to be neutral (example: MFI Si/Al = 1000, silicalite). Substitution of aluminum for silicon creates a charge imbalance and requires other metal ions to be present in relatively large cavities of the framework.

The presence of aluminum is the reason for the Brønsted acid sites on the zeolite surface. The Brønsted acid sites are the location for any catalytic activity in the zeolite, including oligomerization and cracking [6]. The catalytic activity is derived from the hydroxyl groups that bridge between Si- and Al-substituted tetrahedral lattice sites. Such sites exhibit Brønsted acidity, the strength of which varies with zeolite composition and structure [7].
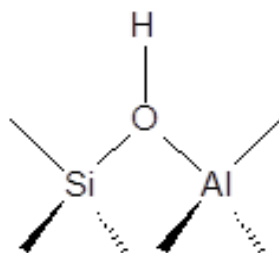
Figure 1-8: Reactions occur at the H$^+$ acid site.

Extensive research by chemical engineers and chemists at Union Carbide, Exxon, Mobil and Shell has been carried out for zeolite catalysis in the last few decades [8]. Zeolites are widely used as catalysts for several applications such as fluid catalytic cracking and hydrocracking of large gasoil molecules, production of chemicals and fuels, production of olefins and light olefins from methanol, oligomerization of small olefins, isomerization and alkylation of benzene molecules [8][9][10][11][12]. Due to their high selectivity, their reactivity and the presence of Brønsted acid sites, zeolites act as solid acid/base catalysts in a variety of reactions [13].

A major advantage of the use of zeolites as catalysts as opposed to traditional catalysts is that the zeolites can be regenerated and reused after multiple reactions. The used zeolite is sent to an air regenerator where the coke is burned off the surface and the

catalyst can be used again. There are a wide range of zeolite structures and pore sizes to suit each reaction appropriately.

There are various other applications of zeolites in both lab-scale research and industry. Zeolites are extensively used as ion-exchange beds for purification and softening of water where they separate molecules in the water based on their sizes, with the zeolite pores acting as sieves. They are used in purification of air and separation of specific gases from a mixture.

Some zeolite structures find applications in agriculture industry as well. Zeolites loaded with potassium or nitrogen can be used for their slow release into the soil, to provide it with essential nutrients. They also act as water moderators, similarly acting for the slow release of water into the soil, to prevent root rot and moderate the effect of droughts. The use of zeolites is also gaining importance in the nuclear and detergent industry, in recent times.

1.4   Oligomerization of Olefins

Oligomerization and hydrogen transfer are important reactions during interaction of light alkenes with the acidic surfaces on zeolites [14]. The demand for kerosene and diesel in comparison to gasoline is increasing constantly. Thus, maximizing the production of middle distillates in the refining process is of immediate interest. Oligomerization reaction to convert the lighter olefins to middle distillates to incorporate in the diesel pool is a promising process for production of clean diesel fractions [15]. The dimerization, or oligomerization, reaction for light olefins has been studied extensively in the past. Light olefins included in past research are mainly ethene (C_2), propene (C_3) and

butenes (C_4). Catalysts studied for these reactions are zeolites and other catalysts like phosphoric acid, certain ionic liquid catalysts, and mesoporous aluminosilicates.

1.4.1 Oligomerization of Light Olefins over Acid Zeolites

Light olefins typically include ethene (C_2), propene (C_3) and butenes (C_4). The zeolites studied for the oligomerization of light olefins, were mostly MOR (Mordenite) and MFI (ZSM-5). Certain authors have studied the oligomerization of C_3 and C_5 olefins to high quality liquid fuels over modified MFI catalyst. The results showed that in the earlier stages, the modified catalysts are better for converting the olefins but at further durations, the oligomerized products lead to deactivate the catalyst through potential formation of large products with larger coking-pore blocking tendency [16].

The analysis of the products of the reaction of light olefins over MFI provides evidence for oligomerization-cracking-realkylation mechanism. The reactions occur mainly in the bulk of the catalyst (within the pore channels of the zeolite) or at the external surface, depending on the amount of coke developed and deposited inside the catalyst [17]. The catalytic activity is largely dependent on the concentration of framework aluminum (Al), and effectively the Brønsted acid sites in the zeolite.

Studies of ethene and propene oligomerization on MFI have been done by FTIR spectroscopy. Oligomerization was observed to proceed through the following steps: (i) formation of short-lived hydrogen-bonded precursors by interaction of the alkene with the internal acidic Brønsted acid sites, (ii) protonation step and (iii) a chain-growth step [18]. At relatively high pressures and high temperatures, the equilibrium distribution for olefin oligomerization is shifted toward high molecular weight olefins. Isomerization

reactions are also seen to occur relatively faster at these conditions [19]. The olefin oligomerization reaction is strongly dependent on the operating conditions (temperature, partial pressure and contact time) and secondary reactions, like cracking, limit the primary reaction to a large extent. 1-butene oligomerization was also studied over MFI at 150 °C and 200 °C. The data showed that the selectivity toward C_8 olefins increased at higher pressures and at 200 °C. However, at higher temperatures, the cracking reaction dominates as expected. The highest selectivity was observed at 200 °C, 50 kPa of partial pressure and the lowest contact time [15].

Propene oligomerization over MFI of varying silicon to aluminum ratios indicated that for a constant space time per active site, a decrease in Si/Al resulted in a corresponding decrease in the rate of oligomerization per site but an increase in selectivity to dimers relative to cracking products. It also showed that an increased proximity of the acid sites in a zeolite improved the rate of formation of aromatic species. The authors also reported that with an increase in temperature the selectivity toward the desired products (C_6 olefins) decreases for reactions over MFI of all silicon to aluminum ratios. At low Si/Al ratios, the steric constraints imposed due to the adsorption of newly formed oligomers restricts formation of trimmers, leading to a greater selectivity toward the dimers [20]. Propene oligomerization has been studied over H-mordenite, which is a one-dimensional channel system zeolite. The reaction is the predominant process which proceeds very rapidly even at room temperature. This process was studied in the past by fast FTIR spectroscopy [14]. This paper also showed that although the Brønsted acid sites on MFI and MOR show relatively similar activity, the protonation of propene proceeds faster on H-MOR.

Isolation of C_5 olefins in the refinery gasoline by oligomerization and dimerization has also been previously studied. A large pore, acidic zeolite – mordenite (MOR) – has been the primary zeolite studied for this process. Zeolites with higher silica to alumina ratio were found to give increased C_5 conversion. [2].

Olefin reactions of ethene, propene, isobutene and 2-methyl-butene-1 over MFI at 300 and 373 K were investigated using high-resolution solid-state ^{13}C-NMR spectroscopy. It was seen that at 300 K, only linear oligomers were observed and at 373 K, branched heavy oligomers were formed. The catalyst caused oligomerization and further isomerization as well at higher temperatures [21].

MFS was a specifically designed catalyst for light alkene oligomerization, to favor a cross-wise arrangement of the alkene and the alkylcarbenium ion to suppress hydrogen transfer. Feedstock of C_3+C_5 and C_4+C_5 alkene mixtures was introduced. At shorter times, dimers were formed while at longer durations, higher olefins were observed [22].
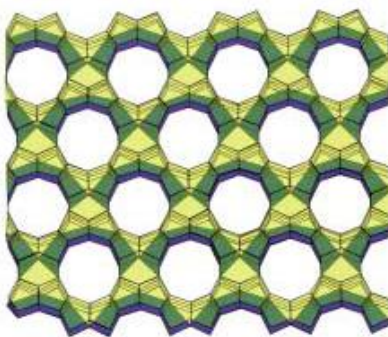
Figure 1-9: Representation of MFS framework topology. [22]

1.4.2   Oligomerization of heavy olefins over acid zeolites

There is fairly little research for oligomerization of heavy olefins over acid zeolites due to the relative smaller pore size of most zeolites. Due to this, the acid sites on the zeolites tend to crack long chain molecules as opposed to oligomerization.

Heavier olefins like hexenes (C_6) and octenes (C_8) were studied for the oligomerization over faujasite and beidellite. 1-hexene was oligomerized at 200 °C and a pressure of 5 MPa in a down-flow fixed-bed tubular reactor filled with beidellite and ultra-stable faujasite catalysts. 1-hexene and 1-octene underwent rapid oligomerization, isomerization and cracking to a mixture of intermediate olefins [23].

1.4.3   Oligomerization of olefins over other catalysts

Oligomerization of olefins over catalysts other than zeolites was studied extensively as well. Mesoporous aluminosilicates are popular catalysts for the oligomerization of olefins. These are similar to zeolites but with bigger pore sizes (around 10-100 nm) and higher surface areas. Unlike zeolites which are crystalline materials, mesoporous aluminosilicates are amorphous. They have high acidity, and due to the larger pore sizes, they can accommodate larger molecules in spite of pore blockage due to coke deposition. Butene oligomerization was studied over aluminum containing micelle template silica (MTS-type) catalysts at 423 K and 1.5-2 MPa. A number of branched dimers (C_8 olefins) were observed as end products [24]. Oligomerization of C_4 and C_5 olefins was observed to be optimum over mesoporous MCM-41 catalyst, as compared to that of lower olefins (ethylene). Activity increased with a rise in reaction

pressure, temperature and contact time, while higher silicon to aluminum ratios reduced the activity and stability of the catalysts [25]. Oligomerization of heavier olefins, like 1-hexene, was also studied over Al-MTS catalyst. A silicon to aluminum ratio of 30, temperature of 200 °C and pressure of 50 bar were shown to give best yield of the oligomerized products [26].

Further, oligomerization of light olefins was also studied over different homogeneous and heterogeneous catalysts. The selective oligomerization of ethylene to 1-hexene and 1-octene has been studied. Oligomerization of ethylene with Cr (PNP) C_{13}/MAO at 200 psig of ethylene at 25 or 45 °C generates 1-hexene, 1-octene, C_{10}-C_{22} oligomers, and polyethylene. The addition of ZnR_2 increases the productivity and selectivity for C_{10}-C_{22} oligomers and results in a decrease in the amount and molecular weight of the polyethylene generated [27].

N-heterocyclic carbenes (NHCs) are newly developed homogeneous catalysts. They are effectively used as ancillary ligands on homogeneous metal catalysts. A large range of catalytic transformations have been carried out using transition metal carbene complexes. In recent times, their use as catalysts for oligomerization of light alkenes has also become prominent [28].

The oligomerization of light olefins over solid phosphoric acid (SPA) is a popular commercial process for production of "polymer gasoline" and kerosene. Isomerization, skeletal rearrangement, methyl migration, cracking and oligomerization are the reactions observed at the catalyst. This particular study for oligomerization of butenes over solid and liquid phosphoric acid (LPA) indicated formation of trimethylpentene and

dimethylhexene predominantly. In general, it was observed that tri- and tetrasubstituted components are primary components of oligomerization over SPA and LPA [29].

Despite numerous light olefin oligomerization reactions over homogeneous catalysts, it must be observed that heterogeneous catalysts are significantly better to study these reactions. Heterogeneous catalysts can be separated from the reaction mixture and regenerated. The amount of acid sites in the heterogeneous catalyst can be controlled and studied in a better manner. From past research, it was also observed that oligomerization in presence of heterogeneous catalysts, especially zeolites, gave better yields of the desired products.

The objective of the thesis can be stated as follows:

1. To explore the oligomerization of C_5 olefins (pentenes) over commercially available zeolites − MFI, BEA*, MOR, FER and FAU − and study the effect of zeolite pore size and dimensions on the yield and selectivity towards the desired C_{10} olefins (decenes).

2. To study FAU as the zeolite for pentene oligomerization in further detail. Catalytic activity over a wide range of silicon to aluminum ratios for FAU, along with the effect of Bronsted acid sites was essential to be discussed.

3. To determine the effects of external parameters − temperature, time, initial concentration of pentene, zeolite manufacturer − on the pentene oligomerization reaction.

Chapter 2: Experiments

2.1 Preparation of Experimental Set-up

2.1.1 Zeolite pre-treatment

Zeolite samples were purchased from Zeolyst International. All zeolite samples were calcined in a tube furnace. The process for calcination is as follows:

1. The zeolite powder was loaded into a pre-cleaned and dried quartz boat, which was then placed in a quartz tube of 5.08 cm outer diameter and approximately 1 m in length.

2. The quartz tube was placed gently in the tube furnace, with ceramic supports on both ends to keep it securely in place.

3. The furnace was then heated up to 500 °C, with a ramp rate of 2 °C/minute.

4. Air was flowed through the glass tube at a continuous rate of 100 ml/minute.

5. After the temperature of the furnace reached 500 °C, it was maintained at that temperature for 3 hours, under continuous flow of air.

6. After 3 hours, the temperature of the furnace was brought back to room temperature, over a period of time.

7. The zeolite sample was then transferred to a completely dried glass vial, which was stored in a desiccator, before using it for the experiments.

2.1.2 Preparation of stock solution

The starting materials for the reaction – 1-pentene and n-dodecane (inert solvent) – were degassed under vacuum. The process of degassing – removal of air and moisture from the solvents – is done to avoid any external effect on the reaction. The degassed solvents were then taken into the glove box (under argon atmosphere). 1-pentene was dried over NaK or a sodium-potassium alloy (dessicant) for 24 hours. The solvents were stored in the glovebox until further use.

A glove box is a completely sealed container that allows one to work in an inert atmosphere, devoid of air, moisture or other contaminants. The glove box used for this project was under argon atmosphere. The procedure to operate the glove box is as follows:

1. Ensure that both the doors of the ante chamber of the glove box are closed.

2. Purge the ante chamber with argon. Set it under static argon atmosphere (1 atm). Open the outside door that is exposed to the atmosphere. Place the samples in the ante chamber. Close the door tightly.

3. Evacuate the atmosphere from the ante-chamber completely. Wait for two minutes. Flush the ante-chamber with argon once again. Repeat this procedure three times.

4. It is important to note that either door of the ante chamber must be opened only when the antechamber is under static argon atmosphere.

5. Finally, once under argon atmosphere, open the door of the ante chamber that opens to the glove box.

The reactant for the oligomerization reaction was 1-pentene, which is a very volatile compound and evaporates even at room temperature. A stock solution of approximately 300 mM 1-pentene in an n-dodecane solvent was prepared because of the convenience to handle and study the pentene oligomerization. Control experiments have proved that n-dodecane does not undergo any oligomerization or cracking during the pentene oligomerization. The stock solution was then kept in a refrigerator in the glove box. The stock solutions and the zeolite samples were stored in the glove box until further use for experimental purposes.

2.2 Gas Chromatography Analysis and Calibration

Gas chromatography is a process for separation of components in a sample between two phases: One of the phases is a stationary bed with a large surface area, and the other is the gas that percolates through the stationary bed. The sample is vaporized and carried by mobile gas phase (the carrier gas) through the column. The different components in the sample separate out based on their solubilities at the given temperature. Gas chromatography is typically a fast method of analysis and is efficient, providing a high resolution, in addition to being reliable and simple, and hence, quite inexpensive. It is sensitive towards detecting even ppm quantities in the sample [30].

The instrument for analysis of the products of the oligomerization reaction was a Varian CP 3900 Gas Chromatography set-up. The software installed for the gas chromatography was Galaxie Chromatography Data System by Agilent.

The method for the GC analysis was maintained standard for experimental analysis for all the reactions studied during the course of the project. The injector set point temperature is 300 °C, with a split ratio of 90. Split ratio is the ratio of the amount of sample passing through the split vent to the amount of sample passing through the column. The starting temperature for the oven is 38 °C and the maximum temperature is 280 °C. The makeup gas is helium (He) with a flow rate of 25 ml/min. The reference gas is hydrogen (H_2) with a flow rate of 30 ml/min. The flow rate for air is 300 ml/min. The flame ionization detector (FID) range for the detector is 12. The maximum run time for the course of the GC analysis is 52 minutes.

It is necessary to run a calibration for every expected compound in the reaction vessel for the following reasons:

1. To determine what compound each observed peak represents and effectively the retention time for each compound.

2. To determine the amount of each compound observed by calculating the ratio of the area under the peak of the unknown compounds to that of the known standard.

The calibration experiment was performed as follows:

1. Stock solutions of known concentrations of 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene were prepared. N-dodecane was the solvent in all the cases.

2. A known concentration of para-xylene was added to the stock solution, as an external standard.

3. 0.4 µl of the stock solution of 1-pentene was injected in the GC and the standard method was run.

4. The peaks observed were compared to find the internal response factor. **Internal response factor** (IRF) was calculated by:

$$IRF = \frac{Area_{IS}}{Concentration_{IS}} \times \frac{Amount_{SC}}{Area_{SC}}$$

Where, IS = Internal Standard

SC = Specific Compound of Interest

Area = Area under the peak of the gas chromatogram

5. The same process was performed separately for each of the other stock solutions. The IRF was calculated for each compound that was expected to be observed during the actual reaction.

Unknown concentration of a certain compound can be calculated if the IRF is known, by the following formula:

$$Concentration = \frac{Area_{compound}}{Area_{ES}} \times Concentration_{ES} \times IRF$$

Where, ES = External Standard (p-xylene, in this case)

The above formula was used to calculate the concentration of all known compounds in the reaction vessel.

Once the calibration experiments are performed, it was easier to determine the composition of the products after the reaction. The project then moved on to study the oligomerization reaction.

2.3 Oligomerization Reaction

Once the zeolite samples were ready and the stock solution was prepared, the experiments to study the oligomerization reaction were undertaken. The following steps were performed in a glove box under argon atmosphere:

1. The Kontes vials, stoppers, spatula, syringe and zeolite samples were taken into the glove box via the ante-chamber of the glove box.

Figure 2-1: Kontes vial.

2. The antechamber was evacuated and flushed with argon thrice in continuation. This was done to ensure that no air or moisture enters the glove box, via the antechamber.

3. Inside the glove box, a sample of zeolite was weighed and added to the Kontes vial. 200 µl of the stock solution (300 mM 1-pentene in n-dodecane) was added to the Kontes vial.

4. The vial was then stoppered tightly to ensure no contact with outer atmosphere. The reaction vessel was then brought out of the glove box for heating.

A HT110 oil bath was pre-heated to 200 °C and kept under continuous stirring. The reaction vessel was immersed into the oil bath and kept under heating conditions for the desired time (10, 40, 180 or 360 minutes). The 0 minute reaction was recorded without heating the reaction vessel. Once the reaction vessel was heated for the desired time, it was cooled immediately under liquid nitrogen. 2 µl of para-xylene was added as an external standard, because it is unreactive in presence of zeolites, at room temperature. The products in the reaction vessel were analyzed by gas chromatography. 0.4 µl of the products from the reaction vessel was injected into the Varian GC.

The peak positions of the products observed on the chromatograph were matched with the peaks of different products observed during the earlier calibration experiment. The area under the peak for each product was measured and the concentration of each product was thus measured with respect to the external standard (p-xylene).

- Conversion of starting reactant (pentenes) to other products is calculated

$$\text{Conversion} = \frac{(C_{\text{pentene at t=0}} - C_{\text{pentene at t}})}{C_{\text{pentene at t=0}}} \times 100$$

- Yield of decenes is calculated

$$\text{Atom Yield} = \frac{C_{\text{decene at t}} \times 10}{5 \times C_{\text{pentene at t=0}}} \times 100$$

- Atomic Selectivity toward decenes is calculated

Atom Selectivity

$$= \frac{10 \times C_{\text{decene at t}}}{6 \times C_{\text{hexene}} + 7 \times C_{\text{heptene}} + 8 \times C_{\text{octene}} + 10 \times C_{\text{decene}}} \times 100$$

C denotes the concentration of the product (pentene or decene)

The effect of pore size on the oligomerization reaction was studied, in terms of, yield of decenes, conversion of pentenes to products and selectivity towards the decenes amongst other undesired byproducts.

The mass of the zeolite samples for each experiment was determined in such a way that the number of H^+ ions was constant for all the experiments. This can be calculated from the molecular formula of each zeolite.

Table 2-1: Comparison of different samples of zeolite

Zeolite	Si/Al ratio	millimoles of H^+ per gram	Mass of zeolite (mg)	Total mmoles of H^+
FAU	2.6	4.625	**2.57**	0.0119
FAU	15	1.040	**11.43**	0.0119
FAU	40	0.406	**29.29**	0.0119

2.4 Sodium exchange experiment

Certain acid sites in FAU (Si/Al = 6) were substituted by Na^+ ions, to effectively kill those acid sites, and increase the distance between each acid site without reducing the strength [31]. These Na^+ substituted FAU samples are termed as Na_x-FAU. The steps for sodium exchange of NH_4-FAU are [32]:

A. Catalyst Preparation

1. Weigh a plastic boat and set the balance to zero. Load approximately 5g NH_4-FAU into the plastic boat.

B. Sodium nitrate (NaNO₃) solution preparation

2. Using a graduated cylinder, measure 150 ml of deionized (DI) water and transfer it to a beaker.

3. Weigh another plastic weigh boat and set the balance to zero. Load approximately 1.25 g of NaNO₃ into the plastic boat.

4. Transfer the NaNO₃ into the beaker containing DI water and stir it until all of the solids dissolve.

5. Rinse the graduated cylinder with the NaNO₃ solution and measure 100 ml solution using it.

C. Setting the condenser and hot bath

6. Transfer the NH₄-FAU into a new beaker and carefully pour the NaNO₃ solution into the beaker. Transfer all of the solution into the round-bottom flask.

7. Prepare the silicone oil bath: heat the bath until 80 °C. Connect the flask into the condenser and ensure that the flask is positioned in the center of the heating plate.

8. Add a Teflon-coated egg-shaped stir bar into the flask. Set the stir rate to 200-250 rpm. Cover the flask and the bath with aluminum foil and ensure the water is running through the condenser.

9. Heat for 12 hours (make sure temperature has stabilized at around 80 °C).

D. Vacuum Filtration

10. Connect a Buchner funnel to a vacuum flask. Put two sheets of filter paper into the Buchner funnel. Turn on the vacuum and soak the filter paper with DI water.

11. Remove the round bottom flask from the condenser.

12. Slowly pour the solution into the center of the filter paper.

13. While pouring the solution, if black specks are noticed on the filtrate, remove them carefully and as much as possible without losing catalyst material.

14. Use a small amount of DI water to rinse the flask, so that entire solid is collected.

15. Keep the solid in an oven to dry overnight.

E. Calcination of Na_x-FAU

16. Take a small amount of the sample of the completely dried Na_x-FAU and pour it in a quartz boat. Place the boat in a quartz tube within the tube furnace.

17. Calcine the sample to 500 °C (with a ramp rate of 2 °C/min). Hold it at 500 °C for 3 hours. Let the tube furnace cool down after 3 hours.

18. Remove the sample from the quartz tube and transfer it to a glass vial. Label the vial and place it in a dessicator.

F. Repeat of sodium exchange process

19. The sodium exchange process can be repeated as many times as wanted.

20. Repeat steps 1-18 for each time.

Chapter 3: Results and Discussions

3.1 Effect of Zeolite Pore Size and Structure

The effect of the zeolite pore size and structure on the yield of decenes from pentene oligomerization was studied. In addition to oligomerization, cracking and other parallel reactions were observed.

The reaction was studied at 200 °C, with constant stirring of the contents of the reaction vessel at 350 rpm. The starting concentration of 1-pentene was constant at approximately 300 mM. The mass of the zeolite for the reaction was calculated as explained previously in Table 2-1. The volume of the reactants was 200 µl (including 1-pentene and n-dodecane). After the heating began, the reaction was investigated after 10, 40, 180 and 360 minutes. A 0 minute reaction was carried out in which the reaction vessel was not heated and the reaction products (if any) studied.

Oligomerization of pentene was studied over MFI, BEA*, MOR, FER and FAU. The zeolites studied for this set of experiments were over a similar range of Si/Al ratios to compare the effect of only the zeolite structure on the pentene oligomerization.

An overview of the reaction over the zeolite can be illustrated by Figure 3-1. 1-pentene as the reactant undergoes rapid isomerization over the zeolite. Upon heating, the pentenes are oligomerized to several isomers of decene (as the desired reaction) or in certain cases, crack to ethene and propene when the C_5 olefins undergo primary cracking. It is then likely that the newly formed decene isomers by C_5 oligomerization can undergo secondary cracking to hexenes and butenes, and in lesser concentrations, to heptenes and propene or octenes and ethene. The cracked products from decenes and pentenes further

undergo reactions among themselves by way of oligomerization to butene molecules (C_2 oligomerization), hexenes (C_2 and C_3 oligomerization) and octenes (C_2 and C_4 oligomerization). C_9 olefins (nonenes) are not expected to be observed as products during this reaction because of a carbocation mediated mechanism for the expected reactions. A carbocation mediated mechanism favors the formation of more substituted olefins as the carbocation at the end of the chain is less stable.
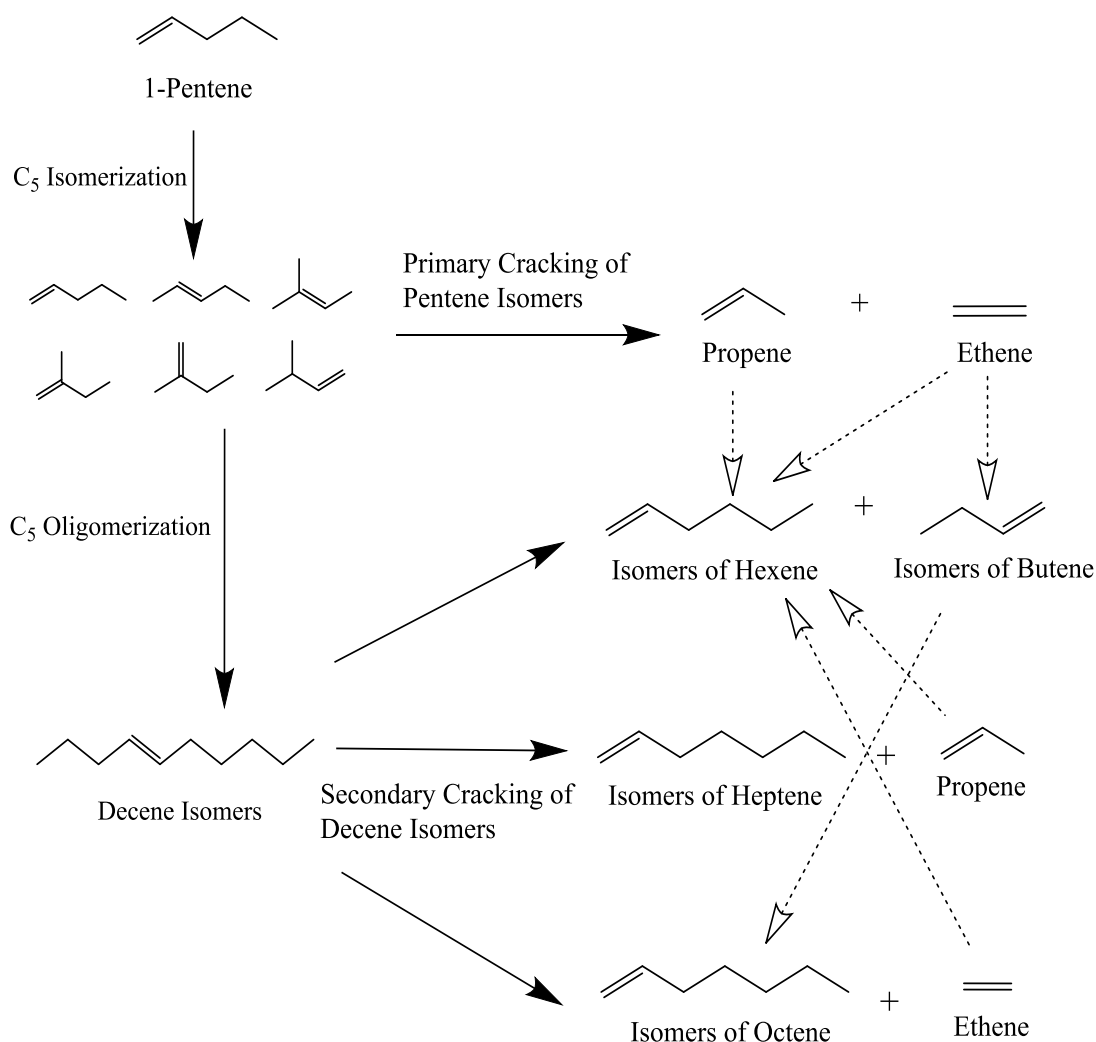
Figure 3-1: Pentene oligomerization and side reactions. Rapid isomerization reactions (not shown) are expected for all olefinic products.

3.1.1 MFI (Si/Al = 15) as catalyst for pentene oligomerization

The first zeolite to be studied was MFI, or ZSM-5, of Si/Al = 15, for its effect on the oligomerization of pentene, as previous studies indicated MFI to be a good catalyst for oligomerization of light olefins [21]. The Table 3-1 shows the conversion of pentene, selectivity toward C_{10} oligomers and yield of the C_{10} oligomers.

Table 3-1: Product distribution for pentene oligomerization catalyzed by MFI (Si/Al = 15) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity to C_{10} oligomers (%)
Blank	320.0	0			
0	298.3	0.0	6.8	0.0	-
10	235.0	11.1	26.6	7.0	26.7
40	193.1	15.3	39.6	9.6	37.5
180	143.5	20.1	55.2	12.6	30.8
360	136.3	16.9	57.4	10.6	19.1

The maximum concentration of C_{10} olefins observed for the reaction, in the reaction vessel was 20.1 mM, after a period of 180 minutes. In addition to C_{10} olefins, a large concentration of C_6 olefins, along with lesser concentrations of C_7 and C_8 olefins were observed in the gas chromatogram representing the products.

The yield of decenes (C_{10} olefins) increased for 180 minutes, and consequently declined, an indication of cracking of the long chain C_{10} olefin molecules after a certain period of time of contact over the zeolite. In contrast, the yield of hexenes, heptenes and

octenes increased throughout the period of observation. The selectivity toward the desired products was fairly low.
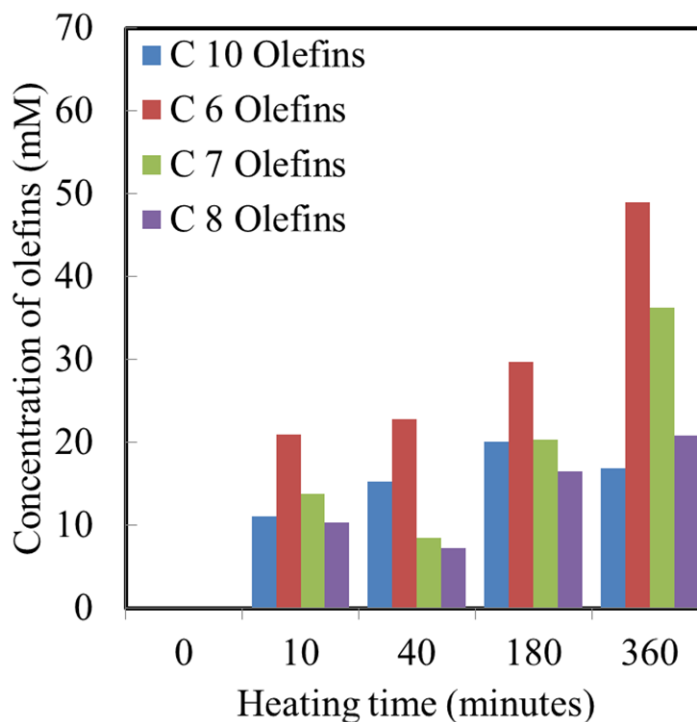
Figure 3-2: Effect of heating time on concentration of olefins for the reaction over MFI (Si/Al = 15). T = 200 °C, $C_{\text{pentene,initial}}$ = 300 mM, m_{zeolite} = 11.4 mg.

The different isomers of pentene were observed for the reaction at 0 minutes in presence of MFI, indicative of the fact that MFI (and other zeolites) cause pentene to rapidly isomerize by way of branching. Zero minutes of heating indicates the time taken from preparation of reaction vessel to injection of the products by gas chromatography analysis. As described in the literature in Section 1.4.1 and Figure 3-1, it is understood that there are two sets of parallel reactions occurring in presence of MFI, due to the high catalytic activity of the Brønsted acid sites with the pores of the zeolite. The first of these reactions is the oligomerization of C_5 olefins to form C_{10} olefins. The more prominent

reaction that takes place is the cracking of C_5 olefins to form C_2 and C_3 olefins, which further oligomerize and react among themselves to form $C_6 - C_8$ olefins. This hypothesis is further supported by Figure 3-2, where it is observed that at all times; a high concentration of cracked $C_6 - C_8$ olefins is accompanied by a significant concentration of C_{10} olefins. The overall yield of C_{10} olefins was very low for the oligomerization over MFI, in spite of a high conversion, indicative of the fact that C_5 cracking and further oligomerization of light olefins is the primary reaction. There is also an expected increase in the concentration of $C_2 - C_4$ olefins from cracking of decene and pentene isomers and reiterated by a carbon balance done for all the reactants and products; however, they are not observed on the gas chromatogram because these light olefins are gaseous at room temperature, and cannot be analyzed from a batch reactor.

Another factor to note for the oligomerization over MFI is the coloration of fresh white colored zeolite to a yellow/brown colored zeolite upon the reaction. This coloration is on account of coke deposition within the pores of the zeolite structure. Coking is caused due to parallel reactions like cyclization and aromatization; and these heavy by-products are deposited within the pores of the zeolite. Products formed due to coke deposition cannot be analyzed by the method of gas chromatography because these are left behind within the pores of the zeolite. Deposition of coke on the acid sites, within the pores of the zeolite, leads to deactivation of the zeolite; a zeolite which undergoes great coke deposition demonstrates less catalytic activity at longer durations.

3.1.2 BEA* (Si/Al = 12.5) as catalyst for pentene oligomerization

BEA* has a structure much alike to that of MFI in terms of pore size and channel system. The oligomerization over BEA* was expected to give a yield similar to that of the oligomerization of pentenes over MFI. The Table 3-2 illustrates the conversion of pentene, along with the yield and selectivity of C_{10} olefins for the reaction over BEA* (Si/Al = 12.5).

Table 3-2: Product distribution for pentene oligomerization catalyzed by BEA* (Si/Al = 12.5) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	308.0	0			
0	281.0	0.0	9.6	0.0	-
10	181.3	6.5	41.2	4.2	19.9
40	186.8	5.8	39.4	3.8	15.0
180	126.8	17.4	58.9	11.3	22.3
360	89.6	19.4	70.9	12.6	18.8

The maximum concentration of C_{10} olefins formed from the oligomerization was observed to be 19.4 mM after 360 minutes. Though BEA* is a large pore zeolite, it is expected that the zeolite tends to crack the C_{10} olefins that are formed, comparable to the reaction in presence of MFI (Section 3.1.1).

The oligomerization of pentene over BEA* depicted similar trends in terms of yield and selectivity toward C_{10} olefins as well as the cracked $C_6 - C_8$ olefins, as the reaction over MFI. Reaction is expected to proceed in a way akin to the oligomerization

over MFI, described in Section 3.1.2. As in the previous case, $C_6 - C_8$ olefins are formed by oligomerization of the products formed by cracking of C_5 olefins. Similar to the reaction over MFI, rapid isomerization of 1-pentene is observed in presence of BEA*, which then undergoes reaction upon heating. Significant coke deposition was observed in the case of BEA* as catalyst for the reaction, with a yellow colored zeolite left behind at the end of the reaction.
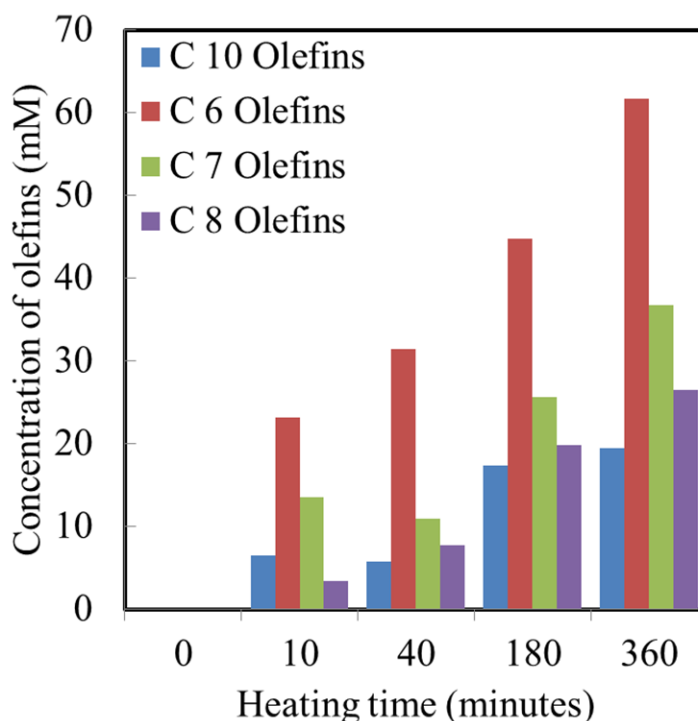
Figure 3-3: Effect of heating time on concentration of olefins for the reaction over BEA* (Si/Al = 12.5). *T* = 200 °C, *C*pentene,initial = 300 mM, *m*zeolite = 9.6 mg.

Due to a low yield of C_{10} olefins and a very high yield of C_6 olefins, along with $C_7 - C_8$ alkenes, it was deemed that BEA* was not a good enough catalyst for the oligomerization of pentene. It was decided to study larger pore zeolites for the reaction.

3.1.3 MOR (Si/Al = 10) as catalyst for pentene oligomerization

MOR has a relatively larger pore size than MFI, but similar to MFI, it possesses a channel type system. MOR, however, has a smaller channel size than MFI (Table 1-1). The products of the oligomerization of pentene were analyzed over a period of 360 minutes.

Table 3-3: Product distribution for pentene oligomerization catalyzed by MOR (Si/Al = 10) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	321.3	0			
0	285.2	0.0	11.2	0.0	-
10	222.8	1.0	30.7	0.6	5.2
40	162.2	2.5	49.5	1.6	11.5
180	154.7	2.8	51.9	1.8	11.2
360	101.2	6.4	68.5	4.0	19.6

The maximum concentration of C_{10} olefins from the oligomerization in presence of MOR as catalyst was 6.4 mM after 360 minutes, much lower when compared to the highest yield (20 mM) in presence of MFI (Table 3-1) and BEA* (Table 3-2).

It has been discussed previously in literature that the smaller 8 member ring pockets (Table 1-1) of 5.7 x 2.6 A° of MOR have unique reactive environments and are the most likely sites for catalytic activity [33,34]. The small 8-MR pockets tend to primarily crack C_5 olefins in the reaction vessel to C_3 and C_2 olefins. These light olefins further oligomerize and react among themselves to give $C_6 - C_8$ olefins, as observed from

Table 3-4. It is suspected that the primary reaction that takes place is the C_2 and C_3 oligomerization to produce C_6 olefins. Further evidence to strengthen this hypothesis is that the concentration of C_6 olefins is higher than that of C_{10} olefins throughout the experiment. It can thus be deduced that hexenes are formed by oligomerization of cracked pentenes and not by cracking of C_{10} olefins. C_5 oligomerization to give a very small yield of C_{10} olefins is reasoned to be a secondary reaction that occurs in the larger 12-member ring channel of the MOR.
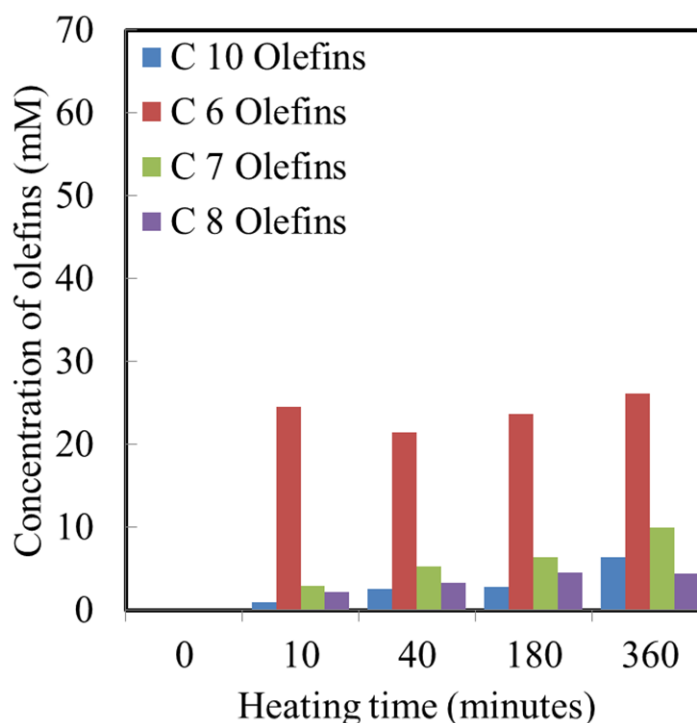
Figure 3-4: Effect of heating time on concentration of olefins for the reaction over MOR (Si/Al = 10). $T = 200\ °C$, $C_{pentene,initial} = 300\ mM$, $m_{zeolite} = 7.8\ mg$.

The amount of light olefins (C_3 and C_2) is expected to have increased, although it is not visible on the chromatogram, as these olefins are in the gaseous phase at standard temperature and pressure. This proposition is based on the fact that there is a reduction in

the concentration of pentene but not an equivalent increase in concentration of other products. A great increase in the concentration of C_6 olefins points to the fact that MOR is better at oligomerization of C_3 olefins to give hexenes.

3.1.4 FAU (Si/Al = 15) as catalyst for pentene oligomerization

FAU, with a super cage of 11.24 A°, was hypothesized to demonstrate a more dominant oligomerization of pentene than in the previous cases. The channels connecting the cages of FAU super cages are also much larger than in the case of previous zeolites that have been studied for this project.

Table 3-4: Product distribution for pentene oligomerization catalyzed by FAU (Si/Al = 15) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	308.5	0			
0	259.9	19.8	15.8	12.9	100.0
10	184.3	25.7	40.3	16.7	58.8
40	94.3	32.6	69.4	21.2	68.3
180	119.8	32.2	61.2	15.7	32.3
360	101.2	22.8	67.2	14.8	35.9

The maximum concentration for FAU as catalyst was 32.6 mM after 40 minutes, which remained relatively constant for further heating periods. There was an evident

increase in the yield of the desired product when compared to the reaction over MFI, BEA* and MOR, along with an improved selectivity at short times.
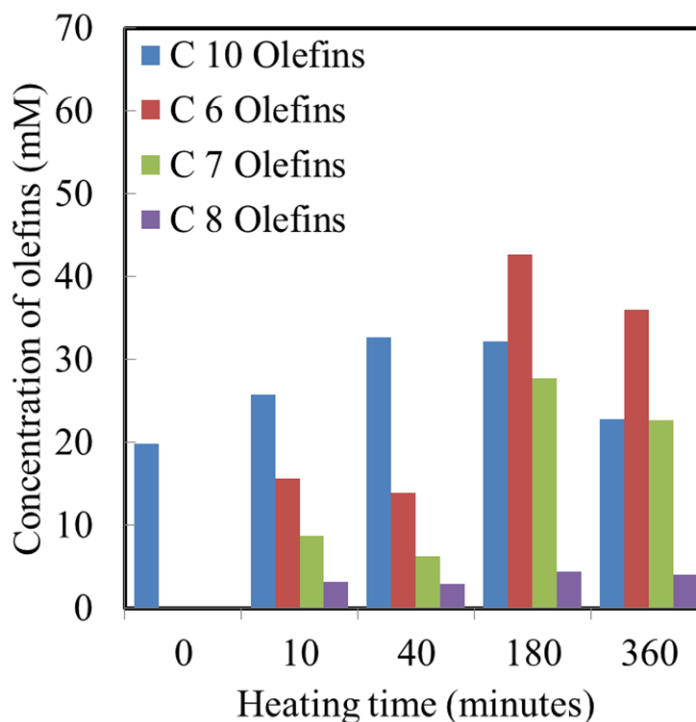
Figure 3-5: Effect of heating time on concentration of olefins for the reaction over FAU (Si/Al = 15). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 11.4 mg.

With an increase in the concentration of C_{10} olefins, there was a growth in the concentration of cracked products, particularly C_6 olefins; an increase in yield of the desired product led to a decrease in selectivity. This highlights the fact that the cracking of decenes was a more dominant reaction as compared to the oligomerization of pentenes at longer periods of heating.

As expected the pore size and zeolite structure plays a key part in the increased yield for the oligomerization over FAU. With a large super cage, it is less likely for the long chain C_{10} olefins to crack as soon as they are formed, as seen in the previous cases.

The formation, desorption and diffusion through the larger pores of the FAU is significantly facilitated in this case. In previous cases, it is likely that bulkier and more branched olefins undergo cracking while diffusion through the comparatively smaller zeolite pores. For a large pore zeolite, the adjacent acid sites are at a much greater distance from each other, thus avoiding rapid cracking of long chain olefins over these acid sites.

At a period of 40 minutes and above, it is observed from Figure 3-6 that the concentration of C_{10} olefins remains fairly constant, with an increase in the concentration of $C_6 - C_8$ olefins. This phenomenon indicates the occurrence of a parallel reaction of cracking of C_5 olefins and further oligomerization of the cracked products. As the production of C_{10} olefins reaches equilibrium certain areas within the pores of the zeolite are inaccessible for oligomerization of C_5 olefins to larger products. At this point, the cracking of the C_5 olefins, along with the oligomerization of these smaller cracked product olefins, takes over as the primary reaction. This explains the increase in concentration of $C_6 - C_8$ olefins, with a decrease in the concentration of C_{10} olefins.

It is known that as the pore diameter of the zeolite is increased; bimolecular reactions (hydrogen transfer and oligomerization), condensation and cyclization are enhanced, yielding more aromatic coke [35,36]. Due to the large super cage of FAU, these reactions are prominent as the reaction goes on. An evidence of coking is visibly seen in the way the spent catalyst is dark brown in color as compared to the fresh catalyst.

A high catalytic activity for FAU is evident after a study of the oligomerization reaction over FAU (Si/Al = 15) [37]. The production of 20 mM of C_{10} olefins by pentene oligomerization even at room temperature was a noteworthy factor during this set of

experiments. The selectivity toward the C_{10} olefins was 80%, with an absence of other products in the reaction vessel.

3.1.5 FER (Si/Al = 10) as catalyst for pentene oligomerization

Ferrierite, FER (Si/Al = 10), was another commercially available zeolite that was considered for the oligomerization reaction. FER, a two-dimensional pore system zeolite, displays excellent activity and stability even when its coke content approaches saturation [38]. Table 3-4 describes the analysis of products observed for the reaction over FER.

Table 3-5: Product distribution for pentene oligomerization catalyzed by FER (Si/Al = 10) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	305.5	0			
0	291.0	0.0	4.7	0.0	-
10	222.9	23.5	27.0	15.4	90.5
40	139.7	39.2	54.3	25.7	80.3
180	106.4	32.8	65.2	21.5	71.4
360	118.5	18.2	61.2	11.9	54.0

The maximum concentration of C_{10} olefins observed for the oligomerization reaction with FER as the catalyst was 39.2 mM after a period of 40 minutes. This was higher than any of the previously studied reactions over MFI, BEA* and MOR.
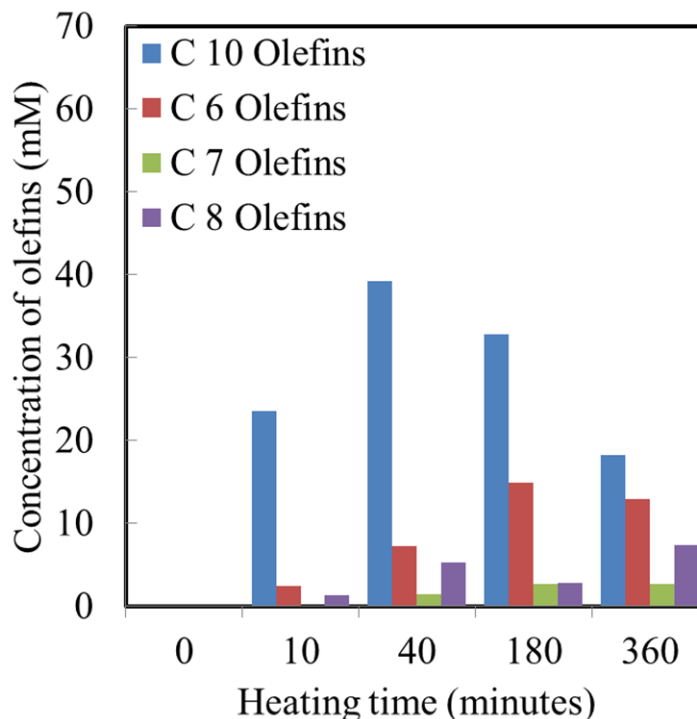
Figure 3-6: Effect of heating time on concentration of olefins for the reaction over FER (Si/Al = 10). $T = 200$ °C, $C_{\text{pentene,initial}} = 300$ mM, $m_{\text{zeolite}} = 7.8$ mg.

It is observed that the amount of C_{10} olefins increased for about 40 minutes before it declined till 180 minutes and onwards. The structure for FER was suspected to be much better for pentene oligomerization as compared to the previous studies. However, it must be noted that the selectivity toward the desired products was fairly low at all times. The low yield at longer duration indicates better cracking of the C_{10} olefins to give C_6 olefins as the primary by-products.

The increased cracking at longer heating times is due to the fact that the diffused pore size of FER is merely 1.56 x 4.69 A°. A sudden decrease in the concentration of C_{10} olefins is indicative of the cracking of C_{10} olefins to give $C_6 - C_8$ olefins. There is an expected increase in the concentration of $C_2 - C_4$ olefins as well, but these olefins cannot

be observed on the gas chromatogram because they are in gaseous state at room temperature. They cannot be injected into the GC from a batch reaction vessel.

3.1.6 Analysis of pentene oligomerization for different zeolites

The comparison of the yield of C_{10} olefins for different samples of zeolites highlights the best zeolite for the oligomerization of pentene.
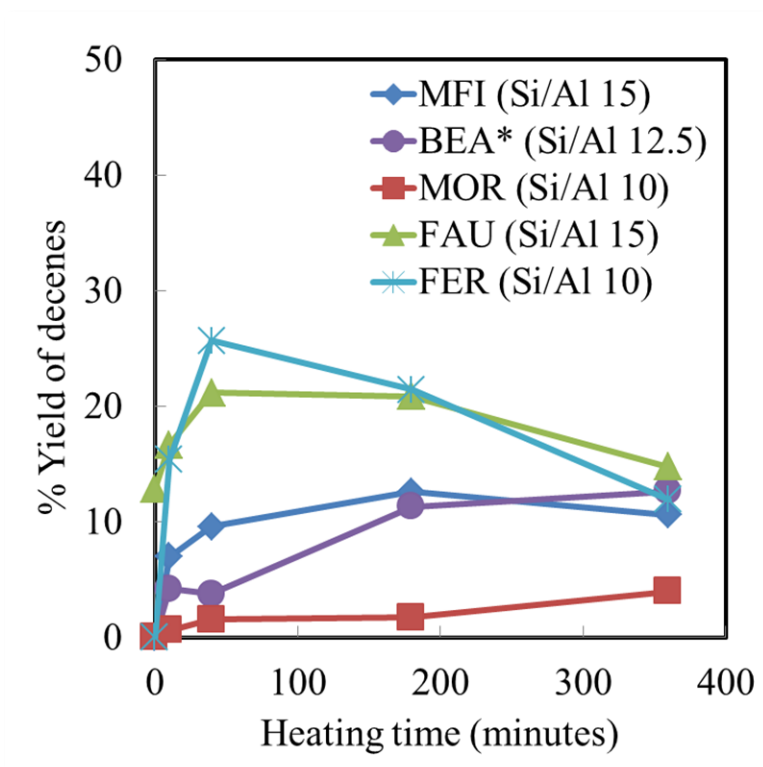
Figure 3-7: Percent yield of C_{10} olefins as a function of heating time for different samples of zeolite (Si/Al = 10-15). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = ~ 8 - 12 mg.

All of the zeolites studied for this reaction demonstrated a significantly low yield of C_{10} olefins. Of these zeolites, MOR was seen to be particularly better at cracking of the pentene molecules and further oligomerization of the lighter olefins. An exception to the

low yield of C_{10} olefins was observed over FER, which showed a high yield at short periods, although that drastically reduced for longer times.
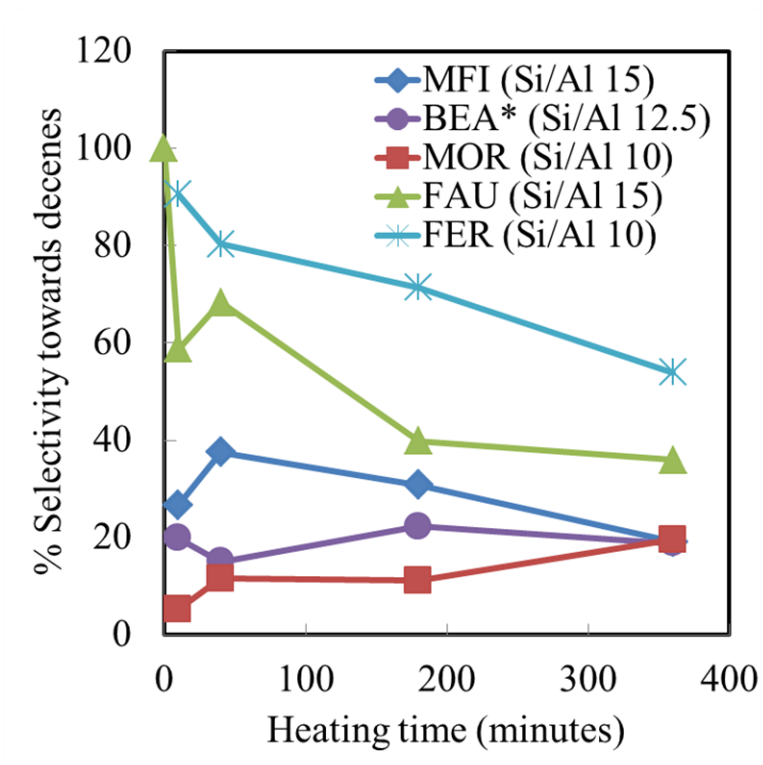
Figure 3-8: Percent selectivity toward C_{10} olefins as a function of heating time for different zeolite samples (Si/Al = 10-15). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = ~ 8 - 12 mg.

In all cases of oligomerization of pentenes over acid zeolites, it was observed that the selectivity toward the decenes reduced at longer periods of time. This was indicative of the cracking reaction taking place at the acid sites within the zeolite pores. As discussed earlier and from Figure 3-1, a number of side reactions were observed during the experiments. Some of these reactions include cracking of C_{10} olefins to give C_6 and C_4 olefins, or C_7 and C_3 olefins, or C_8 and C_2 olefins; oligomerization reactions of light olefins like $C_2 \rightarrow C_4$, $C_3 \rightarrow C_6$, and $C_4 \rightarrow C_8$. It is expected that the most likely product

from oligomerization of 1-pentene is linear 4-decenes as the primary product. As a result, cracking of 4-decenes leads to C_6 and C_4 olefins as primary products, as evident from the results (Figure 3-7). Due to the high activity of the acid sites of the zeolites, all the olefins in the reaction vessel undergo rapid isomerization leading to a number of branched olefins. Larger and more branched olefins are observed to be cracked easier than linear olefins because of the zeolite structures. As a consequence, a variety of C_5 to C_{10} olefins are observed on the chromatogram.
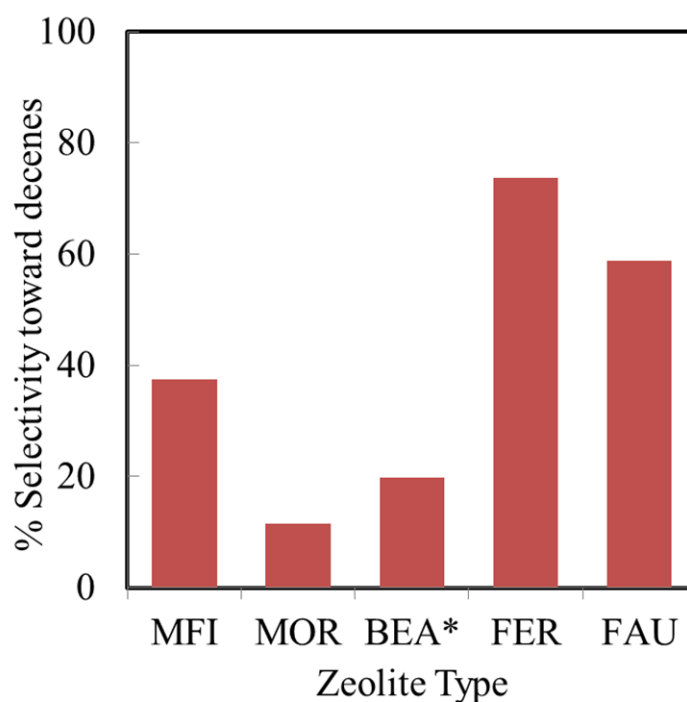
Figure 3-9: Percent selectivity toward C_{10} olefins at around 40% conversion of C_5 olefins. Selectivity for C_{10} olefins by oligomerization over MOR and FER was constant at 30% and 50% conversion. Selectivity at 40% conversion expected to be similar.

The selectivity toward C_{10} olefins over BEA*, MFI and MOR was extremely low, leading to note that these zeolites were not ideal for pentene oligomerization. It was observed that at a similar rate of conversion, the selectivity toward the C_{10} olefins was highest at around 40% for oligomerization over FER and FAU zeolites. This led to the point toward the fact that FER and FAU are the optimum for C_5 oligomerization to C_{10} olefins by catalysis over acid zeolites.

Another factor to be noted for the comparison of zeolites is the amount of coking that is observed in the case of each zeolite. Larger products that are deposited as coke within the zeolite pores are not analyzed by gas chromatography analysis because they are trapped within the pores and are not dissolved in the liquid phase. Coke deposition can be visibly observed in nearly every reaction, as fresh catalyst is white in color and develops a yellow or brown coloration, indicating the presence of coke.

3.2 Effect of Si/Al ratio of FAU on Acid Strength and Acid Site Proximity

The oligomerization of pentene over FER produced the maximum yield of C_{10} olefins, compared to reactions over all other zeolites. However, FER is commercially not available over a wide range of Si/Al ratios. FAU was the zeolite to produce the next highest yield of C_{10} olefins. FAU (Si/Al = 15) showed great promise toward the production of C_{10} olefins, with respect to yield and selectivity. It was decided to study the effect of silicon to aluminum ratio of faujasite by varying the number of Brønsted acid sites for a zeolite of same size and structure. Commercially available samples of zeolite

FAU Si/Al ratio of 2.6, 6, 15 and 40 were studied as catalysts for the oligomerization reaction. FAU with lower Si/Al ratios indicates closely situated, relatively weaker acid sites. Higher Si/Al ratios mean that the acid sites are much fewer per gram of the catalyst and are further apart, with each acid site being stronger. It must be observed that acid strength varies greatly at lower Si/Al ratios and much less at higher Si/Al ratios. Si/Al ratios higher than 10 have similar acid strengths for each acid site; however the average distance between the acid sites is decreased with an increase in aluminum content.

3.2.1 Analysis of pentene oligomerization over FAU with low Si/Al ratio

FAU with Si/Al = 2.6 was studied first for the oligomerization of pentene to yield decenes. The table shows the yield of C_{10} olefins, conversion of pentene and selectivity toward C_{10} oligomers over a heating time period of 0 to 360 minutes.

Table 3-6: Product distribution for pentene oligomerization catalyzed by (FAU Si/Al = 2.6) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	308.5	0			
0	178.6	3.1	41.7	1.8	100.0
10	118.7	15.0	63.0	10.1	36.8
40	122.7	15.3	61.2	9.9	35.6
180	92.9	10.6	70.2	7.0	30.4
360	108.1	13.6	65.0	8.8	31.6

The maximum concentration of C_{10} olefins was 15.3 mM after 40 minutes of heating. The concentration of the decenes gradually reduced slightly as the reaction vessel was heated for a longer duration.
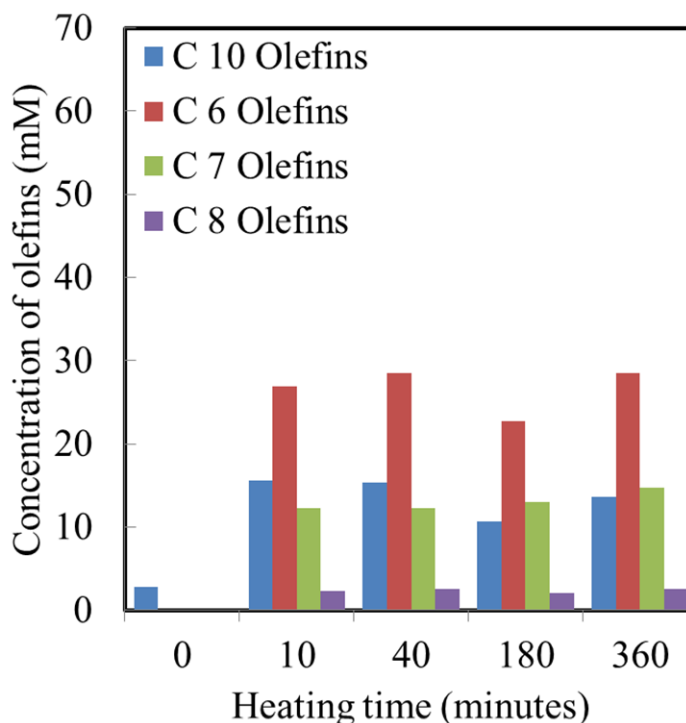
Figure 3-10: Effect of heating time on concentration of olefins for the reaction over FAU (Si/Al = 2.6). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 2.5 mg.

The yield of C_6 olefins was high for all reaction times, indicating a very low selectivity, in spite of a high conversion rate. The proximity of the acid sites, coupled with the high catalytic activity observed for the earlier reaction over FAU, is suspected to crack the pentenes to ethene and propene as opposed to oligomerization. These light olefins then further oligomerize, or react within themselves to give hexenes and other higher olefins. This is further reaffirmed by the low selectivity at 0 minutes, in spite of a high conversion. The pentene was consumed and cracked to lower olefins which are not

observed on the GC. As with the case with reaction over FAU studied earlier, FAU with Si/Al = 2.6 also indicates high activity, though in this case, it is more inclined towards cracking instead of oligomerization, because of the closely situated acid sites.

3.2.2 Analysis of pentene oligomerization over FAU with moderate Si/Al ratio

FAU with Si/Al = 6 has moderately separated acid sites with a reasonable acid strength for each acid site.

Table 3-7: Product distribution for pentene oligomerization catalyzed by FAU (Si/Al = 6) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	316.6	0			
0	140.47	14.5	55.6	9.1	100.0
10	234.61	25.6	25.9	16.1	69.8
40	146.47	38.9	53.7	24.5	61.7
180	112.28	41.5	64.5	26.2	64.8
360	114.26	46.5	63.9	29.3	56.5

The maximum yield of C_{10} olefins was found to be around 46.5 mM after 360 minutes, which is much higher than what was observed in any other previous reaction.

The concentration of decenes gradually increased throughout the period of heating, which was not observed in any of the previous cases of FAU as the catalyst.
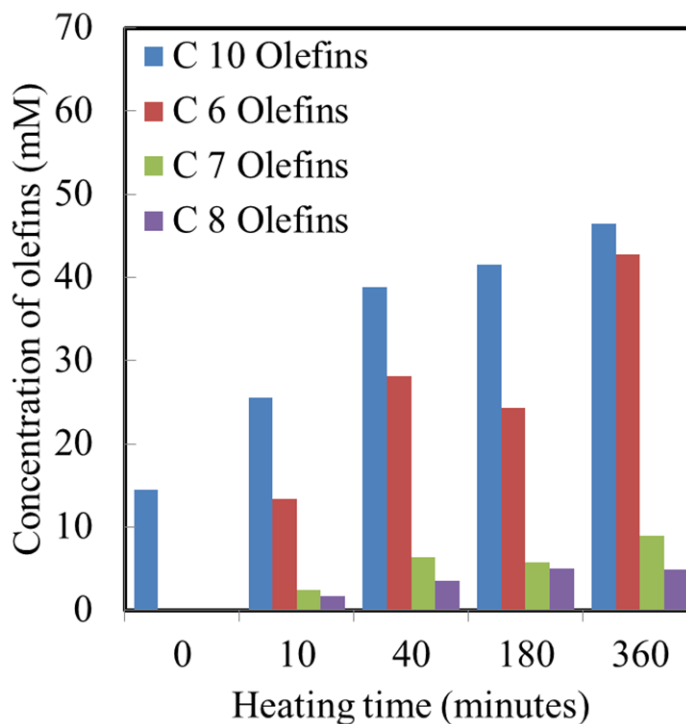
Figure 3-11: Effect of heating time on concentration of olefins for the reaction over FAU (Si/Al = 6). $T = 200$ °C, $C_{pentene,initial} = 300$ mM, $m_{zeolite} = 5$ mg.

As in the case with FAU (Si/Al = 2.6), an increasing yield of the desired product was accompanied by an increase in the concentration of hexenes. The C_6 olefins are likely produced by the cracking of the decene molecules to hexenes and butenes. Unlike in the case of oligomerization over FAU Si/Al = 2.6, the concentration of C_{10} olefins is much higher than that of the cracked products. This observation confirms that $C_6 - C_8$ olefins are formed by the cracking of decenes and not by oligomerization of $C_2 - C_3$ olefins. The concentration of heptenes and octenes remains fairly low for all times.

The moderate Si/Al ratio proved to be better for the oligomerization, without being too favorable for the cracking of the heavier olefins. An increase in the distance of the acid sites, without a significant decrease in the acid strength is indicative of an improved oligomerization of C_5 olefins. As discussed earlier, over time the cracking reaction dominates for all zeolites as catalysts. However, in this case, it is suspected that the favorable structure of FAU coupled with an optimum Si/Al ratio compensates for the cracking reaction with a continuous rate of oligomerization.

3.2.3   Analysis of pentene oligomerization over FAU with high Si/Al ratio

FAU (Si/Al = 15) and FAU (Si/Al = 40) are zeolites considered to have high silicon to aluminum ratio.

Table 3-8: Product distribution for pentene oligomerization catalyzed by FAU (Si/Al = 40) zeolite

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	321.3	0			
0	293.8	10.9	8.6	6.8	100.0
10	206.0	13.9	35.9	8.7	34.3
40	188.7	10.3	41.3	6.7	24.9
180	184.5	19.5	42.6	12.1	35.1
360	172.6	19.3	46.3	12.0	30.2

A maximum concentration of 25 mM of C_{10} olefins over FAU (Si/Al = 15) was observed after 180 minutes, as mentioned in the earlier section (Table 3-5). The reaction over FAU (Si/Al = 40) produced 19.5 mM of decenes after 180 minutes. The maximum concentration of C_{10} olefins observed for both these sets of reactions was fairly low compared to the 46.5 mM of C_{10} observed for FAU Si/Al = 6 as the catalyst (Table 3-7).

The results observed for both samples of FAU with high Si/Al ratio depict a similar trend. The selectivity toward C_{10} olefins is higher at very short times; and for longer heating times, the long chain olefins are cracked very rapidly to give C_6, C_7 and C_8 olefins.
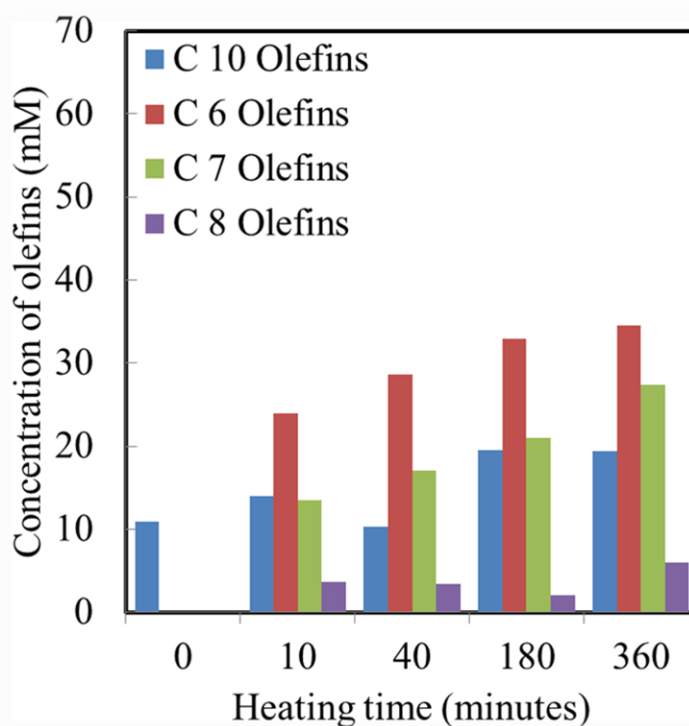
Figure 3-12: Effect of heating time on concentration of olefins for the reaction over FAU (Si/Al = 40). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 29.2 mg.

Having mentioned earlier, zeolites with Si/Al ratios of above 10 have a similar acid strength, this can be clearly seen with a similar yield in terms of value and trend for both FAU with Si/Al = 15 and 40. With greater distance between the acid sites, a number of side reactions were suspected to have occurred because of the increased space within the acid sites. Coking was thus observed to occur faster for FAU with high Si/Al ratios and a dark black colored zeolite was left behind at the end of the reaction.

3.2.4 Comparative study of the pentene oligomerization for FAU across wide range of Si/Al ratios

A comparative summary of all the samples of FAU with different Si/Al ratio, helped determine the FAU sample for which the maximum yield of the C_{10} olefins by pentene oligomerization was observed. The effect of heating time on the concentration and selectivity of C_{10} olefins was studied with a comparison of all the FAU samples.
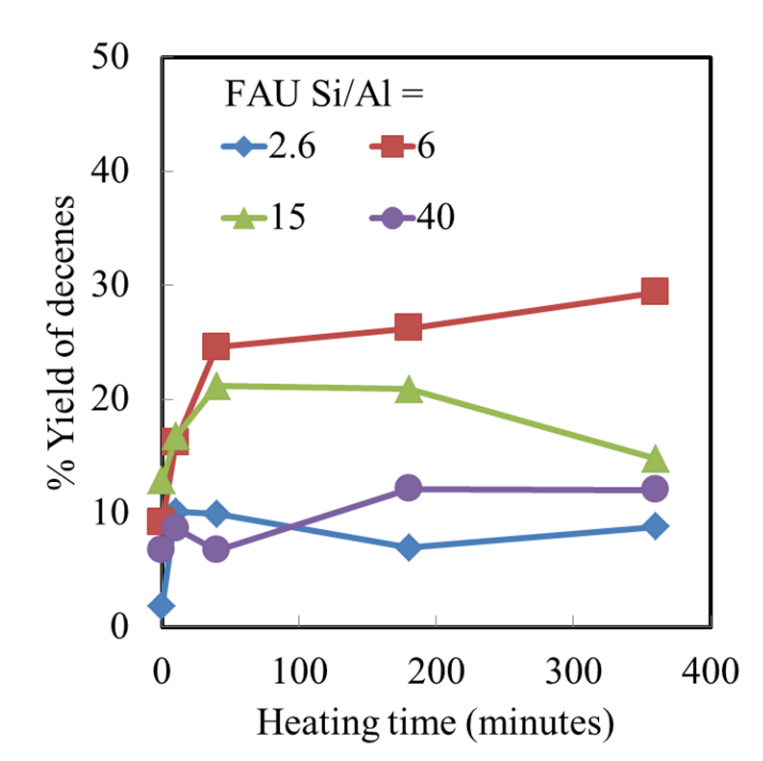
Figure 3-13: Percent yield of C_{10} olefins as a function of heating time over a wide range of Si/Al ratios of FAU. T = 200 °C, $C_{pentene,initial}$ = 300 mM. Mass of zeolite determined according to the Si/Al ratio to maintain constant number of acid sites in each set of reaction (~2.5 – 29 mg).

A comparison of FAU with Si/Al ratios between 2.6 and 40 indicated that a moderate ratio was best for the yield of C_{10} olefins over time. A large concentration of vastly undesired products were observed for low and very high Si/Al ratios, as evident from the graph of the selectivity towards C_{10} olefins as a function of time (Figure 3-14).

The primary reason for greater yield of C_{10} olefins over FAU with moderate Si/Al ratio is that the structure and the proximity of acid sites are favorable for the process. Closely situated acid sites tend to crack the C_5 olefins instead of oligomerization. Acid

sites that are farther apart tend to form heavy olefins through polymerization that clog the zeolite pores by coke deposition and cannot be analyzed by gas chromatography analysis.
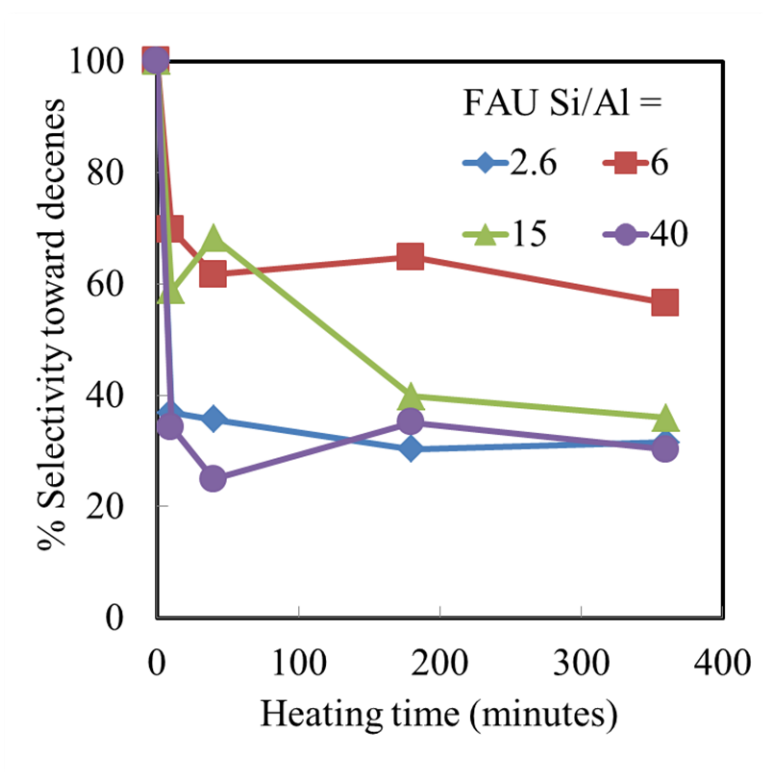
Figure 3-14: Percent selectivity toward C$_{10}$ olefins as a function of heating time for varying Si/Al ratios for FAU. T = 200 °C, $C_{pentene,initial}$ = 300 mM. Mass of zeolite determined according to the Si/Al ratio to maintain constant number of acid sites in each set of reaction (~2.5 – 29 mg).

However, even with a higher concentration of C$_{10}$ olefins observed with the reaction in presence of FAU (Si/Al = 6), the selectivity of the desired products reduced for longer periods of heating. This led to further experiments to attempt to improve the selectivity toward the C$_{10}$ olefins, without reducing the yield.

3.3 Catalytic Effect of Brønsted Acid Sites within the Zeolite:

3.3.1 Analysis of Substitution of Na^+ ions in FAU (Si/Al = 6)

In order to reduce the olefin cracking reaction, the effect of substitution of certain acid sites by Na^+ ions was studied [31]. The substitution of acid sites leads to an increase in the distance between the acid sites, without reducing the individual acid strength. Hence, with the acid sites sufficiently apart in the sodium substituted FAU (Si/Al = 6), the cracking of C_{10} olefins was to be avoided.

The first set of experiments was performed after one exchange of $NaNO_3$ with the NH_4-FAU (Si/Al = 6) by the method explained in section 2.4. The FAU with one exchange of $NaNO_3$ will be termed as Na/H-FAU 6 (single exchange).

Table 3-9: Product distribution for pentene oligomerization catalyzed by zeolite Na/H-FAU (Si/Al = 6) (single exchange)

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	297.9	0			
0	252.4	9.4	15.3	6.3	100.0
10	204.0	24.9	31.5	16.7	68.6
40	180.1	34.5	39.6	23.2	61.5
180	123.3	24.1	58.6	16.2	46.9
360	116.1	14.9	61.0	10.0	36.0

The second set of experiments was performed after an extra exchange of Na^+ ions from the previously exchanged FAU (Si/Al = 6). The FAU with two exchanges of $NaNO_3$ will be termed as Na/H-FAU 6 (double exchange).

Table 3-10: Product distribution for pentene oligomerization catalyzed by zeolite Na/H-FAU (Si/Al = 6) (double exchange)

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	320	0			
0	311.3	0.0	2.7	0.0	-
10	208.5	9.1	34.9	5.7	51.4
40	172.6	20.6	46.1	12.9	65.4
180	143.6	27.5	55.1	17.2	66.1
360	113.1	30.2	64.6	18.9	61.2

The results for the sodium-exchanged FAU as catalyst were compared with the earlier experiments for H^+-FAU 6 as the catalyst. The maximum amount of C_{10} olefins observed with one exchange of Na^+ ions for H^+-FAU was approximately 35 mM (after 360 minutes), and that observed over Na/H-FAU 6 (double exchange) was 30 mM (after 360 minutes). The concentration of C_{10} olefins was lower in both the cases, when compared to 51 mM in case of H-FAU (Si/Al = 6) as the catalyst (table 3-7).

With increase in substitution of Na^+ ions in place of the H^+ acid sites, it was expected that the concentration of C_{10} olefins would increase and the reaction would be

more selective toward the desired product. Contrary to the hypothesis, the selectivity toward C_{10} olefins reduced drastically for Na/H-FAU 6 (double exchange).
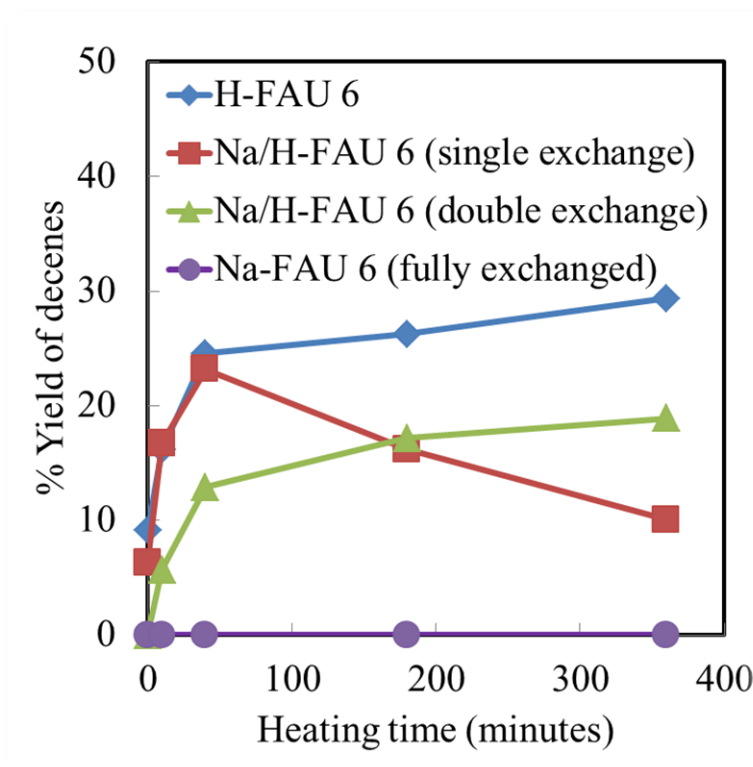
Figure 3-15: Percent yield of C_{10} olefins as a function of heating time for H-FAU and Na-exchanged FAU (Si/Al = 6). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 5 mg.

The mass of the catalyst for the reaction is kept constant for all three sets of experiments. Extra tests with regards to elemental analysis are required to accurately determine the number of H^+ acid sites substituted by Na^+ ions per gram of the zeolite. The reason for the reduction in the yield of C_{10} olefins for increased substitution of acid sites is suspected to be that the total number of acid sites in the reaction vessel reduces. Hence, a reduction in number of acid sites is expected with an increase in the number of sodium exchanges.
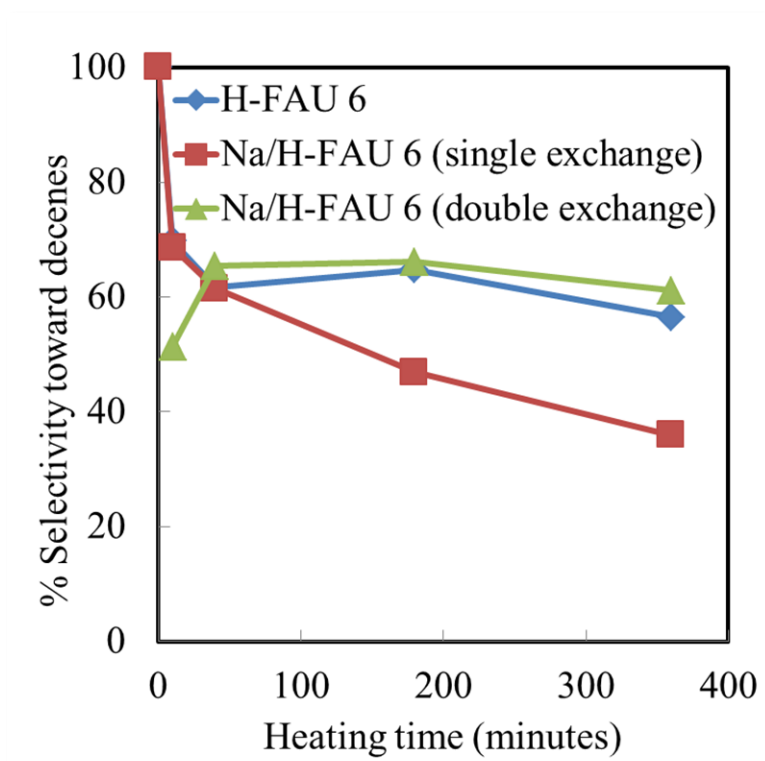
Figure 3-16: Percent selectivity toward C$_{10}$ olefins as a function of heating time for H-FAU and Na-exchanged FAU (Si/Al =6). T = 200 °C, $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 5 mg.

H$^+$ acid sites for FAU of Si/Al ratio of 6 were completely substituted by Na$^+$ ion by the method described in section 2.4 with an excess of NaNO$_3$. This ensured the complete absence of H$^+$ ions in the zeolite, effectively substituting all the acid sites in the zeolite. The table depicts the effect of substituting Na$^+$ ions for H$^+$ ions in FAU (Si/Al = 6). The mass of the zeolite for the reaction was maintained at 5 g, but this is an arbitrary quantity as the number of acid sites per gram of the zeolite is zero.

Table 3-11: Product distribution for pentene oligomerization catalyzed by fully substituted zeolite Na-FAU (Si/Al = 6)

Time (min)	Conc. of C_5 isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity of C_{10} oligomers (%)
Blank	308.5	0			
0	294.9	0	4.4	0	0
10	304.8	0	1.2	0	0
40	295.4	0	4.2	0	0
180	296.7	0	3.8	0	0
360	296.0	0	4.1	0	0

An absence of Brønsted acid sites indicates that there are no reaction sites within the pores of the zeolite. Hence, it is not possible for any reaction to take place in a zeolite that has been completely substituted with Na^+ ions. This is observed from the Table 3-11 as C_{10} olefins are not produced, nor is there any significant conversion of C_5 olefins. This phenomenon is discussed further in detail in section 3.3.2.

A very high Si/Al ratio (a complete absence of aluminum atoms within the zeolite) indicated that no reaction took place. This phenomenon coupled with the previous results for the oligomerization over a wide range of Si/Al ratio reiterated the effect of varying Si/Al ratio on any catalytic activity over a zeolite.

3.3.2 Analysis of Complete Substitution of Acid Sites in MFI

As mentioned previously, reactions over zeolites take place at the Brønsted acid sites located within the pores of the zeolite. Experiments were carried out to affirm this by substituting the Brønsted acid sites in the zeolite and study the effect on the pentene oligomerization. Two samples of the zeolite MFI – silicalite (Si/Al = 1000) and completely Na-exchanged MFI (Si/Al = 15) - were investigated for this purpose. A high Si/Al ratio of silicalite indicates the absence of any acid sites in the zeolite. Completely Na-exchanged MFI was prepared by using an excess amount of $NaNO_3$ for the sodium exchange experiment explained in section 2.4.

The concentration of pentene in the stock solution was 540 mM, compared to 300 mM in previous experiments. The mass of the zeolite was kept at 10 mg, but this is an arbitrary choice, as there are no acid sites in these two samples of zeolites. All other parameters were maintained the same as all earlier cases.

The table shows the concentration of C_5 and C_{10} olefins, along with a percent conversion. No other products were observed for the reaction. It clearly shows no production of C_{10} olefins, or any other products. The slight reduction in the concentration of pentenes is considered to be down to experimental error. As no reaction takes place in case of either of the zeolites in consideration, it can be concluded that Na^+ has no catalytic activity and that a zeolite with no acid sites (silicalite) and a zeolite with only Na^+ at the exchange sites behave the same.

Table 3-12: Analysis of products for silicalite (MFI – Si/Al = 1000) and completely exchanged Na-MFI

Heating Time (minutes)	Silicalite (MFI Si/Al = 1000)			Na-MFI		
	Conc. Of C_5 isomers (mM)	Conc. Of C_{10} oligomers (mM)	Conversion (%)	Conc. Of C_5 isomers (mM)	Conc. Of C_{10} oligomers (mM)	Conversion (%)
Blank	542.0	0		542.0	0	
0	538.7	0	0.61	522.6	0	3.58
10	536.6	0	1.01	514.3	0	5.11
40	533.3	0	1.61	513.7	0	5.23
180	524.2	0	3.28	512.6	0	5.43

3.4 Effect of Reaction Conditions

3.4.1 Effect of Temperature

Oligomerization over different zeolites and a wide range of Si/Al ratios has been studied as a function of time so far. However, it is known that the temperature of the reaction also has an effect on catalytic reactions over zeolites. The temperature was varied from 0 °C to 250 °C. The zeolite in consideration was FAU, with a Si/Al ratio of 6. The products were analyzed after a time of 40 minutes of heating. All other parameters were the same as in previous experiments.

Table 3-13: Production distribution for pentene oligomerization catalyzed by FAU (Si/Al = 6) with varying temperature

Temperature (°C)	Conc. of C_5 Isomers (mM)	Conc. Of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity Toward C_{10} oligomers (%)
Blank	316.6	0			
50	205.2	22.4	35.2	14.2	55.9
100	197.5	27.8	37.6	17.6	62.2
150	171.9	36.5	45.7	23.2	67.4
200	146.5	38.9	53.7	24.6	61.7
250	125.8	13.9	60.3	8.8	47.7

Beyond 250 °C, it is expected that the zeolite tends to aid cracking of the olefins more than any other reaction and hence that was the highest temperature studied for the reaction.
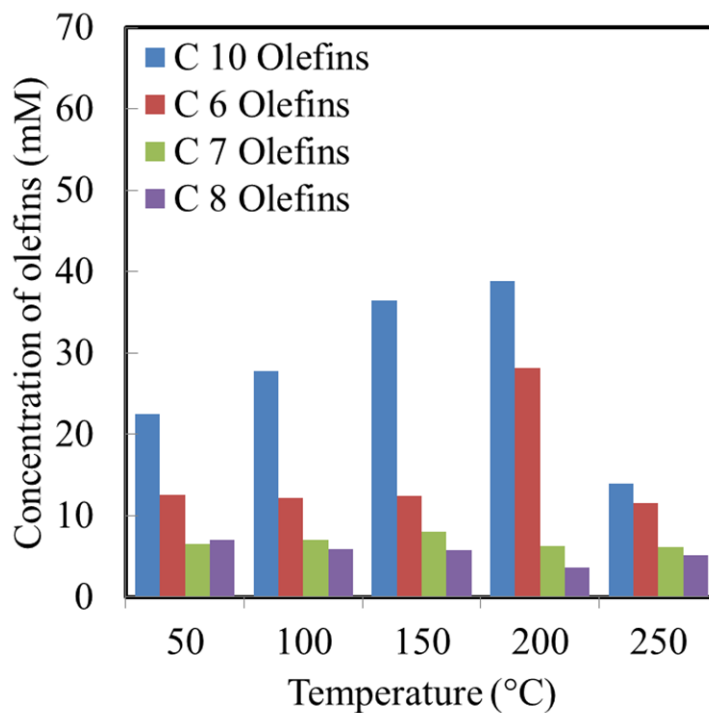
Figure 3-17: Comparison of concentration of olefins observed in the products as a function of temperature, after 40 minutes of heating. $t = 40$ **minutes,** $C_{\text{pentene,initial}} = 300$ **mM,** $m_{\text{zeolite}} = 5$ **mg.**

After a period of 40 minutes, the concentration of C_{10} olefins increased in direct proportion to the increase in temperature. The relatively high concentration of C_{10} olefins at lower temperatures (unusual in the case of zeolite-catalyzed reactions) is an indication of the highly active acid sites and the favorable structure of FAU. However, it can be seen that with an increase in temperature, there is a rise in the concentration of undesired products, an indication of the dominance of the cracking reaction at higher temperatures. Highly acidic acid sites in the zeolite cause the cracking reaction to be the primary reaction at higher temperatures. Hence, the selectivity toward the desired C_{10} olefins goes down.

3.4.2 Effect of Time at Room Temperature

There was significant catalytic activity by FAU, even at room temperature; hence, the oligomerization of pentene was studied at ambient temperatures (without heating) for longer durations as well. The reaction was investigated at up to 72 hours of activity at room temperature.

The zeolite studied for this reaction was FAU (Si/Al = 6) of 5 mg. All the other parameters were kept constant.

Table 3-14: Product distribution for pentene oligomerization catalyzed by FAU (Si/Al = 6) at room temperature

Time (min)	Conc. of C_5 Isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity Toward C_{10} oligomers (%)
Blank	316.6	0			
10	306.1	3.1	3.3	2.1	100.0
40	231.1	19.1	27.1	12.0	76.6
180	89.9	19.6	71.6	12.4	82.1
24 (hours)	100.4	19.6	68.3	12.4	61.0
72 (hours)	107.1	10.7	66.2	6.7	71.6

As observed from the table, it is evident that the oligomerization of pentene is rapid even at room temperature. It can be seen that at shorter durations, the selectivity

toward the desired products is high; it increases up to 180 minutes and is held relatively constant for the next 24 hours. This indicates that a certain amount of C_{10} olefins are formed, and at longer times, there is subsequent C_{10} olefins cracking and formation. C_5 olefins are consumed without further increase in the amount of decenes. This means that due to the limited number of reaction sites on the zeolite, there is an inhibition of the acid sites due to the product formation. Desorption of the decenes from these acid sites is slower than the absorption of pentenes on the sites.
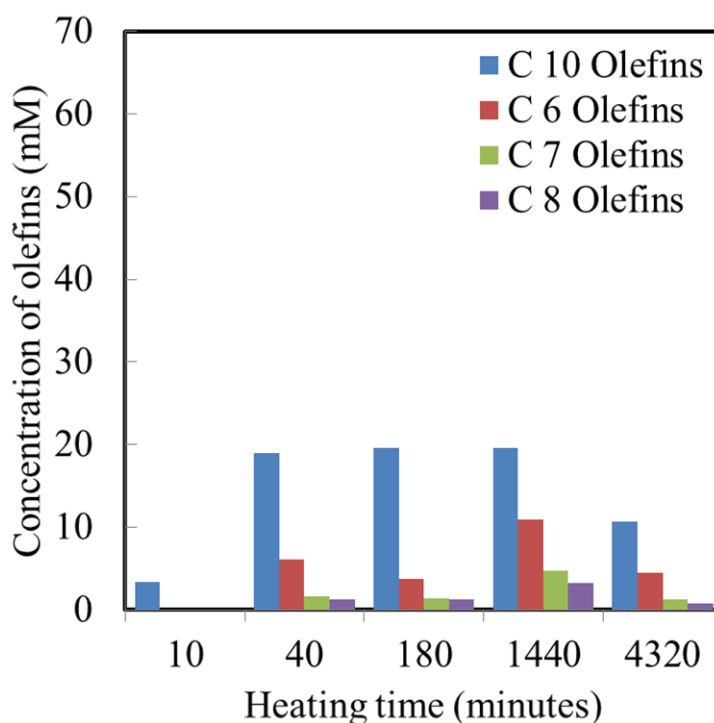
Figure 3-18: Comparison of concentration of olefins observed as a function of time for the reaction at room temperature over FAU (Si/Al = 6). $C_{pentene,initial}$ = 300 mM, $m_{zeolite}$ = 5 mg.

Over a period of 3 days, a reduction in the concentration of C_{10} and the other olefins is observed. It is believed that cracking of all the heavy olefins is observed and it is expected that there is a greater concentration of the lighter olefins not observed in the gas chromatograph. Overall, it must be noted that among all the commercial zeolites that have been studied for this project, FAU is an optimum zeolite for the pentene oligomerization reaction because of the high activity observed at room temperature and also the relatively high yield of C_{10} olefins under heating effect.

3.4.3 Effect of Pentene Concentration in Stock Solution

Stock solutions of 1-pentene in n-dodecane were prepared by varying the concentration of pentene. Pentene concentration was varied from approximately 200 mM to 540 mM. All the other parameters were the same as earlier reactions.

Table 3-15: Product distribution for pentene oligomerization catalyzed by FAU (Si/Al = 6) with varying initial pentene concentration

Time (min)	Conc. of C_5 Isomers (mM)	Conc. of C_{10} oligomers (mM)	Conversion (%)	Yield of C_{10} oligomers (%)	Atom Selectivity Toward C_{10} oligomers (%)
Initial	201.3	0.0	-	-	-
40	55.8	14.9	72.3	14.8	52.0
Initial	316.6	0.0	-	-	-
40	67.8	25.9	78.6	16.4	59.5
Initial	542.0	0.0	-	-	-
40	148.9	31.6	72.5	11.7	60.2

It can be observed that the concentration of C_{10} olefins increases with an increase in the concentration of pentene in the starting stock solution. Also, it must be noted that the percent conversion of pentenes, the yield of C_{10} olefins and the selectivity does not vary much (within experimental error). Thus, it can be deduced that the percent yield of the desired products does not depend on the starting concentration of C_5 olefins.
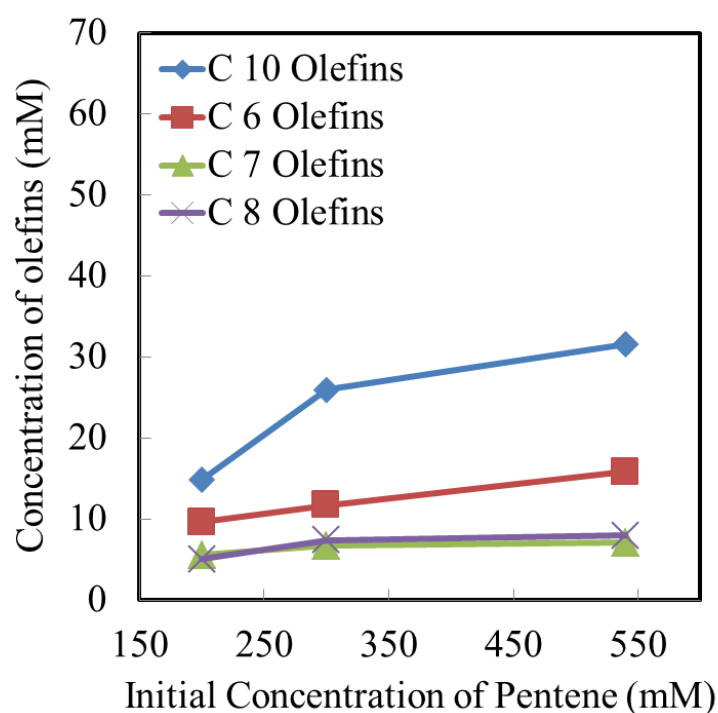
Figure 3-19: Comparison of concentration of olefins observed as a function of initial pentene concentration in the stock solution for the reaction over FAU (Si/Al = 6). *T* = 200 °C, $m_{zeolite}$ = 5 mg.

It must be noted that concentration of all the products in the reaction vessel increases close to linearly with a rise in the concentration of pentene in the stock solution,

further pointing to the fact that selectivity or yield of any of the products is unaffected by initial pentene concentration.

3.4.4 Effect of Zeolite Manufacturer

Zeolite samples were collected from Zeolyst International and Clariant Catalysts. Zeolyst sample MFI of Si/Al ratio = 15 and Clariant sample MFI of Si/Al ratio = 13.5 were the two catalysts considered for the reaction. The table below compares the results observed from the oligomerization over the two samples of zeolites.

Table 3-16: Product distribution for pentene oligomerization catalyzed by MFI zeolites from Zeolyst (Si/Al = 15) and Clariant (Si/Al = 13.5) manufacturers

Time (min)	Zeolyst MFI (Si/Al = 15)			Clariant MFI (Si/Al = 13.5)		
	Conversion (%)	Yield (%)	Atom Selectivity (%)	Conversion (%)	Yield (%)	Atom Selectivity (%)
0	6.8	0.00	-	5.8	0.00	-
10	26.6	5.9	26.7	31.2	6.5	25.7
40	39.7	9.6	37.5	36.9	9.0	28.0
180	55.2	12.6	30.8	44.2	14.4	37.5
360	57.4	10.6	19.1	50.4	13.9	31.4

It is observed that the maximum yield of olefins over Zeolyst MFI is 12.59 % and that over Clariant MFI is 14.4 %, both after a period of 180 minutes. The selectivity and yield both declined after that time, an indication of the cracking reaction dominating over the oligomerization at extended periods of heating. No reaction was observed at room temperature over both zeolites.
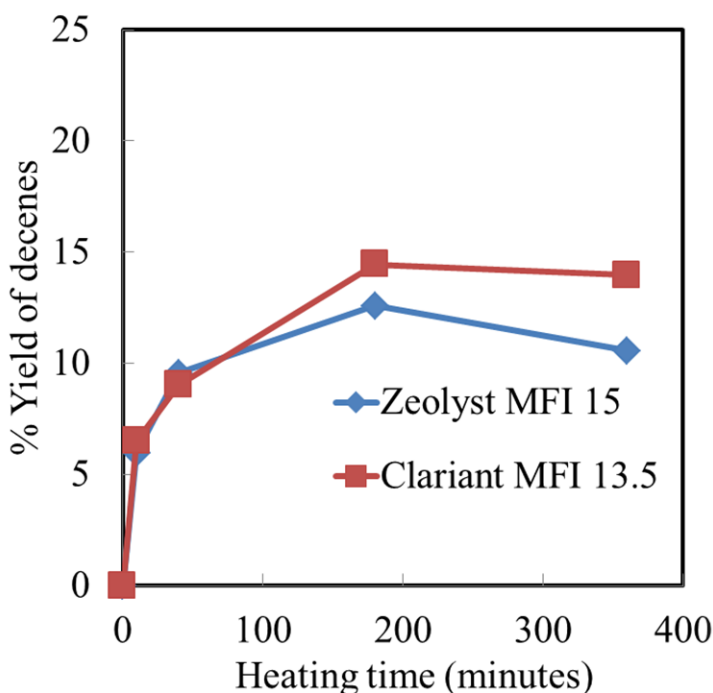
Figure 3-20: Comparison of yield of olefins as a function of heating time for reaction over MFI zeolite from two manufacturers – Zeolyst (Si/Al = 15) and Clariant (Si/Al = 13.5). T = 200 °C, $C_{pentene,initial}$ = 300 mM.

It can be observed that the conversion of C_5 olefins, yield of C_{10} olefins and selectivity toward the desired C_{10} olefins followed a similar trend for both the samples of zeolites. This was an indication that zeolite activity does not depend on the manufacturer

but on the zeolite structure and the acid sites in the pores of the zeolite, as discussed in previous sections.

Chapter 4: Summary and Future Scope

4.1 Summary

The pentene (C_5 olefins) oligomerization reaction, to give decenes (C_{10} olefins), was studied as a comparison over five different commercially available types of zeolites – MFI, BEA*, MOR, FER and FAU. It was noticed that MOR, because of the high catalytic activity environment of the smaller 8-MR channels, predominantly cracked the pentene to give light olefins (C_2 and C_3) and then aided to oligomerize these lighter olefins to give butenes and hexenes as the primary reaction products. MFI and BEA* possess a similar structure and channel system and a comparable catalytic activity toward the reaction was observed over both these zeolites. It was seen that the yield of C_{10} olefins over both the zeolites was not very high, accompanied by a low selectivity toward the decenes. This was on account of cracking of C_{10} olefins (4-decenes, in particular) to give large amounts of C_6 and C_7 olefins. Hexenes have the highest yield in the undesired by-products for the pentene oligomerization reaction. Due to rapid isomerization of all olefins (pentenes and decenes), however, C_7 and C_8 olefins are also observed. The yield of C_{10} olefins was very high for the oligomerization reaction over FER at very short times. But at longer durations, the yield and the selectivity both dropped very low because of the cracking of the C_{10} olefins; this led to a very rapid cracking reaction and a much slower oligomerization. The reaction over FAU showed that the yield of C_{10} olefins was high as well, and there was significant activity even without heating. The high oligomerization activity in presence of FAU, along with a decrease in selectivity over time caused great interest in the catalytic activity of FAU and warranted further study.

The effect of silicon to aluminum for FAU toward the yield and selectivity of C_{10} olefins was studied in the second part of the project. The Si/Al ratio of 2.6, 6, 15 and 40 for FAU were considered. FAU with very low Si/Al ratio showed a very low yield of C_{10} olefins. This was because of the closely situated Brønsted acid sites which effectively crack the pentenes to give lighter olefins. FAU with high Si/Al ratio showed a significantly great yield of C_{10} olefins, but it was insufficient. Along with a low selectivity toward decenes, it was deemed that FAU with higher Si/Al ratio were not good enough for the oligomerization reaction. FAU with Si/Al = 6 showed a considerably very high yield of C_{10} olefins, more than any other previous reactions. The moderate silicon to aluminum ratio indicates that the acid sites are at the right distance, along with the sufficient acid strength for each acid site.

While the yield of C_{10} olefins was high for the oligomerization reaction over FAU with Si/Al = 6, the presence of a host of other undesired products reduced the overall selectivity toward C_{10} olefins. It was attempted to improve the selectivity of the decenes by increasing the distance between the acid sites by replacing some of the H^+ ions by Na^+ ions, effectively deactivating the acid sites. However, it was observed that there was no significant increase in the selectivity of decenes. Instead, the yield and selectivity decreased for each exchange of sodium ions for the FAU 6.

Further reactions were studied by varying certain other parameters like the temperature for heating the reaction vessel and the concentration of pentene in the starting stock solution. It was noticed that for temperatures lower than 200 °C, there was a good yield of C_{10} olefins, and also less of the undesired products. However, with an increase in temperature to about 250 °C, there was excessive cracking of the olefins to

give multiple other products. This was expected as zeolites are very good catalysts for cracking reactions at high temperatures. As decene oligomerization was observed for FAU 6 as the catalyst even without any heating of the reaction vessel, this aspect was studied further. It was observed that there is a maximum of the amount of decenes that are produced till 40 minutes, and thereafter, the reaction reaches equilibrium. By varying pentene concentration in the stock solution, it was seen that there was an increase in product concentration of decenes and other by-products as well. However, it had no direct impact on the percent yield of decenes or the percent selectivity.

4.2 Future Scope

As described earlier, pentanes (C_5 alkanes) and pentenes (C_5 olefins) are major by-products of the crude oil cracking process in the petroleum industry. The overall objective of this project included converting C_5 olefins to higher C_{10} olefins, which are more useful compounds. The aim for research could be broadened for future prospects to include a one-pot conversion of pentanes to higher decanes (C_{10} alkanes), by alkane dehydrogenation, olefin oligomerization and consequent breaking of the double bond (catalytic hydrogenation of alkenes) [39], all in tandem. This research could potentially be ground-breaking for the petroleum industry to convert unnecessary by-products to useful compounds or precursors.

Research can be undertaken for the oligomerization of pentenes over other zeolites or other catalysts as well. As it was observed, zeolites with greater pore size (FAU) gave relatively higher yields of C_{10} olefins, certain zeolites that are not

commercially available but have a similar pore size and structure to FAU can also be studied. One example of such a zeolite is LTL. Other catalysts such as mesoporous aluminosilicates have previously been studied for oligomerization of lighter olefins. These catalysts have pore sizes larger than that of regular zeolites and hence could potentially be really good for the oligomerization reaction. Some examples of mesoporous aluminosilicates include MCM-41 and MCM-48. The oligomerization of C_5 olefins over Ferrierite (FER) produced a very good yield of C_{10} olefins. However, as explained earlier, FER over a wide range of Si/Al ratios is unavailable commercially. FER of varying Si/Al ratios can be synthesized in the lab, and these FER samples can then be studied for the oligomerization.

These are some of the broad research topics for future work for the oligomerization of pentene reaction.

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