Alkylation of Isobutane with Light Olefins Using Mesoporous Superacidic Catalysts

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Abstract

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Philip Kletnieks

A new type of solid catalyst for use in alkylation of isobutene has been developed using a mesoporous support, MCM-41 loaded with an organic superacid, trifluoro methanesulfonic acid (triflic acid). The state of the acid in the pores, catalytic activity and characterization has been studied for this catalytic system.

The organic acid has been found to exist in an adsorbed state within the support as well as in a "free" form without a significant association with the surface. The activity of the catalyst during alkylation reactions has been found to be much improved over traditional solid acid zeolite catalysts. The mechanism by which the reaction proceeds is consistent with liquid phase reactions invoking carbocation based mechanisms and a relatively new type of reaction, self alkylation, appears to be occurring in the reactions. Isobutene delivers much higher conversion levels compared to the linear butenes due to carbocation stability considerations. 1-butene however yields higher than expected selectivites for octanes compared to 2-butene. This phenomenon has been related to the self alkylation regime.

The catalyst possesses very high surface areas but exhibits some structural collapse as a result of the acid loading. Thermal analysis data has also shown that significant coke deposits begin at reaction temperatures above 200^{0}C.

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Chapter 1

1.1 Literature Review of Alkylation

The dependence of the world's population on products derived from petroleum and its by-products is observable in many facets of our daily lives. Petroleum and petroleum derived products are the basis for synthetic fabrics, adhesives, plastics, and of course fuels. Oil, as it is removed from the Earth is not fit for use in any of these ways and must first be treated and distilled into various fractions which can then be further refined to be used in the above mentioned products. In the general case of fuels, the usual route followed from crude oil to a useable final product involves many steps. A portion of the distilled hydrocarbons in a refinery distillation column contains paraffins which can be used as a fuel in combustion engines. This fraction usually ranges from 5 carbon to 10 carbon molecules and is used in conjunction with various additives to produce fuels with acceptable octane ratings. These hydrocarbons have been mixed with various additives in the past such as tetra ethyl lead (TEL), methyl t-butyl ether (MTBE) as well as benzene and other aromatics. These all have the ability to improve the octane rating of a fuel by providing a more stable combustion. This is achieved by scavenging radicals in the fuel/air mixture as it burns and hence a higher octane number is possible by reducing the production of free radicals which lead to uneven and premature combustion.[1] The one drawback to using these additives is the potential toxicity issue. Specifically, soil contamination and nervous system toxicity effects from lead in TEL [2], carcinogenic properties of aromatic compounds emitted in the exhaust of vehicles and more recently ground water contamination by

MTBE.[3] These concerns have lead to the elimination or proposed elimination of all of these additives in the United States. With increasingly stringent regulations on the content of transport fuels the petroleum industry has been under pressure to develop methods to produce fuels which exhibit good combustion properties without the use of additives. Iso-octane or 2,2,4-trimethylpentane (herein referred to as 2,2,4-TMP) is arbitrarily chosen to have an octane rating of 100 and is an excellent molecule to use as a blending component in fuels. This table contains a list of hydrocarbons and their corresponding RON (Research Octane Number) and MON (Motor Octane Number). [4,5] MON and RON are quantities to express the anti knock properties of a molecule upon combustion in an engine. The difference being that RON is tested under higher engine compression ratios than MON. The octane numbers are improved when the molecule contains higher branching as in the TMP series. As comparison, 2-methyl heptane is much lower although the number of carbon atoms is the same and 2,3-dimethyl hexane is better still. N-octane which is completely linear has very poor octane numbers reaching below zero.

Compound	MON	RON
2,4-dimethyl hexane	70	65
2-methyl heptane	13	33
2,2,3-trimethyl pentane	99.9	109.6
2,3,3-trimethyl pentane	99	106
2,2,4 trimethyl pentane	100	100
2,3,4-trimethyl pentane	96	103
n-heptane	0	0

Table 1.1

Octane numbers for various hydrocarbons

2,2,4 TMP exhibits low Reid vapour pressure, high octane number and as such does not cause engine knock, a symptom of using low octane fuel which is caused by premature combustion. This being the case, it only makes sense that to improve the octane rating of fuels without using additives it would suffice to produce more 2,2,4-TMP and add it to the gasoline pool in place of additives. An even more interesting proposition would be to be able to synthesize this product from easily available compounds which do not have a high demand in the world market. This would allow the transformation of compounds that the refiner would not have much use for into a product that has immense utility. This takes us to the present state of alkylation in industrial settings. To better understand this process and it's implementation in a refinery it is logical to look at the chemistry behind it as well as the current technology in use in industry to perform this reaction.

1.2 The Chemistry of Alkylation

Fundamentally, alkylation is a term applied to any reaction which involves the addition of an alkyl group to other molecules. For the case of alkylation, in the petrochemical sense of the word, isobutane is made to react with an olefin under acidic conditions. The olefin used can in fact be any number of molecules depending on what products are desired and which ones are available but typically consist of one of the following; propylene, 1-butene, isobutene and the cis/trans isomers of 2-butene. The reaction requires an acid catalyst and the easiest mechanism to invoke in following the alkylation reaction is that of the classical carbocation type. So, we begin with the reactants, which for the sake of simplicity will be isobutane and 2-butene. We also require an acid to catalyze the reaction. The reaction can be represented in a cyclical fashion to better depict the relation between the various intermediates and reagents. [6]

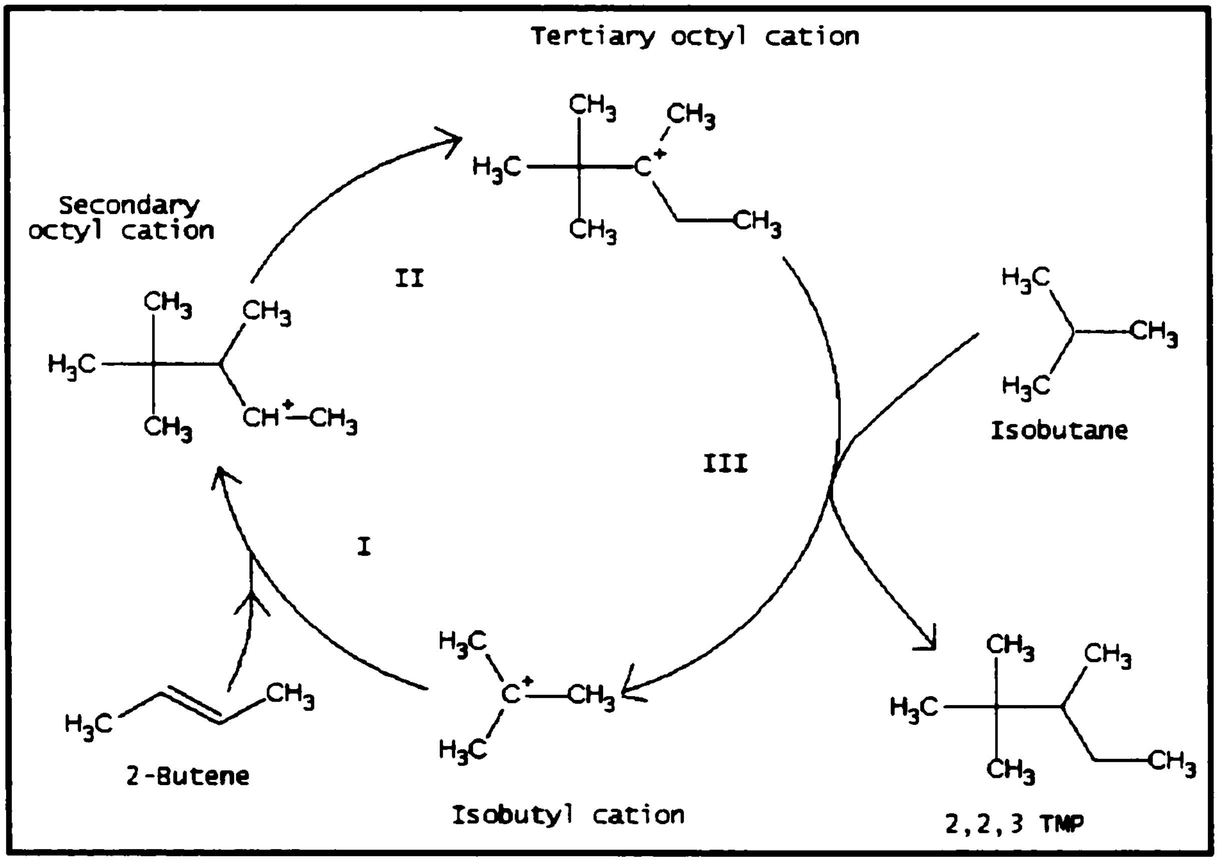


Figure 1.1
Alkylation reaction mechanism

This simple mechanism shows the steps required for the production of the 2,2,3 TMP molecule. There are 3 main steps here.

Step I

This step is the actual alkylation step in the reaction because it leads to the first C8 intermediate, the secondary 2,2,3 trimethylpentyl cation.

Step II

A secondary carbocation is formed and it can react through an intra-molecular hydride transfer to form the tertiary carbocation.

Step III

The tertiary carbocation now undergoes hydride transfer to obtain the actual 2,2,3 TMP product. This will occur by the attack of an isobutane molecule on the trimethylpentyl cation through the tertiary C-H bond. This step then forms the expected 2,2,3 TMP as well as forming a new isobutyl cation which completes the cycle.

The cycle above accounts for the formation of 2,2,3 TMP in an alkylation reaction but one shortcoming of this mechanism is that it fails to account for many other products formed during the reaction. If this was the only reaction, 2,2,3 TMP should be formed exclusively although in reality the product distribution of an alkylation reaction typically shows at least 6 major C8 components and a number of smaller and larger alkanes. To understand why this is, it needs to be emphasized that the olefin feedstock is a mixture of the 4 carbon olefins and under acidic conditions these can undergo isomerization reactions resulting in a mixture of the 4 carbon olefins in a ratio governed by the thermodynamic equilibrium. If the reaction cycle were to be done using isobutene it is clear that indeed 2,2,4-TMP would be formed and so we can see that the alkylation reaction is capable of producing various types of 8 carbon products depending on the feedstock and the amount of isomerization going on. However, this still does not answer for the molecules which are smaller or larger than eight carbon atoms. There are other reactions that occur which will alter the product spectrum from that predicted by the mechanisms. As they are secondary reactions, the products are a variety of C5, C6, C7 and C9s.

Since there are many products and reagents in the reaction medium during an alkylation reaction it is to be expected that side reactions will also occur. In fact this is the case, alkylation reactions result in the formation of products other than the 8 carbon TMP type. The reaction cycle for the production of 2,2,3 TMP does not include the pathways for any products other than the one observed. Even if we were to predict the product distribution using all possible 4 carbon olefins we would still not be able to explain the presence of many of the products in the product spectrum. The reason for this is that the actual alkylation where 2 molecules join together is only one of many complex and inter-related reactions occurring. What we really have in this reaction is a subset of competing reactions which reduce the eight carbon product yield by producing lighter and heavier products. [7]

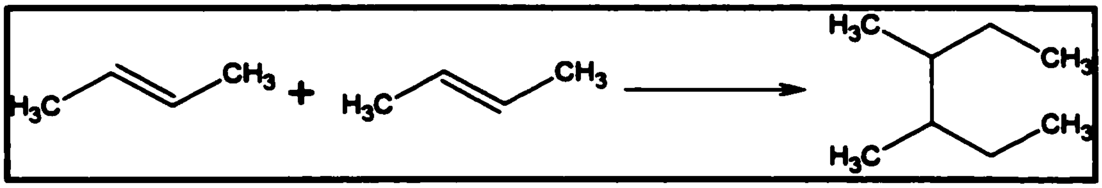
Primary Reactions	Secondary Reactions
Alkylation	Methyl shift
Isomerization	Oligomer cracking
Oligomerization	Disproportionation

Table 1.2

Reactions occurring in alkylation reactions

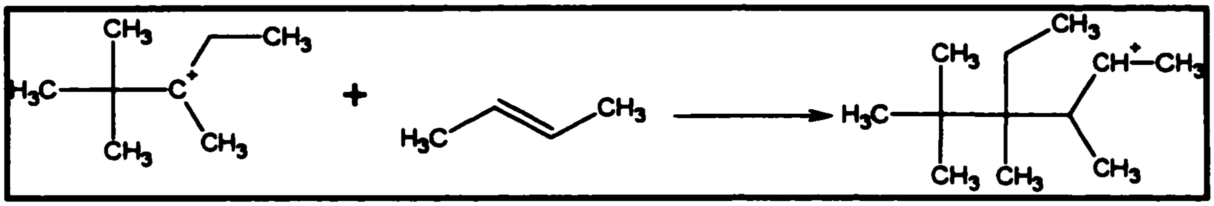
The reactions involved in the formation of these other products are most often dimerization, oligomerization, cracking and disproportionation. These reactions all result in a loss of C8 product yield and are considered detrimental to the process. The reactions can be briefly outlined. [8]

Dimerization



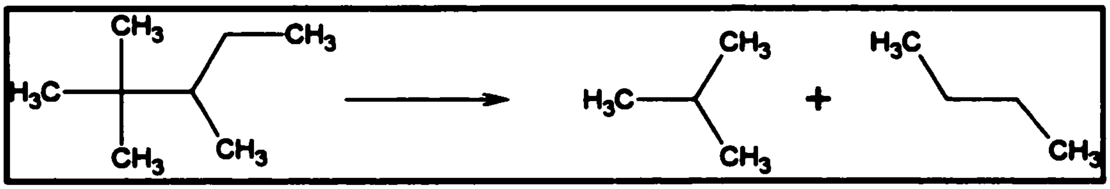
Now, it seems that this is in fact a beneficial reaction to have occurring due to the formation of a C8 molecule. While this may be true it does present an important problem in alkylation. The goal of the process is to react one molecule of isobutane with one molecule of olefin to form products. In this way, isobutane will be consumed in the reaction and the products thus formed will have good octane ratings due to the branched nature of the isobutyl group. When dimerization occurs, the reactants are both olefin molecules and the products will have a lower octane rating due to less branching in the molecule. The main points are that dimerization reduces the isobutane consumption and as a result produces lower quality alkylate. It is obvious that this side reaction will decrease the efficiency of the reaction.

Oligomerization



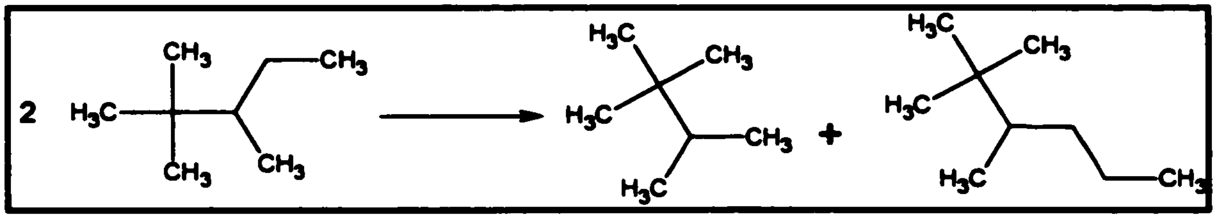
Oligomerization can be considered as a sequential alkylation on a formed C8 cation. This produces larger products of the C12 variety and higher which becomes particularly problematic due to reasons to be mentioned later.

Cracking



Cracking is quite simply the scission of a large molecule into a two smaller ones. In alkylation it can mean the cracking of a C8 product molecule back into many kinds of fragments or also the cracking of oligomers such as a C12, C16, C20 etc... Clearly this is not a beneficial reaction to have occurring.

Disproportionation



Disproportionation is a slightly more complex version of cracking where two C8 molecules can react together to form a lighter product and a heavier product. [9]

Previously, it was stated that the formation of larger products is problematic and indeed this is so, not only because it reduces yields but also because it precedes the deactivation of the catalyst by producing carbonaceous deposits commonly termed "coke". If we take the case of oligomerization to an extreme level where molecules are successively made bigger and bigger through addition of olefin molecules we would end up with enormous hydrocarbon molecules. Now, this is normally a problem which is not very serious in industrial settings since, in that situation, the reaction is done in the liquid phase and large molecules are free to diffuse through the reaction mixture. Where this does become more acute is in the case of solid acid catalysts where pore size constraints can lead to these large molecules becoming trapped in the structure of the solid and thus blocking the acid site from being attained by further reactants. Once the acid sites are blocked no further reactants can diffuse into the pores to react and the conversion level will fall off dramatically. [10] This coking phenomenon will be important in explaining some of the trends in the catalytic data for zeolite catalysts.

Having reviewed the general chemistry of the acid catalyzed alkylation reaction from reactant conversion, mechanisms, side reaction and briefly, deactivation, the means of carrying out this reaction in an industrial plant will now be considered.

1.3 Alkylation in Industry

Alkylation is an attractive process to the petroleum industry for it allows the isobutane produced as a fraction in distillation to be mixed with some light olefins to produce gasoline grade hydrocarbons. The reaction is acid catalyzed and the simplest way to get this acidity is to use a liquid mineral acid as catalyst and then introduce the reactant streams with careful mixing under appropriate conditions. The acids traditionally used industrially are concentrated sulphuric acid and hydrofluoric acid. Both of these are very strong acids and have been used for quite some time in alkylation processes. The use of sulphuric acid is at the heart of the Exxon sulphuric acid technology. [11] This process involves many steps but can be simplified to the following main points. Reactants, acid and refrigerant are introduced into the reactor system. This solution is thoroughly mixed and alkylate is formed. Heat is also released during the reaction and is removed by evaporating isobutane present in the reactor which is subsequently condensed and recycled back to the reactor as refrigerant. The solution containing the product alkylate is then routed to a settler where acid is separated and sent back to the reactor as well. The hydrocarbon stream is corrosive and is washed with water before being sent to the de-isobutanizer. The distinguishing characteristics of the process parameters are high isobutane concentration, low space velocities and low temperature. These are all to maximize octane rating of the product and to minimize cost.

The use of hydrofluoric acid is the basis of UOP HF alkylation technology. The concept here is similar to the Exxon process with the main difference being the type of acid used. Essentially the reactants are mixed as in the sulfuric acid process but here the cooling is accomplished via heat exchangers as opposed to condensed isobutane. Both processes enjoy widespread use worldwide and account for the vast majority of alkylate produced annually. [12]

The product distribution of both liquid phase reactions are presented from industrial reactions using liquid phase conditions. The reactants here are a mixture of all the C4 alkenes as used in industrial conditions.

Compounds (% vol.)	Sulfuric	Hydrofluoric
2,2,4-Trimethylpentane	24.2	38.02
2,2-Dimethylhexane	0.04	0
2,4-Dimethylhexane	2.89	4.19
2,5-Dimethylhexane	4.94	3.57
2,2,3-Trimethylpentane	1.53	1.35
3,3-Dimethylhexane	0	0
2,3,4-Trimethylpentane	13.15	9.63
2,3-Dimethylhexane	3.41	4.9
4-Methylpentane	0	0
2-Methylpentane	0.08	0.09
2,3,3-Trimethylpentane	11.47	8.14
3,4-Dimethylhexane	0.26	0.59
3-Methylheptane	0.23	3.2

Table 1.3

Composition of C8 fraction in liquid acid catalysis

The table includes all observable C8 isomers from the two reactions. [13] The most useful trimethylpentane isomers make up the majority of this fraction indicating that pure alkylation occurs with few side reactions. In the sulfuric acid reaction the TMPs make up 72% by volume of the C8s. Hydrofluoric does better at 77% and it has a higher overall conversion to C8s as well at 57% compared to sulfuric acid which has 30%. These methods offer excellent alkylate selectivity as well as high octane products but there are drawbacks to using reactions catalyzed by liquid acids.

1.4 Drawbacks of Current Industrial Processes

It seems that using the current technology available to undertake alkylation plants is a perfect answer to the question of how to cope with the demand for higher alkylate quantity, lower RVP, and higher octane fuels with an end of removing additives from transport fuels. However, upon closer inspection the sulfuric and hydrofluoric acid methodologies present several problems. The most severe issue is the toxicity associated with these acids. Clearly, using very large quantities of these acids is a dangerous proposition from a transportation point of view as well as a handling point of view. Moving around many tons of acid is a risk and a spill of such a volume of acid will have serious consequences. The reaction itself produces acidic hydrocarbon residues arising from partial solubility of the acid in certain oils formed in the reaction that must be disposed of and these residues are also exceedingly toxic. The final concern is one related to cost. To run these reactors requires a constant input of fresh acid to maintain a constant concentration. Failing to do so will result in a decrease in the octane number of the product. So, it is obvious that there are several difficulties in dealing with alkylation catalyzed by these acids.

Chapter 2

2.1 Research Work and Thesis Presentation

The research into alkylation encompassed by this project is aimed at finding alternative ways to produce a high quality alkylate product using catalysts which have the requisite acidity but do not have the problems tied to conventional liquid acid catalysis in alkylation. Having enumerated the hazards of H_2SO_4 and HF based reactions as well as observing the beneficial properties of these reactions the following criteria may be proposed as the requirements for a new viable alkylation catalyst.

1) The catalyst will be able to provide activity and selectivity surpassing that of the present processes.
2) The catalyst will not require continuous fresh catalyst input to maintain catalytic performance.
3) The catalyst will not form hazardous by products.
4) The catalyst will not pose a threat during transportation and handling throughout the plant.

The goal of this project is to develop a catalyst which meets these requirements. This entails finding a way to use the acidity available in liquid acids and some how eliminating the negative aspects so that the new catalyst adheres to these requirements. This project has looked in detail at many solutions to this complex problem. Generally speaking this work has focused on 2 main ideas, zeolite catalysts and mesoporous silica based catalysts. In the next chapter both types will be explained in detail including their behaviour under alkylation conditions, their physical properties and their chemical properties.

2.2 New Concepts in Alkylation Technology: Zeolite Based Catalysts

The petroleum industry makes routine use of catalysts for a wide array of reactions. One type ubiquitous throughout are the zeolites. Zeolites are inorganic solids composed of silicon, aluminium and oxygen. There are exceptions but more often than not these are the building blocks for most zeolites. The structure of a zeolite depends on the type being dealt with but they all have a structure which contains a network of channels and voids which contain sites that are acidic in nature. One thing to emphasize with zeolite catalysis is that they differ from liquid catalysts due to the way in which the reactants attain the active sites and then leave the site as a product. The diffusion in zeolites and their properties will be covered in this section.

2.2.1 Diffusion in Solid Catalysts

Liquid phase reactions catalyzed with an acid such as in alkylation are relatively simple systems. Their rates are dependant on the concentration of the catalyst as well as the concentration of the reactant and the rate constants are a function of temperature. The reaction proceeds via simple carbocation chemistry as in most solutions. The reactants form products and the products are removed from the reaction vessel. This is straight forward enough but if we compare this scenario to what is occurring in a similar reaction with the sole exception being that the catalyst is a porous solid the reaction becomes more complex due to various diffusion processes.

This is how diffusion occurs in a solid.

1) External diffusion of the reactants to the catalyst interface.
2) Internal diffusion of the reactants into the catalyst structure.
3) Adsorption of the reactants onto the surface of the catalyst.
4) Chemical reaction to form the products.
5) Desorption of products from surface.
6) Internal diffusion of products to catalyst interface.
7) External diffusion of the products away from the catalyst surface.

These processes display the complexity of diffusion in a solid catalyst and can be placed into two categories. Diffusion steps and reaction steps. The diffusion steps are those where molecules are navigating through the catalyst. Each step has an activation energy which will vary with the structure of the channels as well as the particle interface and of course temperature. These energy barriers can be attenuated by making diffusion easier. In this case, by increasing the space molecules have to move within the pores the diffusion steps are less demanding. The reaction steps consist of the adsorption/reaction/desorption steps. The adsorption occurs when a reactant molecule comes into contact with an active site and becomes adsorbed. Since we have 2 reactants there should also be a second molecule adsorbed so the alkylation can take place. This situation where two adsorbed molecules in close proximity react is typical of Langmuir-Hinshelwood kinetics. [14] The reactants react with each other once adsorbed and then desorb as one product molecule into the channel.

Let us consider the reaction of reactant A to product B through an absorbed state on a catalyst surface.

There are 3 elementary processes that occur here.

1) Adsorption onto the surface
2) Reaction of adsorbed species A to adsorbed species B
3) Desorption of product B

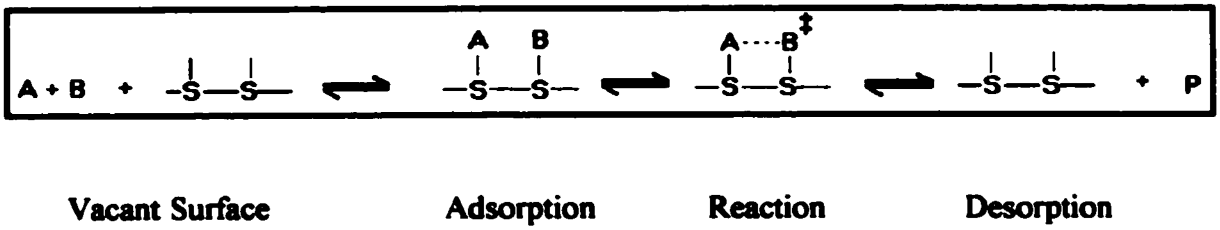


Figure 2.1

Surface phenomena

2.2.2 Acidity

Zeolite acidity is due to the charges within the zeolite that reside on the aluminum sites. Although zeolites are 3 dimensional structures they are often represented in a 2 dimensional format to more easily understand their chemistry. This is because to examine the chemical properties, the individual atoms need to be seen as well as their orientation with respect to each other. A typical structure is shown in figure 2.2 part a.

It can be seen that there is a charge on the tetravalent aluminum site. This charge is extremely important to the acidity of zeolites. The framework charges present due to this extra valency are countered by cations such as Na^+ of Ca^{2+} in zeolites. Now, these cations are quite mobile within the zeolite structure and this means that other ions can be substituted at these locations. To obtain an acidic form of a zeolite an ion exchange is done whereby ammonium ions are substituted for the metal cations. Once the ammonium is in place near the aluminum it can be decomposed under heat to produce ammonia which leaves the structure while leaving behind a proton. This proton can now form a bond to the oxygen atom which destabilizes the Al-O bond and results in a silanol group which is acidic. This is the cause of zeolite Brönsted acidity.

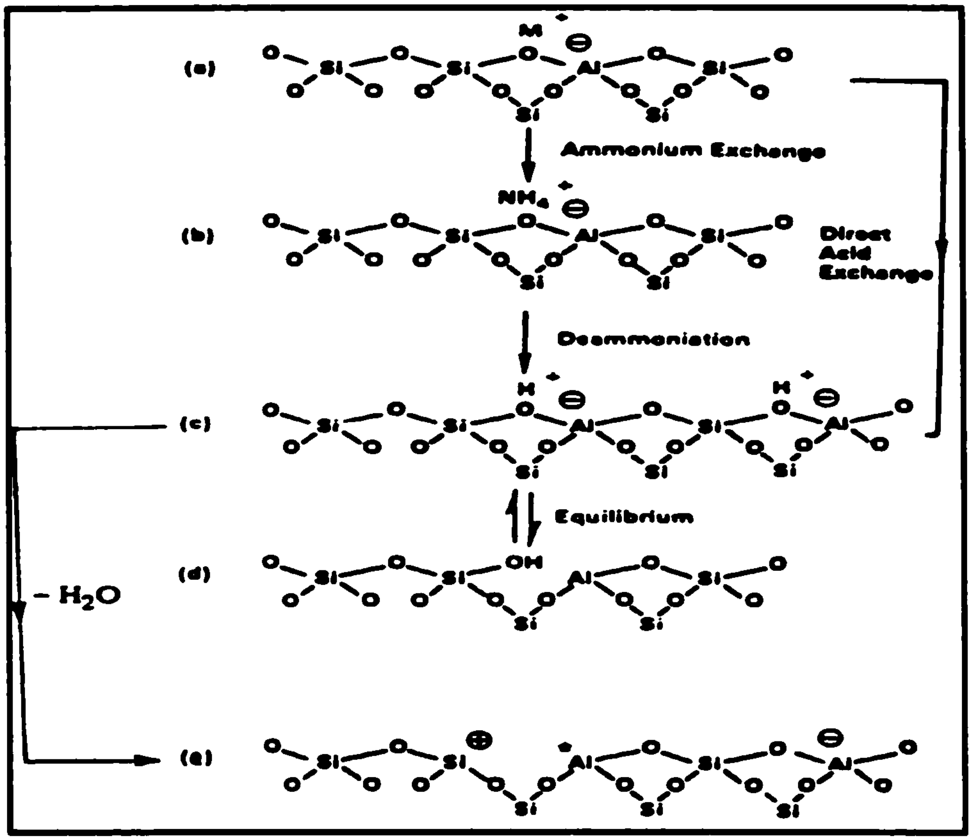


Figure 2.2

Ion exchange and acid site formation in zeolites [15]

This situation means that wherever an aluminum atom is present in the framework, an acid site can form and this is how acid site density and strength can be modified in zeolites depending on the needs of the reaction. By increasing the aluminum content the number of acid sites goes up (aluminum hydroxyls have Bronsted acidity) and the acid strength of the sites goes down. This decrease in the acid site strength has been explained by drawing an analogy between solid acids and inorganic oxyacids.

The general form of an inorganic oxyacid is $XO_n(OH)_m$. As the value of "n" increases, the acidity increases. The value of "m" has little effect on acidity. To apply this idea to zeolites it is necessary to write the formula of the zeolite in the same form. The zeolites are built from Si and Al tetrahedra which will be considered as the X group in the above formula. Doing so changes the formula to $TO_n(OH)_{m.w}$ where T represents the tetrahedra. By increasing the (Si,Al) tetrahedra the value of n increases and as a consequence the m value must go down. The value of m is also equal, in theory, to the number of Al sites which means that by lowering the content of alumina and thereby the number of acid sites the n value goes up. [16] Acid site density and strength can be modified or chosen so as to optimize reaction efficiency. The ability to choose from numerous acid strengths makes zeolites amenable to many petrochemical reactions.

2.2.3 Surface Area

Using a solid acid catalyst means that there is a finite amount of space on which reactions can occur compared to solutions where there is no such restriction and the acid is available very easily. By increasing the surface area in a solid catalyst the amount of product attainable is increased. The amount of surface area ranges widely in zeolites from tens of square meters per gram to thousands of square meters per gram. The more porous a solid the higher its surface area. A typical value for HZSM-5 is approximately 450 m^2/g. When low reaction temperatures are used a higher surface area is usually warranted because the rate of reaction is determined by the number of free active sites and the number of reactant molecules (assuming Langmuir-Hinshelwood kinetics) up until saturation occurs. This means that a low conversion from lower temperature can be offset by using a higher surface area with more active sites. At high temperatures lower surface areas can be used without any drop in activity.

2.2.4 Pore Size and Shape Selectivity

The channels in a zeolite traverse the particles and open at the interface of the particle. The opening at this interface governs the size of molecules that will be able to diffuse into the zeolite. This pore mouth changes in size depending on the number of oxygen atoms contained in the pore mouth. This factor plays a key role in zeolite selectivity. The internal cavities of the zeolite are also important to the shape selective effects observed. By considering a cavity in the zeolite bounded by two surface openings 3 types of selectivity can be proposed.

a) Reactant shape selectivity where the size of a reactant or other species in the reactant stream must be small enough to be able to diffuse into the pore.

b) Transition state selectivity is the limitation of any transition state formed in the pores to the size of the cavities in which it formed. In other words, if a transition state it too large to exist in the cavity, it will not form.

c) Product state selectivity dictates that any product capable of forming within the cavities must also be able to diffuse out of the pore mouth otherwise it will remain in the cavity.

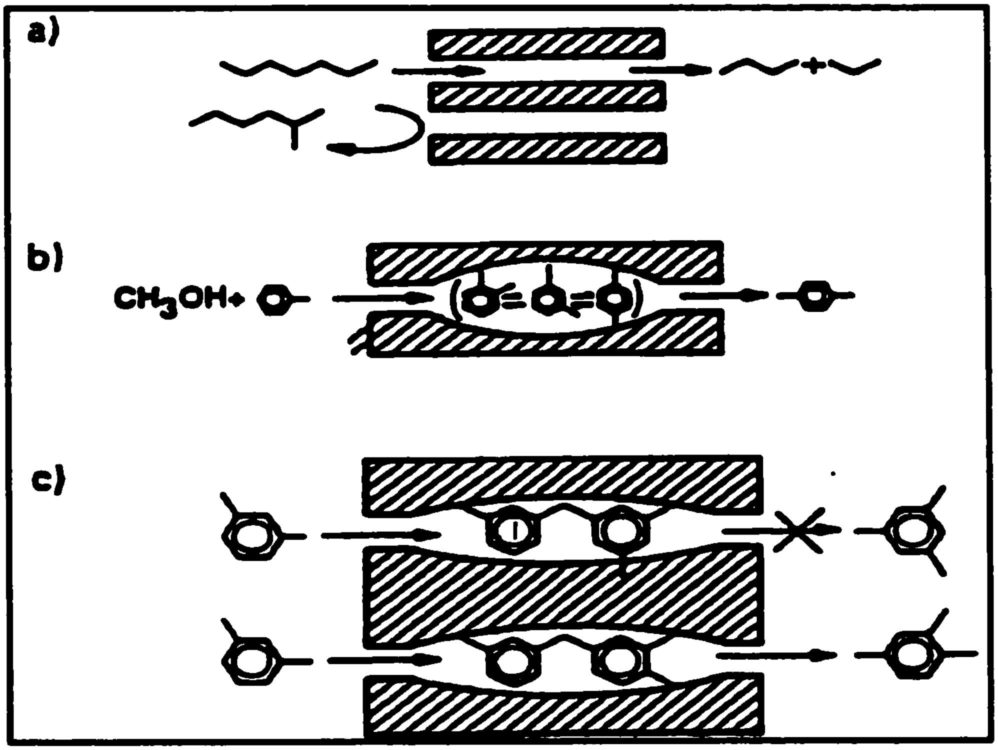


Figure 2.3

Shape selectivity in zeolites [17]

These aspects of zeolites may seem trivial but the implications are profound. A zeolite can be selected such that only the desired reactants are admitted to the structure, unwanted by-products will not be able to form in the cavities and only the desired products will diffuse out of the zeolite. These properties are well documented and are put to great use in many reactions.

2.2.5 Limitations of Zeolites vis a vis Alkylation

Having gone over the properties of zeolites and the many aspects which make them desirable catalysts for petrochemical processing, attention will now be directed at the limitations of zeolites when applied to alkylation. Zeolites have had great success in other reactions and as a result there is ongoing research into the possibility of using them for alkylation reactions to supplant liquid acids. Research is ongoing but very often pursues zeolites of Y type, and mordenite. [18] These are characterized by intermediate surface areas and medium acidity. The unfortunate findings without exception have been that zeolites of any kind do not perform well under alkylation conditions. The most common ailments of the zeolites in this demanding reaction are rapid deactivation and diffusional limitations. These two issues stem from the properties that normally make zeolites such an attractive catalyst choice. The causes for the diffusional limitations and deactivation can thus be simply explained.

Understanding how catalytic failure occurs means looking at the basic reaction scheme as well as the conditions used. In an alkylation reaction the temperatures needed are low so as to favour the formation of larger molecules. Since larger molecules are being favored by the conditions used it stands to reason that the formation of coke will have a larger rate constant with respect to other reactions. So to obtain the products desired the implication is that using the appropriate conditions will also favour the very reactions responsible for deactivation. On the other hand high temperatures will provide energy which can lead to extensive cracking activity. This is in contrast to other reactions such as cracking where larger size molecules are split into smaller products. The conditions are chosen to favour smaller molecules and the corresponding coke formation should be relatively suppressed. Why should this matter? In reactions where small molecules are the product, appropriately chosen zeolites can allow easy passage of the molecules in and out of the pores. The products are smaller and the reactants can diffuse without hindrance. Also, reactor temperatures are higher in these cases so the kinetic diameter of the molecules is even lower still. In alkylation we are encouraging larger molecules to form where smaller pores can prohibit diffusion and the lower reaction temperatures do not provide any kinetic energy to allow these large molecules to push their way through the pores. So, the diffusional limitations are due to very simple size mismatches between hydrocarbons and catalyst, coupled with unfavourable thermodynamics.

The deactivation of the zeolite catalysts goes hand in hand with the diffusion issues from the previous paragraph. Deactivation is the loss of activity in a catalyst whereby the rate of conversion of reactants into products is diminished. This most often means that the reactants are no longer able to reach the active sites within the pores and so the conversion suffers. If time on stream stability suffers as the reaction progresses, the logical conclusion is that products are being formed which inhibit the reaction. The "products" in question are more commonly referred to as "coke". Coke is a carbonaceous deposit which can consist of any large carbon based structure whether it be aromatic or aliphatic. These coke particles can reach sizes in excess of the pore sizes present which effectively locks them in the structure from which they cannot escape. This deposit blocking the pore also blocks access to the active sites and this is the cause of activity loss. If we again consider that in alkylation we are running the reaction under conditions which promote larger molecules it makes sense that some will become trapped in the pores and will deactivate the catalyst.

It is now quite apparent that zeolite based catalysts when taken in the context of alkylation suffer from setbacks which render them all but useless. Although research continues in an attempt to circumvent these difficulties, it seems that the solution must be directed away from trying to correct deficiencies in certain systems to developing systems that don't have these problems from the outset.

2.3 Superacid Catalysis

It has been shown have seen the industrial alkylation methods along with their environmental setbacks and the poor performance of zeolite catalysts. By taking the activity and selectivity of liquid phase catalysts and combining them with the stability of solid catalysts then most problems encountered to date would be solved. To eliminate the health issues a catalyst is preferably solid to eliminate spills and transportation dangers while remaining highly acidic. The evidence in the literature has proven that small pore size is the main cause of zeolite deactivation so the solid component must have larger pores which improve diffusion and higher surface areas will improve the conversion levels. The acid component must be chosen carefully as well. With a large pore size solid support the acid must be large enough to not simply pass in and out of the structure but rather to adhere to the surface. This is necessary so as to have a catalytically active surface. Also, the acid must be very strong to be effective in the reaction. The solution now becomes more evident. By using a mesoporous solid which has much larger pores than zeolites and incorporating acidity either in its framework or simply adsorbed on its surface it should be possible to eliminate all of the current troubles.

This introduces the topic of mesoporous supports using organic superacids as catalytic agents. Specifically, in this project a support was chosen which possesses tremendously high surface area with large pores and a liquid superacid is incorporated to provide the necessary acidity. Explanations of the two components follow.

A mesoporous material is one that displays average pore sizes in excess of 10 angstroms. The support chosen is called MCM-41 and is a silica based material first synthesized by researchers at Mobil. Hence the name Mobil Crystalline Material-41. This is a relatively new material which has garnered much attention as a support for many reactions owing to its unusual properties. [19] Not only does it have large pore diameters which can range from 15-100Å, it exhibits extremely high surface areas regularly above 1000 m^2/g, and in the case of the type we use it is approximately 1200 m^2/g. The pore morphology in MCM-41 is a hexagonal tubular type. Essentially, it is built of tubes of silica in a hexagonal packing arrangement.

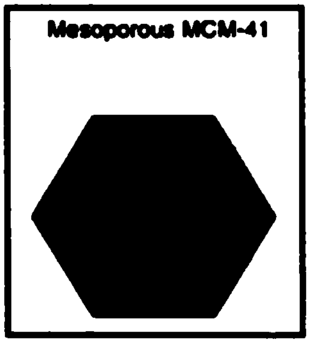


Figure 2.4

Schematic representation of MCM-41 pore structure

MCM-41 is synthesized using a micelle template crystallization process. The addition of a surfactant creates a solution which coalesces to form clusters of micelles. Using an alkaline environment to dissolve a source of silica the micelles act as scaffolding onto which the silica can attach and crystallize. These newly formed tubes are in a disordered state and eventually form a regular ordered system as the crystallization proceeds. Once the silica is completely crystallized the templating agent is removed by calcining the material in air which pyrolyzes the organic surfactant. Once the organic molecules are gone all that is left is the silica tubes which are very stable under high temperature.

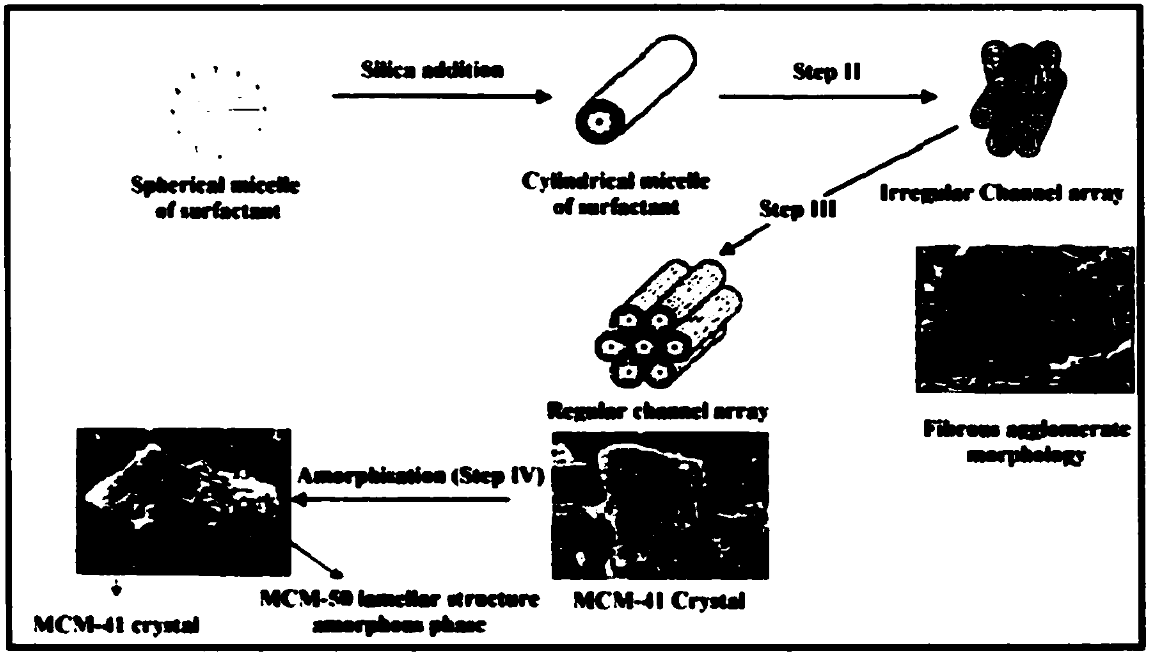


Figure 2.5

MCM-41 synthesis [20]

This micelle process is the reason for the regular pores in MCM-41. What makes MCM-41 a very attractive support is its uniform pore size distribution and ease of modification. It can be synthesized to have varying pore sizes which allows great control over the shape selectivity which occurs and the tubular shape easily accepts dopant species such as acids or transition metals. These tubular channels admit molecules very easily, a phenomena which we can use to our advantage in loading an acid into the MCM-41.

The actual catalytic species in our formulations is trifluoromethane sulfonic acid commonly known as triflic acid. It is an organic super acid which is well know for its strong acidity. A superacid is an acid which displays a Hammett acidity function of less than -12.0. This value has been taken arbitrarily as being the sole criteria for superacidity and since sulphuric acid has a value of -12.0 it means that any acid with a value below that of sulfuric acid qualifies as a superacid. A brief explanation of the Hammettt acidity function and its origins will assist in clarifying its need as a means of gauging acidity. The Hammett acidity function is used as an alternate means of obtaining a quantitative measure of acidity as opposed to the pH scale. The Hammet function rather than considering the -log of the number of protons in solution as the acidity uses a completely different approach. A weakly basic indicator is added to the acid and the degree of protonation of a series of these indicators is compared spectrophotometrically. Hammett and Deyrup were the first to suggest a method of measuring the degree of protonation of weakly basic indicators in acid solution. [21] This organic superacid has a Hammett acidity function of -14.1 making more than a hundred times stronger than sulphuric acid. It is a very stable acid although it is rather volatile. This acid fumes in moist air to form the monohydrate which is a solid at room temperature. It has found use in alkylation catalysts before with silica supports of less crystalline nature using complex impregnation procedures to seat the catalyst within the pores. These techniques, although somewhat effective do not have very high alkylate production and the acid tends to travel out of the supports due to partial solubility in the alkylate phase.

2.3.1 MCM-41/TFA

The catalyst components have now been chosen and the triflic acid must be added to the MCM-41 to obtain useable and active material. In this system the acid is incorporated into the pores of the support where it adsorbs to the surface. It remains there and forms layers of acid on the surface. The outermost layer will be the active catalyst surface. A benefit of this multi layer adsorption is that when coke deposits form over the acid layer it may be possible to remove them using water vapour at higher temperatures. This could provide for an easy and economical regeneration of the catalyst. This is a diagram showing the loading of the acid into the channels.

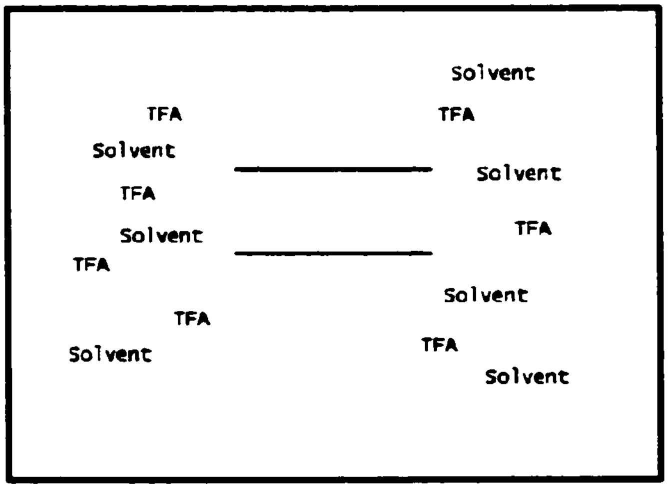


Figure 2.6

MCM-41 synthesis

This figure displays a single MCM-41 channel which has been immersed in a solution containing triflic acid and a solvent which in this case is water. The channel is empty and the acid and water are at the interface of the channel.

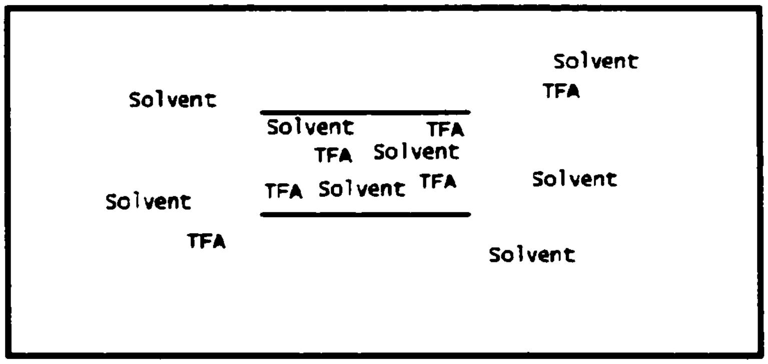


Figure 2.7

MCM-41 accepting acidic solution into channel

It is expected that the solvent molecules and triflic acid molecules begin to migrate into the channels. The channels will accept some of the acid along with solvent while some of this solution remains outside. At this point the acid may be physisorbed to the surface of the channel.

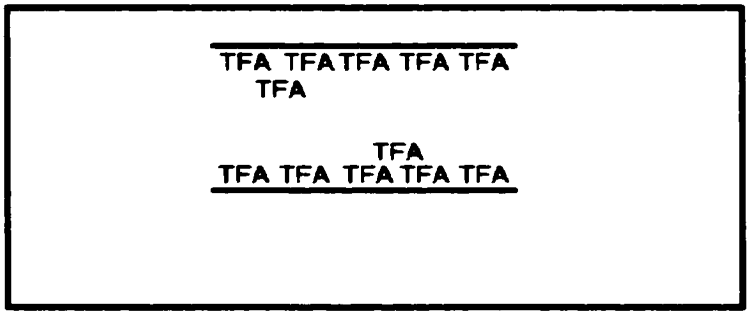


Figure 2.8

MCM-41 with adsorbed triflic acid

The solvent has now been driven off by a heating step and the triflic acid which remains is now on the surface of the channel and is fairly strongly adsorbed on the surface. There are also some loosely bound acid molecules on top of the first monolayer. This is the final form of the catalyst as it is used in the reaction.

Chapter 3

Experimental

3.1 Source of Materials

Chemicals	Supplier
Tetrapropylammonium hydroxide	Aldrich
Myrisityltrimethylammonium bromide	Acros
Sodium hydroxide	ACP
Silica Gel	J.T. Baker
Trifluoromethanesulfonicacid	Aldrich
Bentonite	Aldrich
Potassium Bromide (FT-IR grade)	Aldrich
Alumina	Fisher
ZSM-5	Chemie Uetikon AG
Y	Chemie Uetikon AG
USHY	Chemie Uetikon AG
Mordenite	Chemie Uetikon AG

3.2 Catalyst preparation, characterization and testing

In this section the various synthetic routes employed in preparing the catalysts will be outlined. Specifically, the zeolite type including modifications with various dopants. The characterization of the physico-chemical aspects of the catalyst will be outlined for techniques applicable to understanding catalytic structure, nature of the acid loading and coke deposition. The catalytic testing for MCM-41 will be studied since it provides important information about how the catalyst behaves in terms of product distribution, deactivation and stability. The data acquisition methods and analysis are shown to demonstrate the techniques used in quantifying the performance characteristics mentioned above.

3.3 Catalyst Preparation

3.3.1 Zeolite preparation

3.3.1.1 HZSM-5

ZSM-5 purchased from Chemie Uetikon AG, is a powder present in the Na^+ form. It is first subjected to an ion exchange process whereby the powder is placed in a solution of ammonium chloride at 80^0C which displaces the sodium cations in favour of ammonium ions. The process is done 5 times to ensure complete exchange and after each time the solid zeolite is dried by vacuum filtration followed by heating at 120^0C in air for a period of at least 12 hours. The ion exchanged zeolite is heated at 500^0C overnight in order to have the H^+ form (HZSM-5) through the following decomposition reaction:

$NH_4^+Z^- \rightarrow NH_{3\,(g)} + H^+Z^-$

The powder is not fit for catalytic testing since a powder would block a plug flow reactor tube where gases are being passed through, so it is formed into thin cylindrical extrudates. This is accomplished by mixing the powder with a cementing agent (bentonite) in an amount of 20% by weight. The addition of water then results in a malleable paste which is placed in a syringe and extruded. This new form of the catalyst is again activated overnight at 500^0C to yield the final formulation.

3.3.1.2 H-Mordenite

H-Mordenite zeolite is purchased from Chemie Uetikon and follows similar steps compared to HZSM-5. The powder is already present in the protonic form so no ion exchange is necessary. The powder is mixed with 20% by weight of bentonite as a binder and is then extruded. The extrudates are allowed to dry at room for 1 hour followed by activation at 350^0C overnight.

3.3.1.3 USHY

USHY is a derivative of HY and possesses a higher silicon to aluminum ratio. This is achieved by steaming the catalyst which results in a loss of framework aluminum. The resulting catalyst called ultra stable HY is purchased as a powder form and requires the synthesis according to the H-Mordenite protocol.

3.3.2 MCM-41 Mesoporous Support Preparation

MCM-41 is not purchased but rather synthesized in the lab. A 20.8 ml volume of tetrapropylammonium hydroxide is mixed with 3.3 g of sodium hydroxide.

To this is added 110 ml of distilled water and 18.3 g of silica gel. The resulting solution is stirred for 30 minutes at 80^0C. Separately, 17.2 g of myris ityltrimethylammonium bromide is dissolved in 66 ml of distilled water. Once this dissolution is complete, the solution is added to the silica gel solution and this new mixture is again stirred for 30 minutes at 80^0C. The final step is a crystallization which calls for the reaction mixture to be heated at 95^0C in a water bath for 72 hours. Once the crystallization period is over the solid material is rinsed with 1.5 L of room temperature distilled water during vacuum filtration to assist in removing species used as templating agent as well as residual sodium. The filter cake is then dried overnight at 120^0C and is then heated at 550^0C for at least 6 hours to pyrolyze any residual organics left in the MCM-41 structure.

3.3.2.1 Incorporation of Triflic Acid onto MCM-41

The MCM-41 support does not possess any acidity of its own so the addition of triflic acid solves this problem. The incorporation is done by dissolving triflic acid into distilled water. The amount used is such that a 30% by weight loading is achieved with respect to the amount of MCM-41 used. The solution is then mixed with the MCM-41 so a slurry which can be mixed is obtained. The slurry is mixed for 20 minutes and then placed in an oven at 120^0C to dry overnight. The resulting powder is then mixed in with bentonite binder to form extrudates where bentonite is added in a 30% by weight amount. The higher amount of bentonite is due to the fact that MCM-41 forms unstable extrudates with lower amounts of bentonite.

3.4 Characterization

3.4.1 FT-IR

Fourier transform infra-red spectroscopy is a tool often used by chemists to elucidate structural features of organic molecules by looking for absorbances corresponding to certain bond vibrations. This technique can also be used to probe the surface of a solid provided the technique is modified to account for the opacity of a solid sample such as a zeolite. The technique used in this case is called DRIFTS. Short for diffuse reflectance infra red fourier transform spectroscopy. Rather than trying to send the radiation through the sample as in the case of liquid IR spectroscopy, this method allows the beam to hit the surface of the solid and to diffusely reflect off the surface.

Mesoporous catalysts were tested on the instrument to investigate the acid on the catalyst as well as coke deposits on spent catalysts. Samples are prepared by mixing catalyst and KBr with the sample making up 1% by weight of the mixture. The solid mixture is then ground with a mortar and pestle. This step is critical to ensure that the beam does not diffract when impinging on the powder surface. Spectra are normally obtained by obtaining a spectra of a suitable background and then the spectra of the sample. The actual spectra is a difference between the background and the sample spectra. The background used is most often a simple air background of the atmosphere in the room but it can also be taken as an unmodified MCM-41 sample so that samples can be tested with acid or coke to see just those species. The region seen is between 600cm^{-1} to 4000cm^{-1}. Spectra are all taken as the average of 120 scans at a resolution of 4cm^{-1}.

3.4.2 Nitrogen Porosimetry

One of the fundamental principles in this project is the idea that large surface areas and pore sizes are necessary in catalysts for alkylation. To evaluate these parameters of a catalyst use is made of nitrogen porosimetry. The technique provides a wealth of information concerning the pore diameters and surface areas as well as void volume of the catalysts. The surface area is made up of the internal pore surfaces and the external surface area derived from the particle boundaries. In this way it can be proven that the MCM-41 has the requisite properties and the addition of triflic acid can be evaluated in terms of its effect on these properties.

3.4.2.1 Surface area

The area as determined by the BET which is an abbreviation for Brunauer, Emmett and Teller is based on the adsorption of nitrogen at low pressure assuming a Langmuir site coverage model. It is a measure of the accessible surface per unit mass of solid. To determine the area an isotherm is measured for the volume of nitrogen adsorbed as a function of its relative pressure. From the isotherm, the monolayer capacity (V_m) can be found which is the value used to calculate the area (A).

The BET model assumes the following points. [22]

1) The surface contains a constant number of identical adsorption sites.
2) There is no interaction of one adsorbed molecule with the next.
3) Once the first monolayer is formed, the heat of adsorption of subsequent molecules is identical to the heat of condensation. (Only the first monolayer is affected by the surface)
4) An adsorbed molecule can serve as an adsorption site for further molecules which gives rise to multi layer coverage.

A second technique known as BJH can be used based on a sequence of stepwise adsorption and desorption equilibria in the solid which often gives more accurate values. Most surface properties reported here will be done for BJH treatment because the BET method has been subject to criticisms for not following the assumptions of the model in use above P/P_0 values of 0.35. [23]

Porosimetry using nitrogen involves out-gassing the sample to remove any water or atmospheric gases which may have adsorbed to the surface. Once this is done the sample is dosed with nitrogen gas until it is saturated. The volume adsorbed is measured while the pressure is increased and from this an adsorption isotherm is collected. A desorption isotherm is also collected by allowing the nitrogen to leave the catalyst and again taking pressure reading versus the amount desorbed.

3.4.2.2 Pore Size

Pore size is another characteristic that can be derived from BET data. While the pores are filled with condensed liquid nitrogen the desorption of the liquid adsorbate occurs at a pressure related to the pore size by the Kelvin equation. The equation assumes cylindrical pores and known values for the nitrogen surface tension, contact angle and molar volume. The pore size distribution is calculated from desorption data by applying the Kelvin equation.

$$\ln P/P_0 = -2\, nV/RT \times 1/r_K \cos\theta$$

P/P_0 = The relative pressure of vapor in equilibrium with the meniscus in the pore.

r_k = The curvature radius of the meniscus

n = Surface tension of the liquid nitrogen

V = Molar volume of liquid nitrogen

R = Gas constant

T = Absolute temperature

θ = The contact angle formed by the liquid nitrogen in the pore with the surface adsorbed nitrogen of the pore. [24]

3.4.2.3 Sample preparation for porosimetry

Samples are generally left in an oven at 120°C overnight to prevent any water vapor from adsorbing on the surface. The samples are then loaded into a quartz tube and are subjected to low pressure for 4 hours at a temperature of 220°C. This is to thoroughly remove any remaining adsorbate on the surface. When conducting tests on triflic acid loaded samples the low pressure heating step is modified. Since the triflic acid boils at 162°C under atmospheric pressure it would certainly evaporate under normal outgassing conditions. For these samples, a temperature of 120°C is used and the time spent under vacuum is 16 hours. Once the outgassing steps are completed the quartz tube containing the sample is connected to an analysis port on the instrument where the pressure readings are taken. The procedure is non destructive and the samples can be used after the test.

3.5 X-Ray Diffraction

X-Ray diffraction is a technique where a solid sample is placed in the path of an incident beam of x-rays and the beam is diffracted. When the diffracted beams happen to interfere constructively the diffracted beams can be observed at the detector. This occurs when a crystalline or periodic structure is being analyzed. It is this periodicity which gives rise to some of the incident waves diffracting in phase with each other. Since the higher the amount of crystallinity in the sample the more detected beams there are we can determine the degree of crystallinity of one sample compared to another. This is done by integrating the peak areas from an XRD pattern for 2 samples and comparing the areas. Specifically, patterns were obtained for a sample of pure MCM-41 and another MCM-41 sample that had been impregnated with triflic acid. If there is any loss of crystallinity in the sample as a result of the acid, then the change will appear as a lower degree of crystallinity. XRD data can also be used to characterize an unknown compound by comparing a pattern of the unknown to a reference pattern. If the peaks coincide then there is evidence that the unknown is very possibly the same compound as the reference.

Samples for XRD analysis are simply heated at 120^0C for a period of 48 hours and are then packed into a plastic sample holder and placed into the instrument. The instrument used is a Siemens X-ray diffractometer with patterns obtained for a 2 theta range of $1.35\ ^0\ \theta$ to $71^0\ \theta$. The region of interest for MCM-41 materials is below $5\ ^0\ \theta$. These are the incident angle of the x-rays on the sample surface.

3.6 Differential thermal analysis/thermo gravimetric analysis

3.6.1 Theory

This technique, abbreviated DTA/TGA operates on 2 very simple principles. By heating a sample and observing changes in mass (TGA) and differential changes in temperature (DTA) information can be obtained regarding transformations occurring to the sample due to the heating as well as whether these changes are exothermic or not. By using nitrogen or air atmospheres these changes can be ascribed to combustions or non oxidative processes too. The mass changes are obtained by collecting data from a microbalance holding the heated sample.

Differential changes in the temperature are obtained via a thermocouple connected to the sample tray. If a change occurs in the sample relative to the furnace temperature the thermocouple will register it as a voltage either positive or negative. An increase denotes an exothermic process and a decrease indicates an endothermic process.

3.6.2 Instrumentation

The instrument in use is a Stanton-Redcroft STA equipped with a 1500^{0}C furnace unit capable of variable atmosphere conditions. A DTA/TGA consists of a zero seeking microbalance which has two sides. The sample and counter balance sides. The sample side is built from a ceramic hangdown containing inside the microbalance arm and thermocouple leads. A furnace is assembled such that it can be raised to completely enclose the sample hangdown. The actual sample is placed in platinum crucibles which prevents melting at high temperatures. Platinum also eliminates potential reactions from occurring between the crucible and the sample. Once a test is started, the furnace is heated at a rate dictated by the operator and sufficient to obtain resolution of separate events. When a temperature is reached where a reaction or change begins in the sample, the mass can change and the temperature can drop or rise as measured by the thermocouple which is part of the sample hangdown. The system is more clearly understood by referring to the image below.

3.6.3 Sample Preparation

Collecting DTA/TGA data requires careful sample preparation and controlled environmental conditions due to the extreme sensitivity of the microbalance assembly. Before a test is initiated the location must be free of drafts and the lighting must be constant throughout due to photosensitive components in the balance. The microbalance is then zeroed by adding counter balance weights so the BCU (balance control unit) reads zero within 0.01 milligrams. Samples are prepared by gently grinding a small portion of catalyst (~0.02 g) in a mortar and pestle. The powder is carefully loaded into a platinum crucible and is settled so the powder is evenly distributed in the crucible. This is to be able to obtain reproducible data. Uneven packing may change the results. With the powder loaded and placed onto the sample hangdown the furnace is raised and the mass is allowed to stabilize. Fluctuations persist for several minutes after loading and must be allowed to stop before proceeding. At this point, an appropriate temperature profile is chosen and if an atmosphere change is needed it can be added to the profile. Atmosphere changes are most often from nitrogen to air. This will prevent any compounds that may oxidize during the ramp from actually burning. Switching to air near the end of the ramp causes all combustibles to burn at once and give a precise value of how much weight loss occurred due to combustion. Other atmospheres can be used by connecting gas cylinders to the instrument but nitrogen and air are the most common for combustion data.

3.7 Catalytic Testing

3.7.1 Reactor Design

The ability to evaluate a catalyst's performance is important in conducting research. Testing is done using catalyst extrudates loaded into a plug flow tubular reactor made of quartz seated in a furnace with inlets for reactant streams as well as an exhaust side gas sampling manifold. The reactant streams originate from compressed gas cylinders equipped with regulators to reduce pressure. The heating chamber at left is present in the event that water is introduced to the reactor. Once the reactant stream has passed this stage they enter the reactor which is the quartz tube seen filled with catalyst within the furnace. Products exit to the left side and are trapped in the three chambered glass manifold.

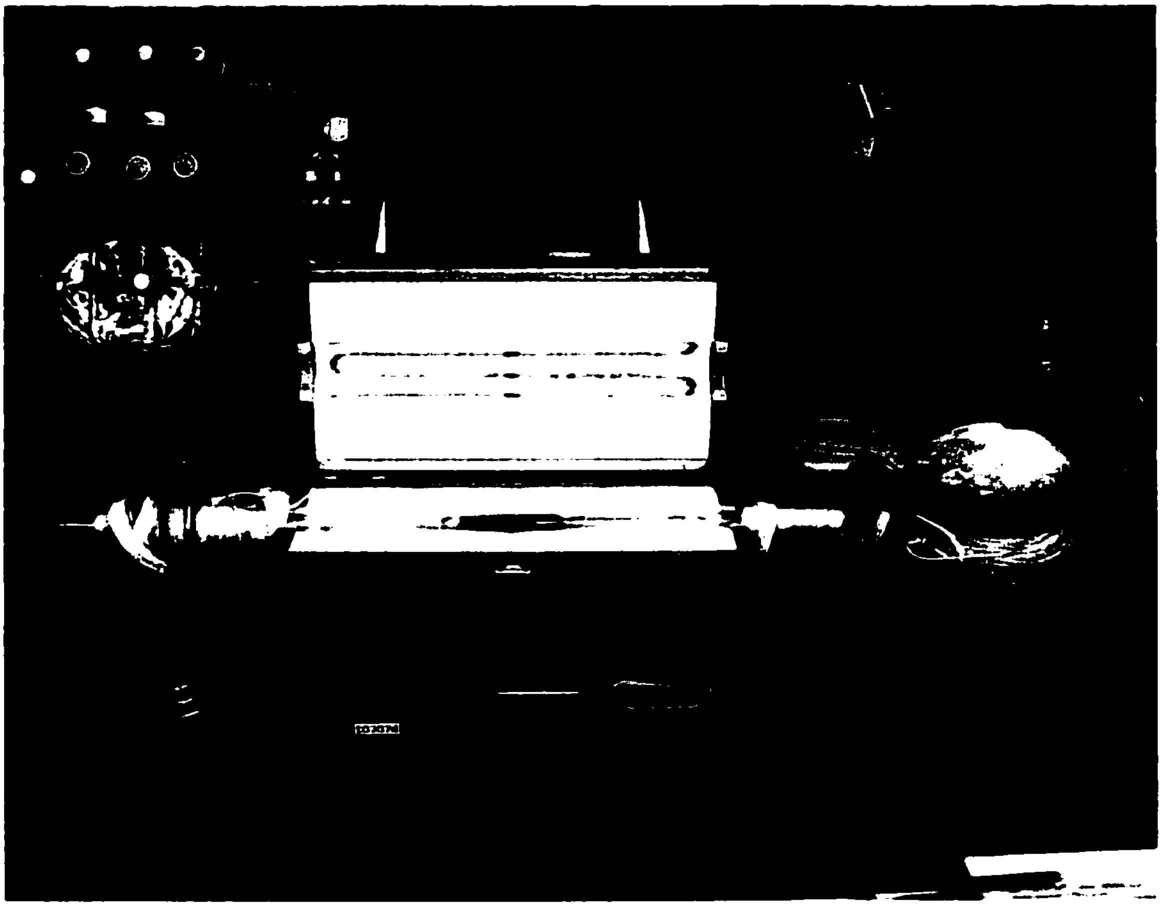


Figure 3.1

Reactor setup

This set-up allows for easy changing of catalyst and simple operation as well as sample collection. The reactor temperature can be regulated via a control panel and the reactant flow rates are controlled using needle valve flow controllers. The samples are taken of gas phase hydrocarbons exiting the reactor and are held in gas syringes.

3.7.2 Reactor parameters

The catalytic data covered the variation of some key operating parameters of the alkylation reaction. These parameters are listed in the table below.

Reaction Parameter	**Description**
Reactor Temperature (^0C)	The temperature at which the catalyst bed is maintained during a reaction.
Isobutane/Olefin (mol/mol)	The ratio at which the two feedstock are mixed and then passed into the reactor
Contact time (hr)	The amount of time a reactant molecule spends within the catalyst bed.
W.H.S.V. (hr-1)	The inverse of the contact time, used to express the mass of reactants passed through the reactor with respect to the mass of catalyst loaded/hour.

Table 3.1

Description of reaction parameters

3.7.3 Gas Chromatographic Analysis of Product Stream

The samples are tested using gas chromatography. This method allows the components of a mixture to be separated and quantified. The technique relies on the varying properties of the products and their partitioning within the column to obtain a separation. The samples are injected at a heated injector port and the carrier gas then sweeps the molecules onto the column. Once on the column the molecules will partition themselves to varying degrees within the alumina packing. The variable partitioning means that molecules that do not have strong affinities for the alumina will elute from the column more quickly than those which have more affinity for the stationary phase. The G.C. in use is a Hewlett Packard HP 5890 GC equipped with a 30 m Alltech gamma alumina column using a hydrogen carrier gas. Once the molecules exit the column they are detected by a flame ionization detector. The detector burns the hydrocarbon products as they exit the column. Ions are produced in the flame and a filament carrying a charge attracts the ions. The voltage change due to the ions is proportional to the amount of hydrocarbon exiting the column at that time. The signal output is sent to a Hewlett Packard 3392a signal integrator which reports the quantity of each hydrocarbon in the product stream as a percentage of the total amount of hydrocarbon in the sample. The temperature ramp used for the chromatography is given.

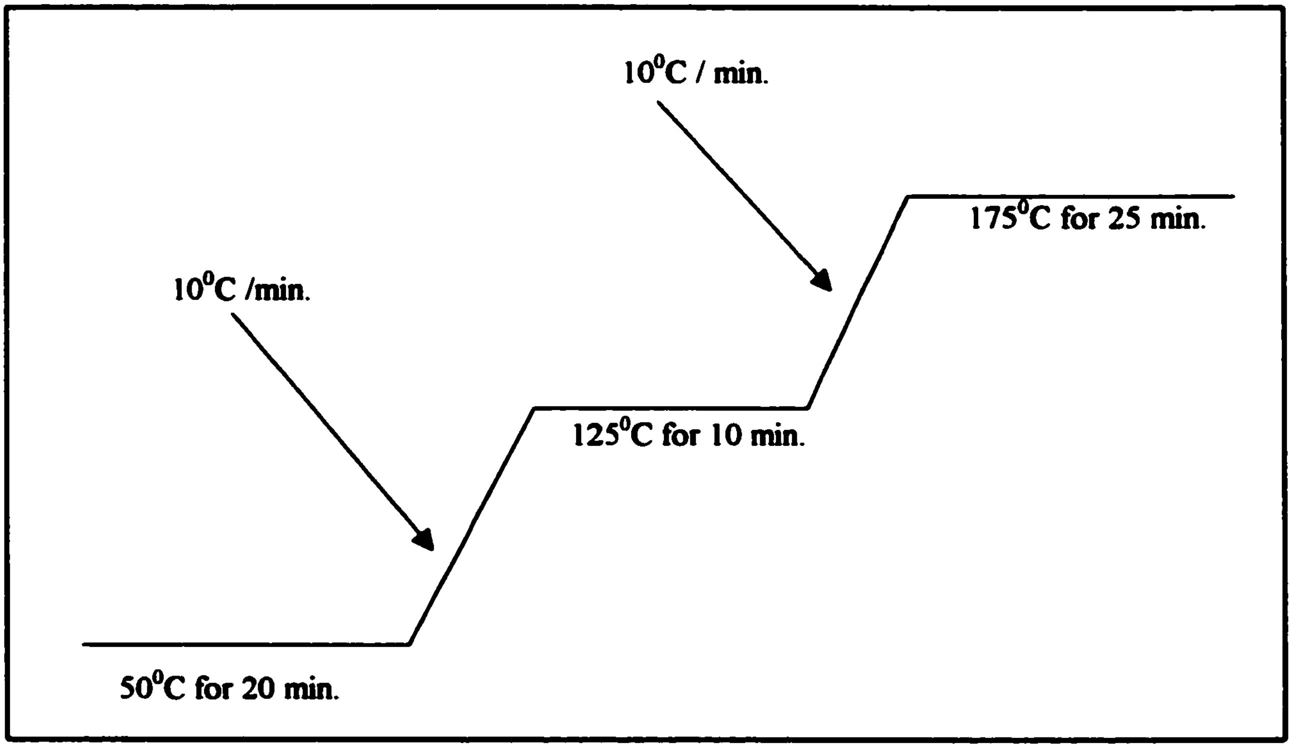


Figure 3.2

G.C. temerature profile

3.7.4 Interpretation of catalytic data

Analysis of the catalytic data is done by performing a series of calculations based on the raw gas chromatographic printouts. The conversion is a measure of how much reactant is converted in the reactor. The olefin feedstock is taken as the limiting reagent in the reaction and is used to calculate the conversion. The olefin isomerizes to four compounds; 1-butene, cis/trans 2-butene and isobutene. This process is very rapid and is not considered actual conversion due to the ease with which the process occurs. It is essentially due to the thermodynamic equilibrium established by the molecules. Thus, the amount of reactant consumed is done relative to the total of all 4 carbon alkenes in the exhaust stream.

$$\% \text{ Conversion} = [100 - \Sigma \text{ C4 isomers (area)}]$$

The selectivities (S_i) represent the percentage amount of a product with respect to the total amount of product formed in moles of carbon atoms.

$$\% S_i \ (x) = \frac{\text{\# of moles of product carbon atoms (x)}}{\text{Total \# of moles of products}} \times 100$$

At this point in the project the selectivities are grouped into classes of compounds according to the number of carbon atoms they have. C5-C7 products are considered cracking products, C8s are considered alkylation products and C9s are taken as oligomerization/dimerization products.

Chapter 4

Results and Discussion

4.1 Introduction

This chapter will include two sections; a brief review of selected results obtained with zeolite catalysts and results of mesoporous catalyst. The zeolite section covers the performance of 3 zeolite catalysts in alkylation reaction conditions. The mesoporous section is further divided into two subsections; characterization/physico-chemical properties and catalyst performance in alkylation reactions. The characterization section will go over all of the data pertaining to the structure, acid sites, and deactivation while the catalytic performance section will deal with the data obtained for alkylation reactions using various feedstocks and reaction parameters.

4.2 Zeolite Performance

The numerous properties of zeolites have been given in the introduction. To further demonstrate the points raised in the introduction some general results from the literature and experimental work will be given. The specific cases of HZSM-5, USHY, H-Mordenite and their derivatives will be briefly discussed.

It is now established that zeolites deactivate quickly during alkylation reactions. This has been linked to diffusion problems as a result of insufficient pore size. This information meant that pursuing a zeolite path would at the very least necessitate modifications to the zeolites. The very first zeolite tested was HZSM-5. In our lab we had seen in the past excellent results using HZSM-5 in catalytic cracking and MTO reactions. [25] Consequently HZSM-5 became a candidate for testing to see if it could work in alkylation. Unfortunately the success did not transfer over to alkylation. HZSM-5 demonstrated conversion levels less than 1% and stability of less than 30 minutes. Regardless of temperature the conversion and stability was unsatisfactory. For us this was proof that the pores in HZSM-5 could not accommodate the size of any transition state or product that may form on the active sites. Furthermore, it may even be possible that the reactants were not able to gain access to the pores in HZSM-5. Although the conversion was unacceptable, that is not to say that it was zero. We did see a small amount which seemed at odds with the pore size explanation. In theory there should be absolutely no conversion. The answer lies in the fact that H-ZSM-5 has active sites on the external surface of the particles as well. These active sites are available to any molecule that can adsorb on the particle surface. Estimates of the quantity of surface area due to external surfaces in HZSM-5 are approximately 1%. This explains why there was some small amount of conversion at all.

4.2.1 Y-type and mordenite zeolite

Another zeolite tested was HUSY type. It differs from HZSM-5 in that it has larger pores that can definitely accept reactant molecules and allow product molecules to diffuse out to an extent. Below is a graph demonstrating the stability of a Y type zeolite using butenes and isobutane as feedstock from the literature.

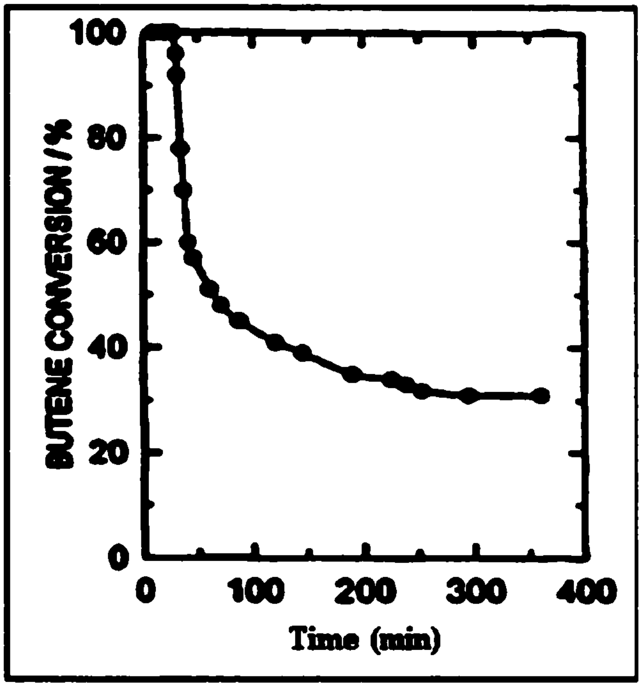


Figure 4.1

Butene conversion as a function time on stream in minutes for a Y type zeolite[26]

The graph shows that the initial level of conversion is 100% but this quickly drops down to 40%. In addition to this large loss in conversion the authors report that the pure alkylation process stops after a time and oligomerization of the butene feedstock predominates.

In our lab ultra stable Y type zeolites were tested as well. Initial levels of conversion are high but the results are not very stable and the overall numbers are not indicative of a useful catalyst. We confirmed that Y type zeolite is not an option for this reaction as presented in the literature. Another catalyst used in the lab was H mordenite which has similar acid strength to the ultra stable HY catalyst. It gives unsatisfactory results compared to the HUSY zeolite but in both cases the tests gave poor results. This placed a rather serious constraint on the research and the conclusion was that further investigating zeolite systems would not lead to significant improvements. Many papers had already dealt with the issues we were seeing from our results, so a completely new catalyst was needed. This of course leads to the choice of the MCM-41/triflic acid catalyst. To contrast the zeolite catalysts with the MCM-41 catalyst the conversion and selectivities are given for a set of identical conditions using 3 catalysts. All 3 tests were done at a reactor temperature of 140^{0}C using an isobutane/2-butene ratio of 10.

	H-Mordenite	H-USY	MCM-41/TFA
Conversion (%)	2.82	21.1	25.04
Cracking (%)	73.27	37.27	41.99
Alkylation (%)	19.02	18.19	45.28
Oligomerization (%)	7.71	44.54	12.74

Table 4.1

Comparison of micropore and mesopore catalysts

The table shows without a doubt that the zeolite catalysts do not have nearly the same level of effectiveness compared to the mesoporous MCM-41/TFA catalyst. Mordenite conversion is all but negligible and the products it does manage to form are predominantly cracking products. USHY conversion is many times higher than mordenite and somewhat lower than MCM-41/TFA. While this is an interesting result the selectivity shows that the primary tendency of this catalyst is to yield oligomers whereas the MCM-41/TFA produces much more alkylate than the zeolites. There is another critical difference between the zeolite and the MCM-41 catalyst as well. It is accepted in the literature that one of the primary difficulties in zeolites with regards to deactivation is the difficulty of accomplishing the inter molecular hydride transfer to regenerate an isobutyl cation needed for successive alkylation steps. [27] Since the alkylation step occurs on the catalytic surface on an active site, the octyl cation so formed must be in close proximity to adjacent active sites in order for the hydride transfer to occur. It is thought that the acid site density in MCM-41/TFA is higher than in most zeolites. If this is the case, the adsorbed octyl cation will more likely be in close proximity to an acid site with an adsorbed isobutane. This closeness will allow easier hydride transfer compared to a low acid site density where the octyl cation will not be as close to adjacent acid site on the surface since the cation must be adsorbed for this to occur. This will slow the hydride transfer step and decrease the activity of the catalyst.

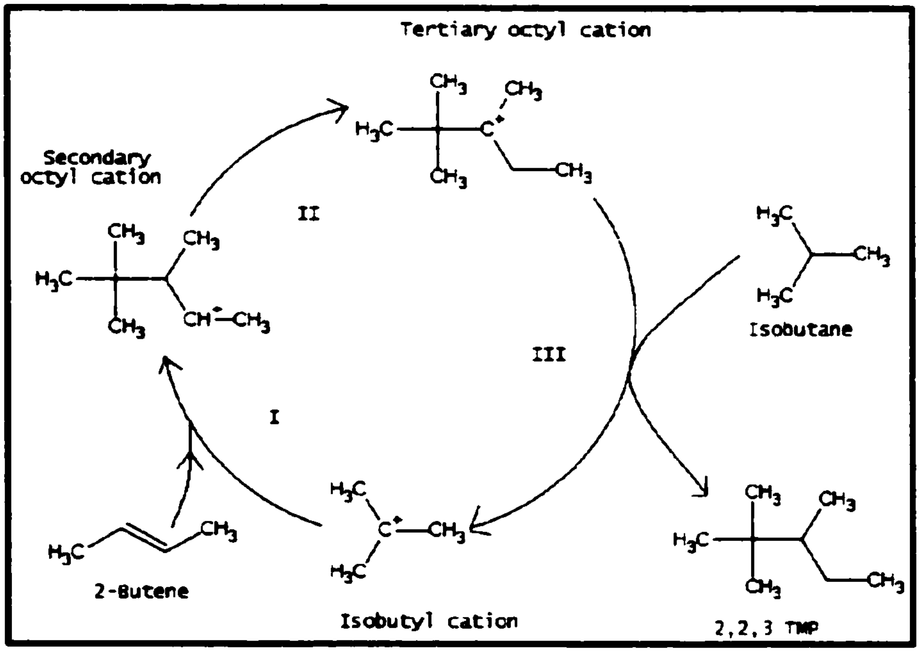


Figure 4.2

Hydride transfer in alkylation

This explanation concerns step III from the above mechanism. This step is the one believed to be most difficult in zeolite catalysts and without it the isobutyl cations will not form which lowers activity.

4.3 MCM-41/TFA Characterization

The characterization of a catalyst is crucial to understanding how it works. By knowing as much as possible about its structure and how it behaves under different conditions the determination of what improvements need to be made is easier. This is especially true of a new catalyst which is what we have here. Many techniques were used to study the catalyst for several parameters. Nitrogen porosimetry is one of the most important tools available to us and it gives data on MCM-41 in terms of surface area, pore size distribution, changes upon acid loading and void volume to list a few. DTA/TGA data will show what type of species may be present in the catalyst due to acid loading as well carbon deposits on the used catalysts. X-Ray diffraction allows the identification of the structure and provides data on the crystallinity of the sample. It can also be used to identify an unknown compound by its peaks if they can be matched to a reference sample. DRIFTS is a FT-IR technique developed for the study of surfaces and powders. For this project it allows the investigation of the MCM-41 support, the supported species (triflic acid) and eventually the species deposited on the catalytic surface during the reaction. These may consist of coke or other chemisorbed species.

4.3.1 X-ray diffraction

Since MCM-41 is meant to be a highly ordered and crystalline material and it is this order which gives it its useful properties, having XRD data will provide insight into the structure of the material including any structural change with acid incorporation. Framework destruction has been documented from previous research in our lab concerning HY type zeolites which were loaded with triflic acid. When the framework of the solid is damaged the structure is said to be less crystalline and as a result the pore networks will be damaged which decreases surface area. Depending on the amount of acid used the damage may be more or less pronounced. Studies on HY where 3% triflic acid was loaded showed a small loss in crystallinity but a large decrease in surface area. This quite clearly indicates that at low quantities of acid a zeolite structure can resist the superacidic conditions and retain much of its crystallinity although the acid can physically block some of the pores which will decrease the apparent surface area. [28] In the case of MCM-41 the acid loading was higher by an order of magnitude than the previous example and the XRD shows that the structure was much more affected by the treatment.

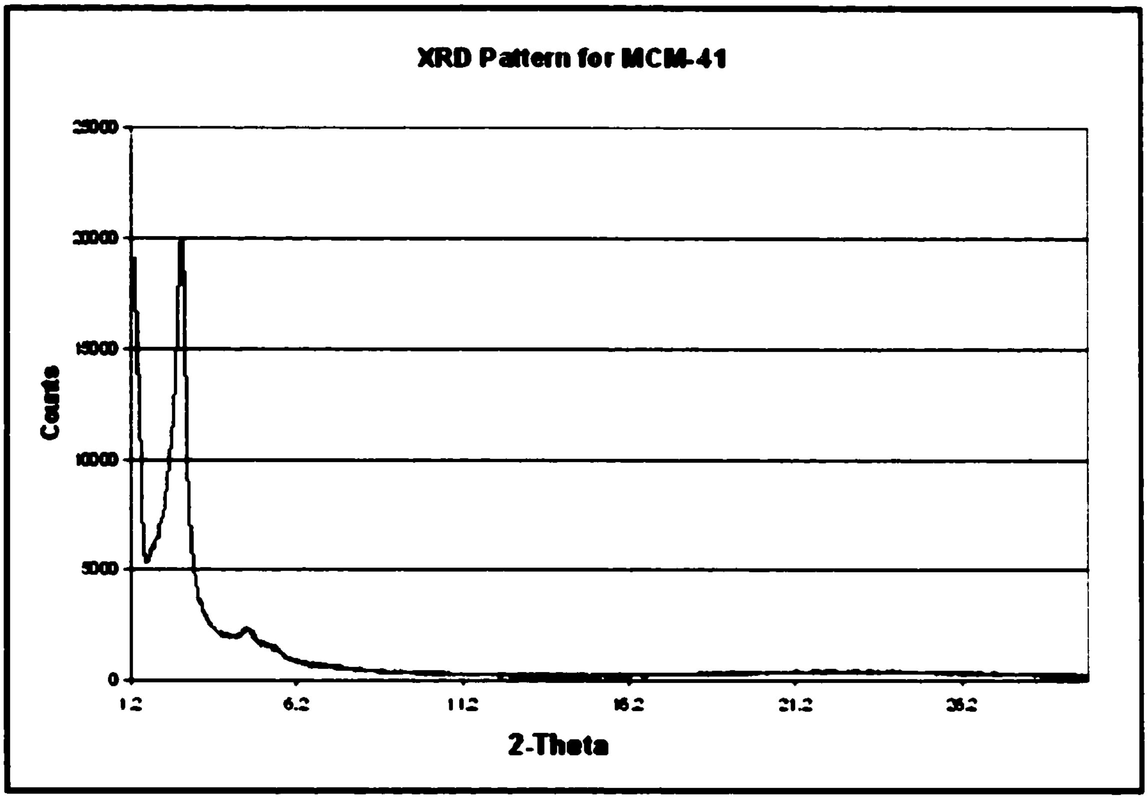


Figure 4.3

XRD pattern of MCM-41

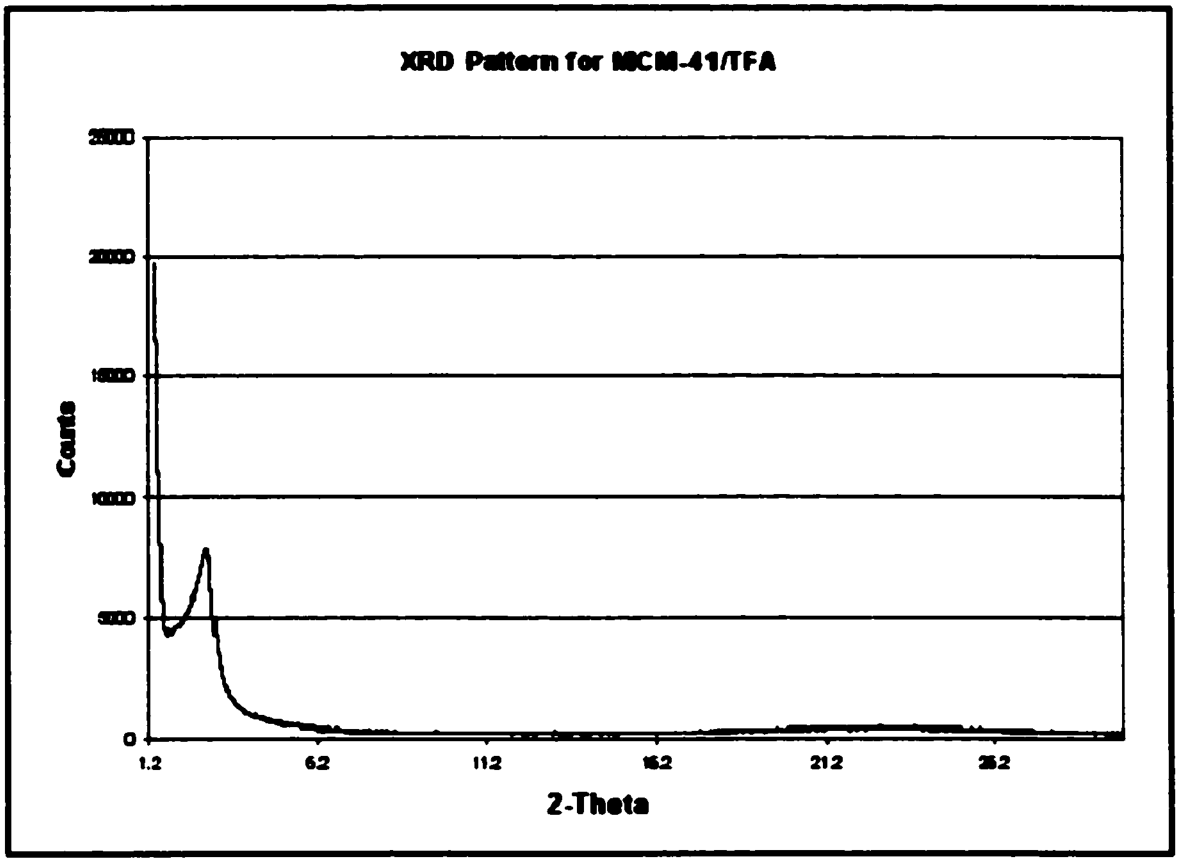


Figure 4.4

XRD pattern of MCM-41/TFA

The patterns presented here were used to determine relative degree of crystallinity which is done by integrating the area under the curves. The major peak in both patterns at 2 degrees has been attributed to the [1,0,0] plane of MCM-41. There are also 2 much smaller peaks in the MCM-41 pattern which are due to the [1,1,0] and [2,0,0] planes. [29] These are absent in the MCM-41/TFA sample. Definite evidence that structural collapse has occurred. In fact the relative degree of crystallinity of the MCM-41/TFA compared to the pure MCM-41 suffered a loss of 55% crystallinity. This amount of structural collapse although significant does not render the catalyst useless. By starting with surface areas in excess of 1500 m^2/g we are still able to retain a sufficient amount of pore structure and surface area available for reaction despite the acid's corrosive nature. Ideally however, there would be no loss of crystallinity in the catalyst and a new method should be found to mitigate this damage. From the study of HY zeolite with TFA at low concentrations it is known that minimal structural collapse occurs which suggests that a sequential loading process could allow MCM-41 to accept TFA in smaller amounts while retaining its structure. [30] In this way a 30% loading could be split into 3, 10% loadings to see if the crystallinity was more stable. This could further improve the diffusion in the catalyst and give longer on stream stabilities.

4.3.2 BET analysis

Porosimetry data is obtained for various samples of catalyst to see how successful the synthetic procedure is as well as the effect of acid incorporation on the morphology of the MCM-41 structure. We will look at pore size distribution, surface area, pore volume and pore size for the catalysts.

The first type of information that we will look at is the pore size distribution of the parent MCM-41. A pore size distribution shows the amount of nitrogen adsorbed by the material being analyzed as a function of the relative pressure of the nitrogen being introduced to the sample. It gives a graph which shows how much of the porosity in the material is attributed to each size of pore opening.

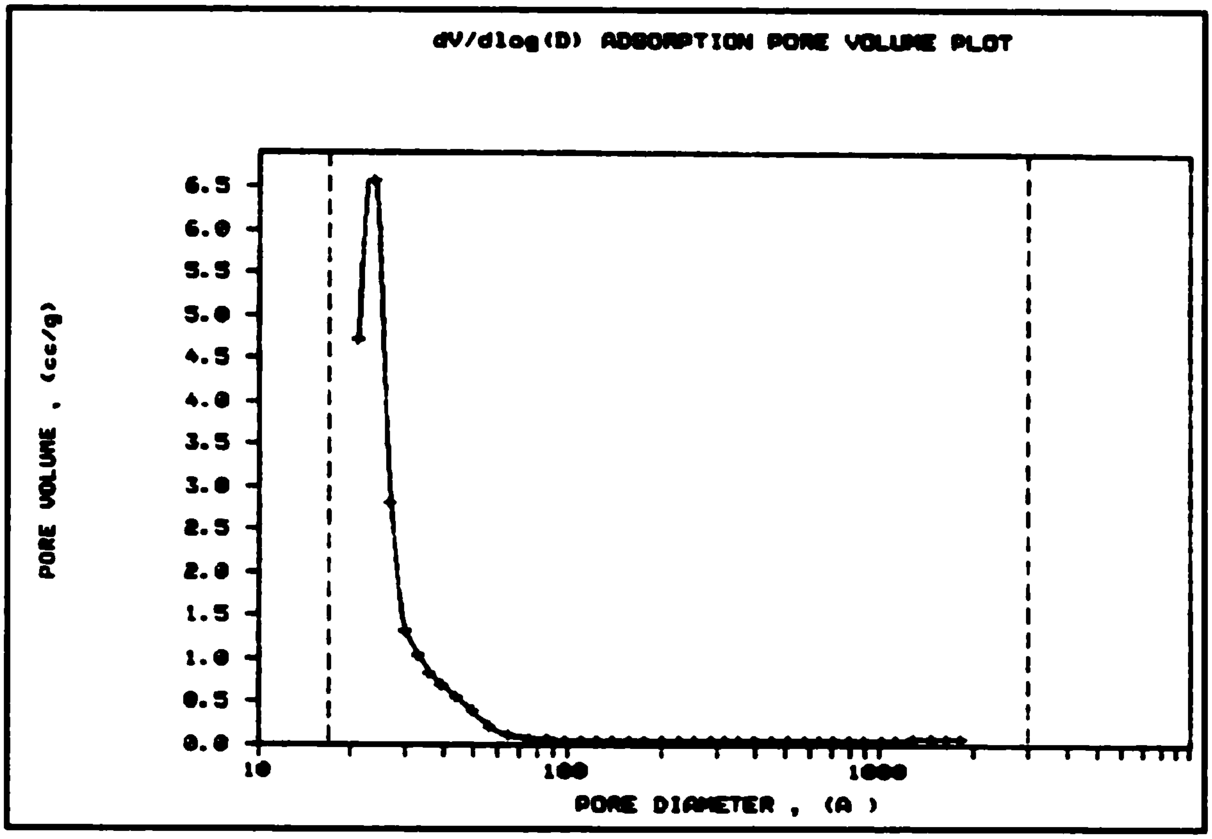


Figure 4.5

Pore size distribution in MCM-41

The graph shows that the majority of the pores have a diameter of approximately 26 Å without any other sizes being represented in significant amounts. This value has an uncertainty in it though due to the lack of data points much below 26Å but it is still considered as fairly close to the actual value since the unit cell parameter from XRD data is 26Å. The MCM-41 synthesized is thus very uniform in pore size distribution, a quality that is helpful when compounds are being passed through the channels. Having a narrow distribution of pore size ensures uniform diffusion properties through the whole solid.

We know that the MCM-41 in its unmodified state is very uniform in terms of pore size and it also has high surface area. Adding the triflic acid will alter the characteristics of the material to a great extent. In table 4.2 below the surface area, pore sizes and pore volumes are given for 3 different samples.

Sample	Surface Area (m^2/g)	Pore Diameter (Å)	Pore Volume (cm^3/g)
MCM-41	1519	26.6	1.01
MCM-41/TFA (1)	494	26.3	0.32
MCM-41/TFA(2)	769	25.9	0.50

Table 4.2

Morphological characteristics in MCM-41

There are several interesting things to note in this table. The MCM-41 stock sample does in fact have the high surface area and pore sizes we were trying to attain for the synthesis so as to alleviate some of the diffusion difficulties. Also, the pore size is significantly higher than zeolites. In fact it is more than 3 times the size of the USHY and H-Mordenite samples. This is also what was hoped for in the final material. So, the support has the desired characteristics and will then be loaded with the triflic acid. The 2 remaining entries in the table are for MCM-41 which was treated with triflic acid. All three samples were derived from the same batch with the only difference being the heat treatment given to each one. This was done to eliminate any potential variation in acid content from the loading procedure. The data for MCM-41/TFA (1) was collected for a sample which contained triflic acid and was heated at 120^{0}C for 48 hours. The MCM-41/TFA (2) entry was also heated at 120^{0}C for 48 hours and was then subjected to a further heating process involving an initial temperature of 200^{0}C which was increased to 450^{0}C in 50^{0}C increments every 2 hours. The reasons for choosing the heating steps used are as follows. The MCM-41/TFA samples can accept water vapour upon exposure to the atmosphere just as MCM-41 alone is capable of. To eliminate this water all samples tested were subjected to a 120^{0}C heating for 48 hours. Had water vapour been allowed to remain, the results would be skewed to lower values since water will occupy some of the pores. The MCM-41/TFA (1) sample with the same heating as above was tested to note the difference in characteristics from acid occupying the pores. We want to observe how much of the surface area is lost by adding the acid, how much the pores are narrowed and how much internal volume remains after this loading. The third sample, MCM-41/TFA (2) was heated with the stepwise process. It is known from thermal analysis that at temperatures above 350^{0}C, all acid species present in this catalyst will have desorbed and all that remains is the MCM-41 support. Structural damage is often a problem when incorporating certain acid species into catalysts and by removing all triflic acid from the MCM-41 the extent of this damage can be seen. There are two effects to be seen from the data here, structural collapse and occlusion of pores by triflic acid. The effect of pore occlusion is the difference in values between the MCM-41/TFA(1) values and the MCM-41/TFA(2) values. Structural collapse is evident from the difference between the MCM-41 and MCM-41/TFA(2). The two effects can be isolated in this way to assess the extent of each in reducing the surface area, pore volume and pore diameter.

Taking the case of surface area, there is a clear decrease in value upon acid addition. The reason for this is two fold. The acid has a damaging effect on the MCM-41 as evidenced by the XRD data showing less crystallinity. There is actually a correlation between the morphological characteristics and crystallinity. Both surface area and pore volume drop by roughly 55% as does the degree of crystallinity. The damage as caused by the triflic acid will result in some collapse of the pores. The second reason is the occlusion of the pores by the acid. This is the result of acid coating the pores and thereby decreasing the effective surface area available for nitrogen to adsorb and at the same time some pores can be entirely blocked by the acid. The term used to describe this is occlusion. A visual representation of this is shown in figure 4.6.

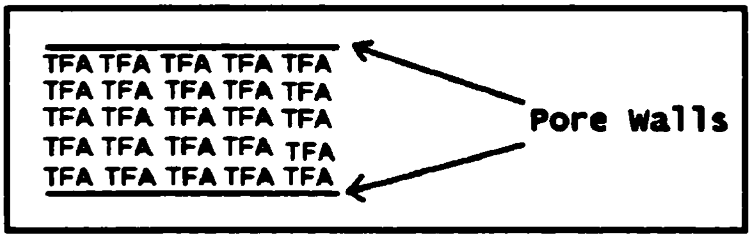


Figure 4.6

Occlusion of MCM-41 pore by triflic acid

In effect, the pores are reduced in radius and some are totally blocked. As a result the actual area must drop since the nitrogen has less space to adsorb. By then removing all the acid in the pores by heating, the effect of the acid on the structure will be seen with respect to the area. The data shows that the acid has definitely damaged the structure which is evident from the lower surface area. A mesoporous material is more affected by structural collapse compared to a microporous one as well since it has larger pores and volume. So, collapsing some of them will lower the area and volume compared to a zeolite where the pores are much smaller and less of them collapse. Had no damage occurred we would expect that the surface area would match the stock MCM-41 value. The triflic acid which was driven off does contribute to an increase of the area but some loss in structure has happened. Doing a porosimetry analysis on this sample will reveal the state of the support with all of the triflic acid present that was able to adsorb to the surface. The data shows that there is a significant loss in the surface area although the amount is only half relative to the MCM-41 alone. The nature of the damage which can lower surface area is the destruction of part of the pores in the material. Under sufficient attack, the pores will no longer have enough structure to maintain an open configuration and they will collapse. Also, silicon species can be removed and that will actually block the pores. Being able to minimize this structural collapse will be beneficial in better controlling the catalyst properties.

The pore volume is a measure of the amount of volume in the catalyst due to any pores able to accommodate nitrogen during the analysis. Again, we see that the MCM-41 stock batch has a high value of 1.01 cm^3/g, which means the structure is highly porous and can accept a large amount of acid. Addition of acid decreases the pore volume as the pores are partially filled with the liquid which accounts for the decrease. Then, after heating and removal of the acid the pore volume partly recovers but not to initial levels. This also shows that there is an acid attack on the MCM-41 which removes some porosity. In fact, if pore volume does not recover and the surface area is also lower, then the explanation is that the pores are being blocked by fragments that have been removed from the structure and then lodge in the remaining pores.

The pore diameter can also indicate changes in the structure of MCM-41. The variations in pore size at the surface of the pore are not significant and are comparable to the error in the actual value. In theory, when acid is added to it the pore diameter decreases slightly. This is due to the acid occupying the surface and thereby shrinking the pore size. The isotherm plots for these three samples are presented below in Figure 4.7. The changes in volume are quite clear .

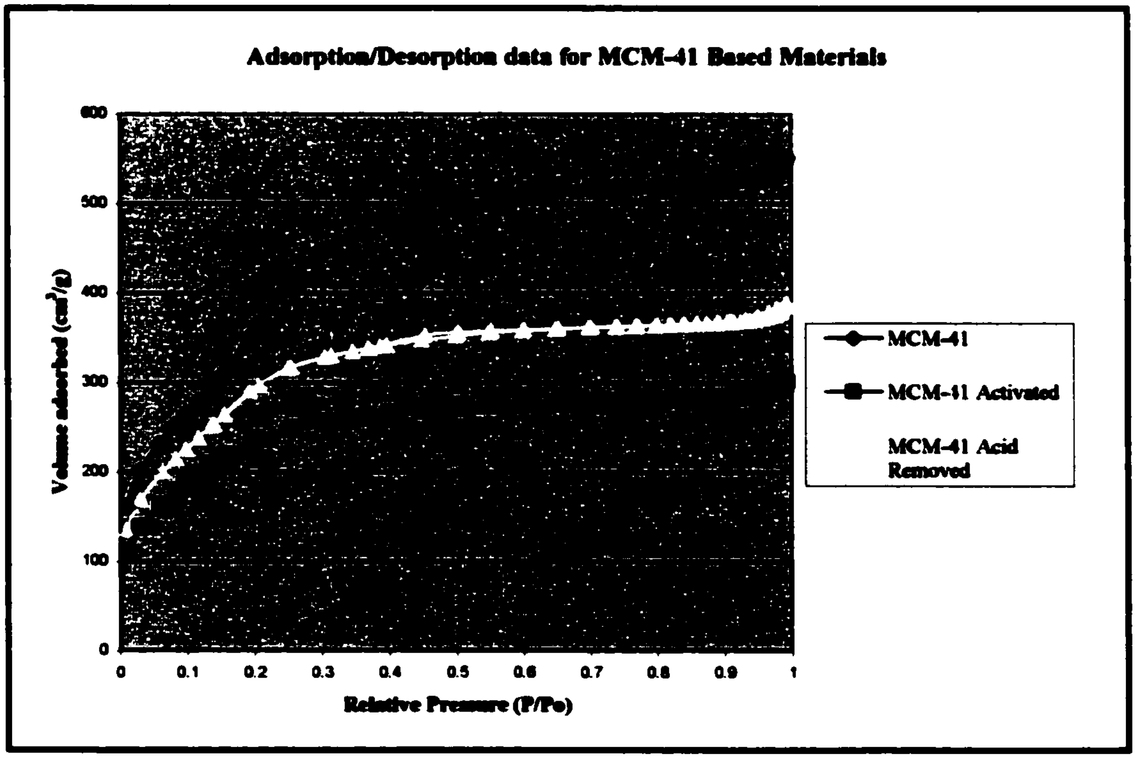


Figure 4.7

Nitrogen porosimetry isotherms for 3 catalyst forms

4.3.3 DRIFTS

This spectroscopic technique is adapted to study the surface of powders and solids with the use of infrared radiation. It is used for studying the fresh MCM-41 as well as acid loaded MCM-41 and used catalysts.

4.3.3.1 DRIFTS on stock materials

The first set of IR spectra are taken for the stock catalysts in the sense that none of them have been used for actual reactions. The first spectra is that of MCM-41 and it shows a few characteristic peaks. Y-axis units are taken as arbitrary with x-axis units as wavenumber (cm^{-1})

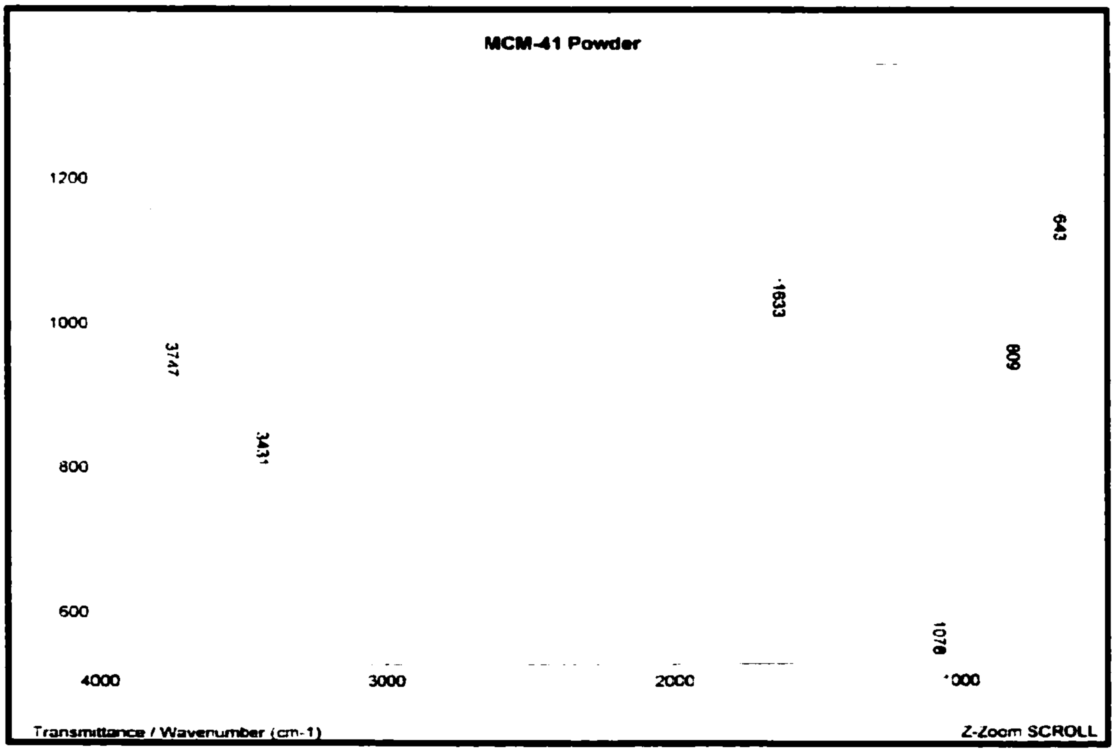


Figure 4.8

DRIFTS spectrum for MCM-41

It can be seen that there is a sharp peak at 3747cm^{-1} next to a broad band in the region of 3431cm^{-1}. The 3747cm^{-1} peak is common and has been attributed to silica hydroxyl or "silanol" groups in zeolites and high silicon content zeolites. [31] The 3431cm-1 broad peak may be due to water in the sample but it is possible there is also some contribution from hydrogen-bonded silanols as stated by Moser et al. Moving to the mid IR region there are more peaks in the spectra. The largest being the 1078cm^{-1} containing a shoulder at 1176cm^{-1}. The former is due to an internal structure asymmetric stretch of O-Si-O in the MCM-41 where the frequency is dependant, in zeolites, on the quantity of aluminum in the framework. As the fraction of Al decreases in the samples from the literature the position of this band is shifted to higher wavenumber. If this data is extrapolated to an Al fraction of zero the band is predicted to appear at 1075cm^{-1} which is very close to the value for the O-Si-O stretch in the MCM-41. The shoulder peak at 1176cm^{-1} has been attributed to the same stretching except that it is linked to the external O-Si-O asymmetrical stretch. The Si-O symmetric stretch also occurs in the spectrum at 809cm^{-1}. The last peak to be assigned is the one at 643cm^{-1} which is associated with Si-Si stretching. Having gone through the major distinguishing peaks in the spectrum of MCM-41 we can compare how it changes upon acid incorporation and other treatments.

If we consider next the MCM-41/TFA powder form, the IR changes as a result of acid incorporation can be seen.

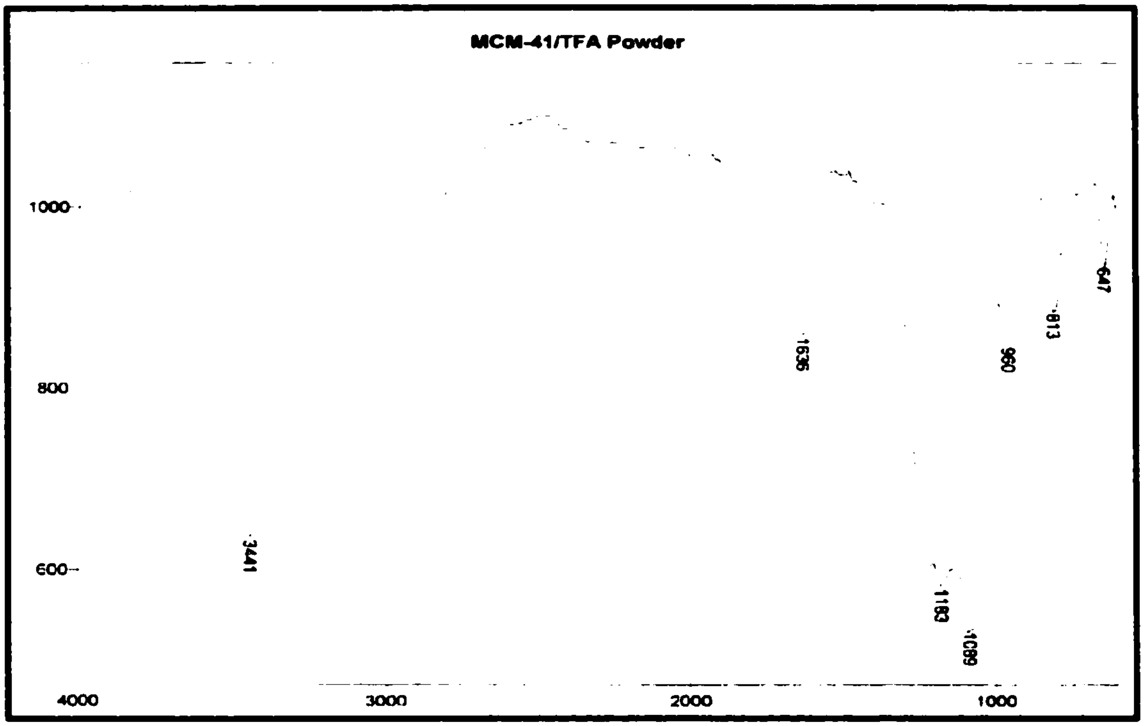


Figure 4.9

DRIFTS spectrum of MCM-41/TFA

The most noticeable difference between the two is the absence of the high frequency silanol peak at 3747cm-1. This characteristic peak should be present whenever silica is present with surface silanols. It is obvious that the MCM-41 is still present after acid loading so the only way for this peak to be attenuated is by preventing the radiation from attaining it. In a DRIFTS experiment the beam is only capable of penetrating through a very thin portion of the sample just below the surface. It may therefore be possible that the addition of the triflic acid results in a covering of the surface where the silanols would normally absorb. Apart from this peak the only other difference of note is the clearer resolution of the peak at 960cm^{-1} when compared to the unmodified MCM-41. The most likely assignment for this peak has been an absorption due to triflic acid, and more specifically the sulfoxide part of the acid. This peak appears as a shoulder of the much larger peak to the right so it is possible the peak from triflic acid happens to absorb in the same region as the MCM-41 siloxane asymmetric stretch.

It seems that the acid does not have very significant effects on the IR spectrum of MCM-41 so a test was also done using the extrudate form catalyst but it is virtually identical to the acid loaded MCM-41/TFA.

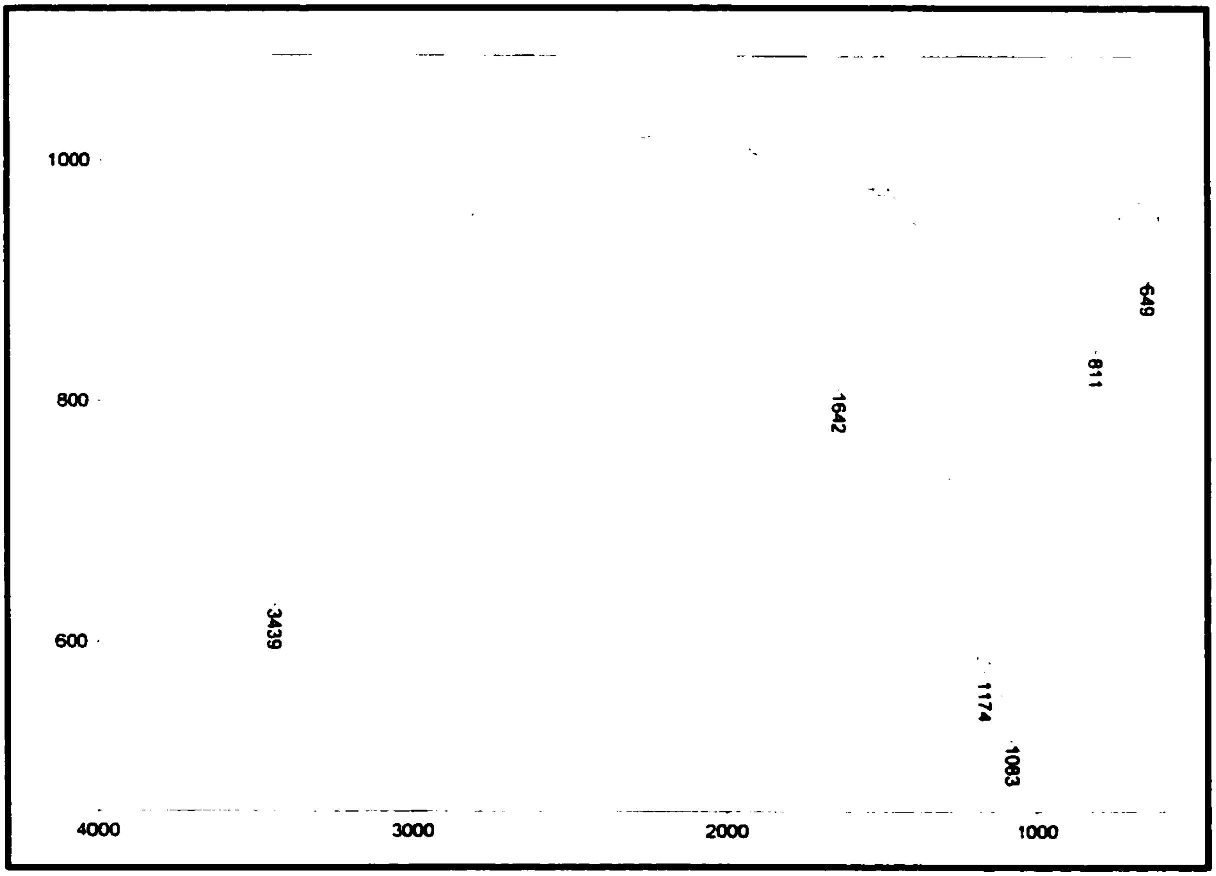


Figure 4.10

DRIFTS spectrum of catalyst extrudates

This indicates that bentonite does not affect the structure in any way. The final IR spectra obtained was on an extrudate sample which had been heated at 140^{0}C for the same amount of time as the duration of a typical alkylation reaction in the actual reactor so as to simulate the conditions with the exception of the introduction of feedstock. The concept here was to ascertain the level of structure change if any following use in a reaction. The spectrum showed that there is no change once again meaning that the reaction conditions themselves do not induce any structural changes in the catalyst.

4.3.3.2 Infrared study of coke deposits

The carbonaceous deposits on the catalyst during a reaction will be various hydrocarbons detectable by IR spectroscopy. The study dealt with a series of 6 catalysts used in the temperature variation reactions for isobutane. All 6 spectra are overlaid on the next spectrum to show the effect of temperature on the nature of coke. The top spectrum is at 200^{0}C and the temperature goes lower down to 70^{0}C for the bottom spectrum.

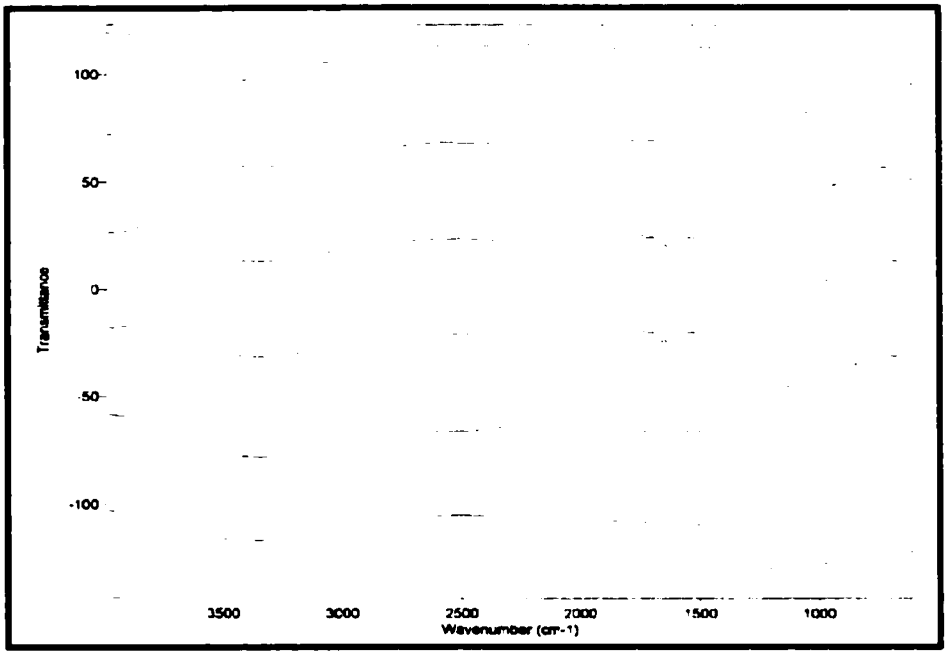


Figure 4.11

DRIFTS spectra on used catalysts

A very gradual peak size change is observed in two regions of the spectra. First the 2900cm^{-1} region and also the 1400cm^{-1}. What is interesting about this temperature induced effect is that the peaks diminish as the reactor temperature increases. We know from the thermal data that coke increases with temperature yet the peaks are smallest at high temperature. This behaviour is counter intuitive since more coke should roughly translate to stronger peaks. Knowing that coke deposits increase with reaction temperature, the IR peaks in the ranges noted must be due to other species. Adsorbed hydrocarbons of smaller size may be the actual cause of these peaks. Assuming the molecules are not completely trapped on the surface of the catalyst which is reasonable to assume since the surface has now physical means of trapping the molecules, they will leave the surface more readily at elevated temperatures. What may be happening is an adsorption of product molecules, reactants, light coke etc... which is only weakly bound to the catalyst surface. As the reactor temperature is increased these more volatile molecules will easily desorb from the surface. The actual IR peaks shown in the spectra coincide with saturated C-H stretches in the $3000cm^{-1}$ range and the lower frequency peaks near $1400cm^{-1}$ are likely due to C=C stretches from aromatic systems containing several rings.

4.3.4 Thermal analysis

Determining how triflic acid interacts with MCM-41 is one of the goals of this research. Thermal analysis is a technique capable of showing various phase changes and mass changes in a material. The technique comprises 2 simultaneous operations, measurement of mass loss and measurement of differential sample temperature as a function of the furnace temperature. Many samples were run on the instrument in order to get as much information about the catalyst as possible. The components of the catalyst are MCM-41, triflic acid (from aqueous solution) and bentonite as a binding agent. MCM-41 and bentonite are thermally stable structures and should not have any change upon thermal analysis. Any residual moisture which may have been present on the surfaces of these materials was eliminated by heating at 110^0C inside the instrument.

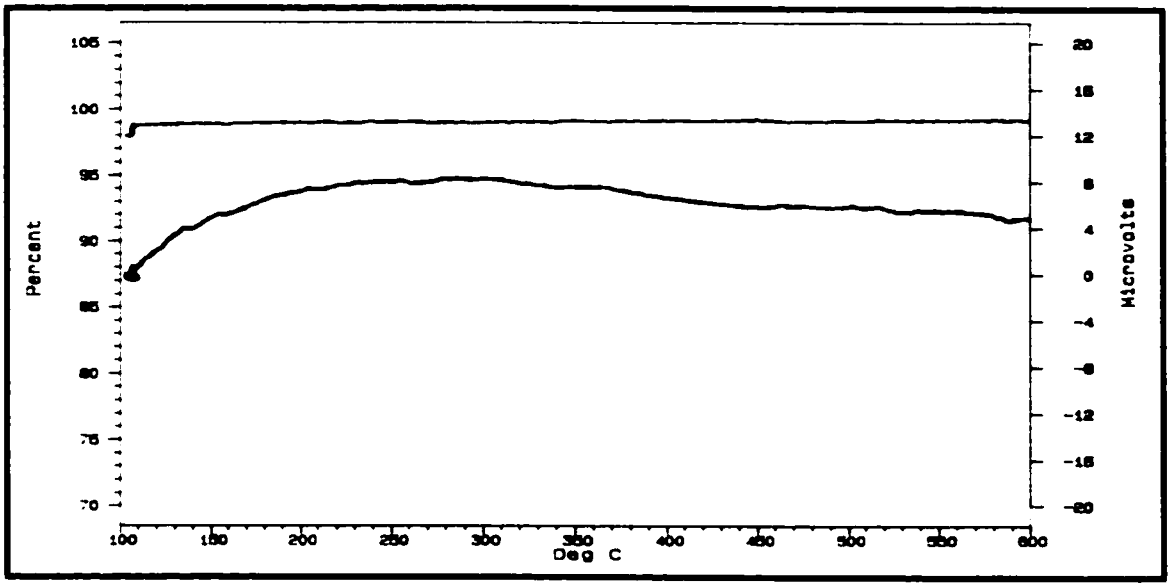


Figure 4.12

Thermal analysis of MCM-41

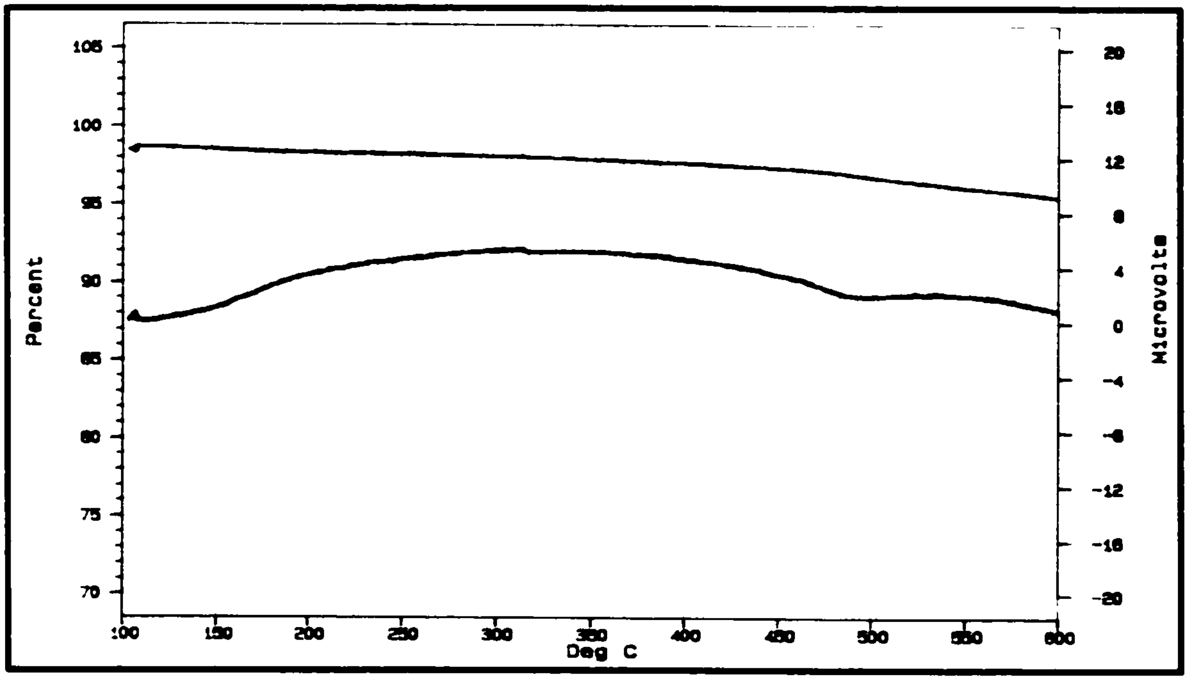


Figure 4.13

Thermal analysis of bentonite

The DTA/TGA traces show no variation throughout the temperature ramp. If the binding agent and support do not contribute to any DTA/TGA signals then any signals during catalyst testing must be due to interactions arising from the triflic acid loading. Recall that before the MCM-41/TFA can be used as a catalyst it must be extruded with a binding agent, bentonite. The extrudates are then heated again. Therefore, there are two forms of the catalyst, powder and extrudate. We now look at the result for MCM-41 which has been treated with the acid and dried for 24 hours.

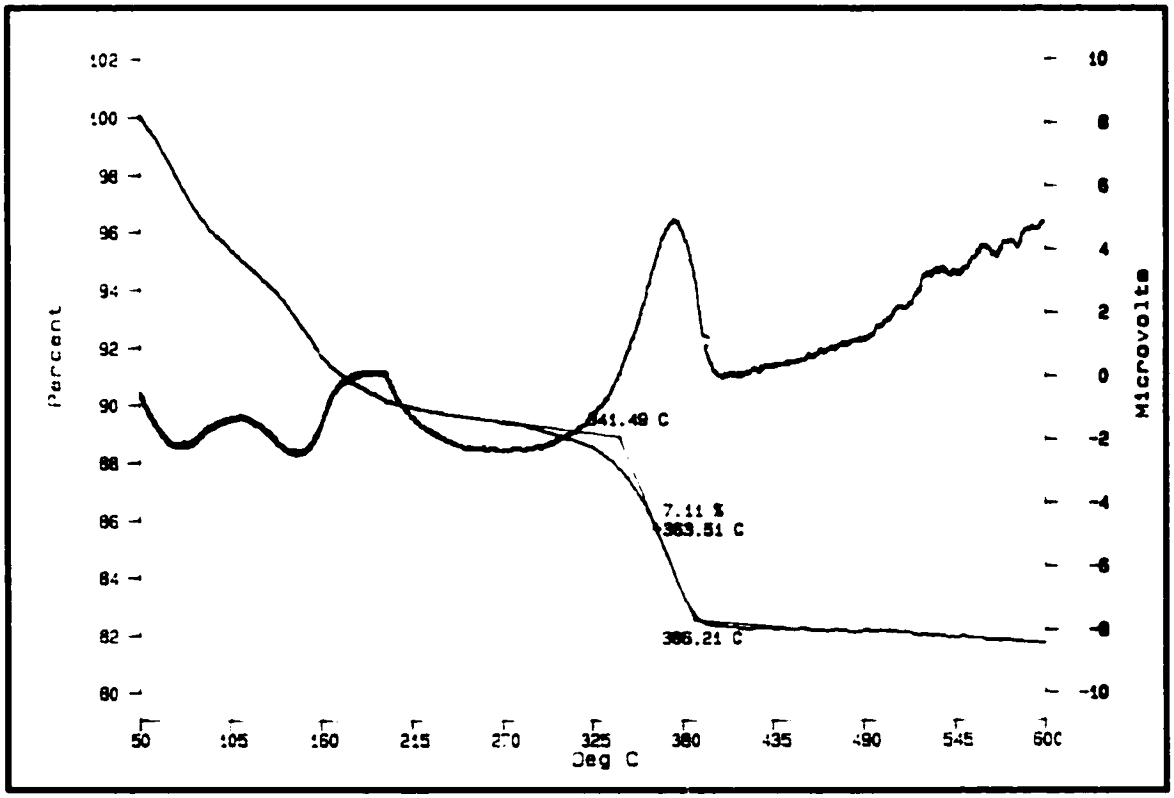


Figure 4.14

Thermal analysis of MCM-41/TFA

There are 2 clear mass changes and corresponding thermal events on the above trace. These have been ascribed to 2 species of triflic acid in the material. The first transition at 160^{0}C is the evaporation of "free" liquid like triflic acid from the MCM-41 pores. It is not bound and with modest temperatures will easily evaporate from the support. The DTA trace also indicates that this transition is endothermic which supports the theory that the evaporation is indeed the cause of the mass drop. The second mass loss is at a higher temperature and is exothermic. For a change to be exothermic it must be either a decomposition or a combustion. Assuming that the free acid has been cleared the only possible remaining species is a triflic acid species more strongly associated to the support. A chemisorbed molecule would need higher temperatures to desorb due to the chemical bond with the surface. Previous work from Le Van Mao et al. has suggested an adsorbed triflate anion species capable of chemisorbing to a silicon atom in a zeolite. [32] It is thought that the same anion is present in this case and is giving rise to the 330^{0}C mass loss in the powder. This is the predicted structure of the chemisorbed anion.

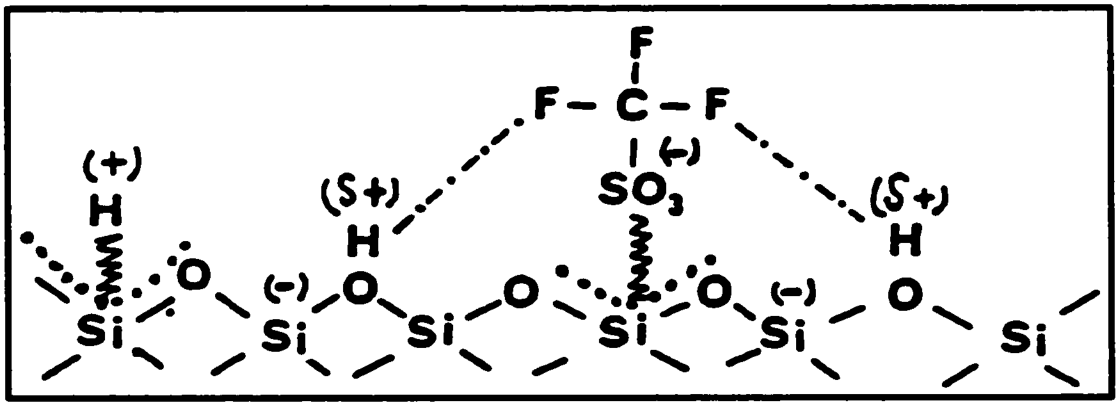


Figure 4.15

Adsorbed triflic acid on MCM-41 surface

Adsorbed triflate ions can lead to an increase in the acidity of the silanol groups on the MCM-41 surface which are normally non acidic. This means that the addition of triflic acid provides two different types of acidity in the form of loosely bound triflic acid and triflate anion functionalised silanol groups which are more resistant to high temperature. Initial testing for this dual acid catalyst system has been obtained by isolating the silanol acidity from free triflic acid. A sample of MCM-41/TFA catalyst was heated in the reactor for 16 hours at 220^0C. These conditions are more than adequate to remove the free triflic acid leaving behind only silanol acid sites. Testing of this catalyst shows activity lower than the non heated sample which is the expected result assuming free triflic acid as the major catalytic component.

Further insight can be gained from the data by calculating the actual mass loss for these events. The thermal TGA trace for the MCM-41/TFA sample experiences a loss of about 7% for the free acid species and 7.1% for the adsorbed species. Knowing that the acid is added in a 30% amount relative to the mass of support we can say that the MCM-41 uptakes approximately 45% of the acid present in the impregnation solution. The remaining 55% most likely stays on the external surface of the particles and quickly evaporates upon heating when drying the sample. Of the 45% successfully loaded into the MCM-41 in the "free" and adsorbed state, the "free" form makes up approximately 30% of this and the difference is adsorbed.

A DTA/TGA test was conducted on an extrudate sample of the catalyst and a drastic difference was noted. Upon addition of bentonite and extrusion into the final catalyst form with a 24 hour heating period at 120⁰C to remove water, the DTA/TGA transition at 160⁰C disappears.

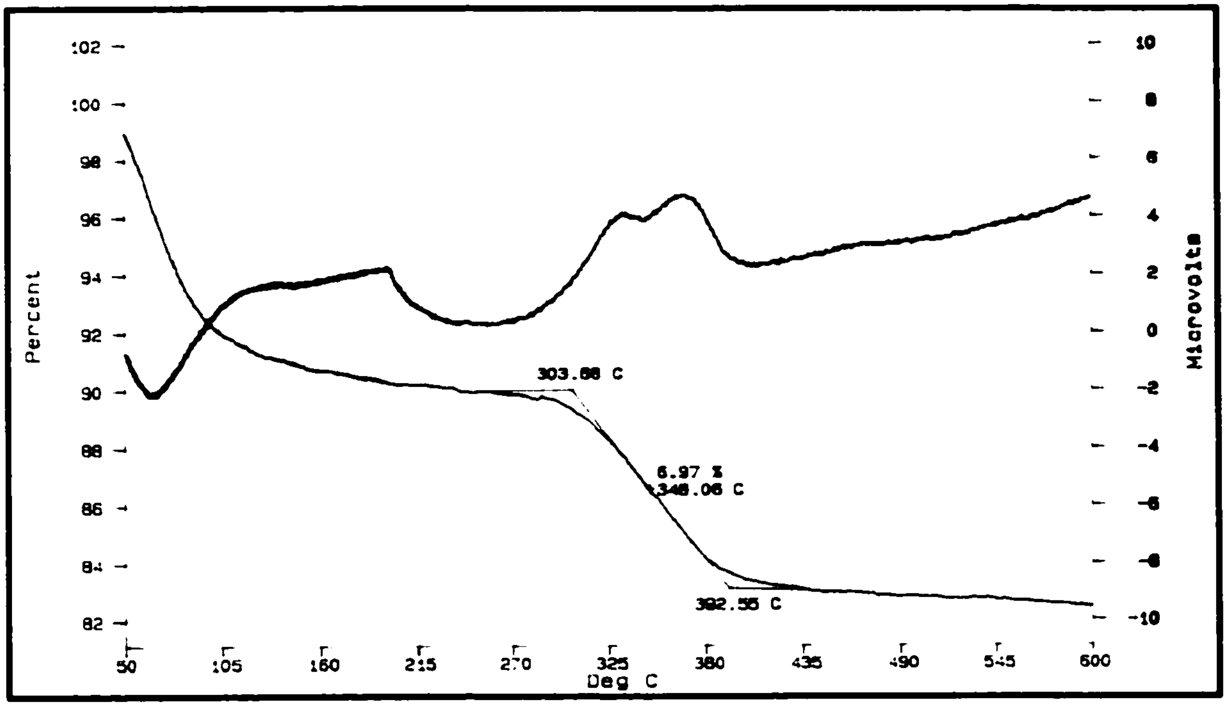


Figure 4.16

Thermal analysis of extrudate form MCM-41/TFA

Absence of this transition which corresponds to the "free" triflic acid evaporation points to either a loss of this acid during the second heating step or the modification of the acid such that it no longer evaporates at the same temperature. Bentonite in the extrudates is known to be capable of adsorbing water vapour and other species onto its surface so the bentonite must be playing a role in the triflic acid adsorption. Careful analysis of the TGA trace reveals that upon addition of the bentonite the mass loss at 360⁰C does not change in quantity to any large extent. With the addition of 30% bentonite this loss should also drop due to dilution of the powder with the inert bentonite. Actually, the loss is the same while the loss at 160⁰C is gone. The only way for the 330^0C loss to be constant is for the "free" acid to become adsorbed to the bentonite as it does to the MCM-41. Essentially, the addition of bentonite provides additional surface on which triflic acid can adhere in some form. These bentonite particles once embedded with the MCM-41 particles can perhaps intercept and adsorb species which diffuse out of the pores of MCM-41 thereby making the release of triflic acid more constant with time. These mesoporous particles will come in intimate contact with the MCM-41 particles and readsorption of desorbed triflic acid may be the phenomenon occurring. Stability of the catalyst was evaluated by heating a sample of the powder form for two weeks at 120^0C to see if with extended times at higher temperatures the acid content would drop off. It was found that the acid is rather stable with negligible fluctuation in acid content despite lengthy heating.

Summarizing the findings using thermal analysis these insights are obtained into the catalyst structure.

1) MCM-41 itself and the bentonite binding agent do not have any noticeable effects on thermal stability of the catalyst.
2) Triflic acid when loaded into the MCM-41 support forms two distinct species thought to be the "free" protonic form triflic acid and a chemisorbed triflate anion coordinated to a silicon atom in the MCM-41 framework.
3) Formation of this powder form catalyst into extrudates using bentonite causes some of the adsorbed protonic form to shift to higher temperatures due to interactions with the bentonite . It seems probable that the

bentonite in some way adsorbs the acid that manages to leave the MCM-41.

4) The catalyst is stable and does not lose acid with time.

4.3.4.1 Thermal analysis on used catalyst

Thermal analysis was predominantly used in ascertaining the state of the acid in the catalyst as well as stability of the catalyst but it is used with equal success to estimate the amount of coke deposited on the catalyst after a reaction is completed. We are interested in seeing coke deposition on the catalyst depending on the temperature used in the reactor since this phenomenon leads to loss in catalytic activity. It is well known that higher reaction temperatures lead to faster deactivation due to coke formation. By using a variable atmosphere DTA/TGA scenario where air is sent into the furnace at high temperature following nitrogen atmosphere the combustible coke deposits can be burned off and the weight loss noted. A set of 6 catalysts were tested all having been used in alkylation reactions of isobutane with isobutene. Each catalyst was used at a different temperature for the reaction so the DTA/TGA should show an increase in coking as the reactor temperature increases. A thermal analysis trace is shown for the catalyst at 200^0C. The sharp mass loss at 600^0C corresponds to air being sent into the system and the coke burning. This is the cause of the large exothermic spike in the differential temperature data.

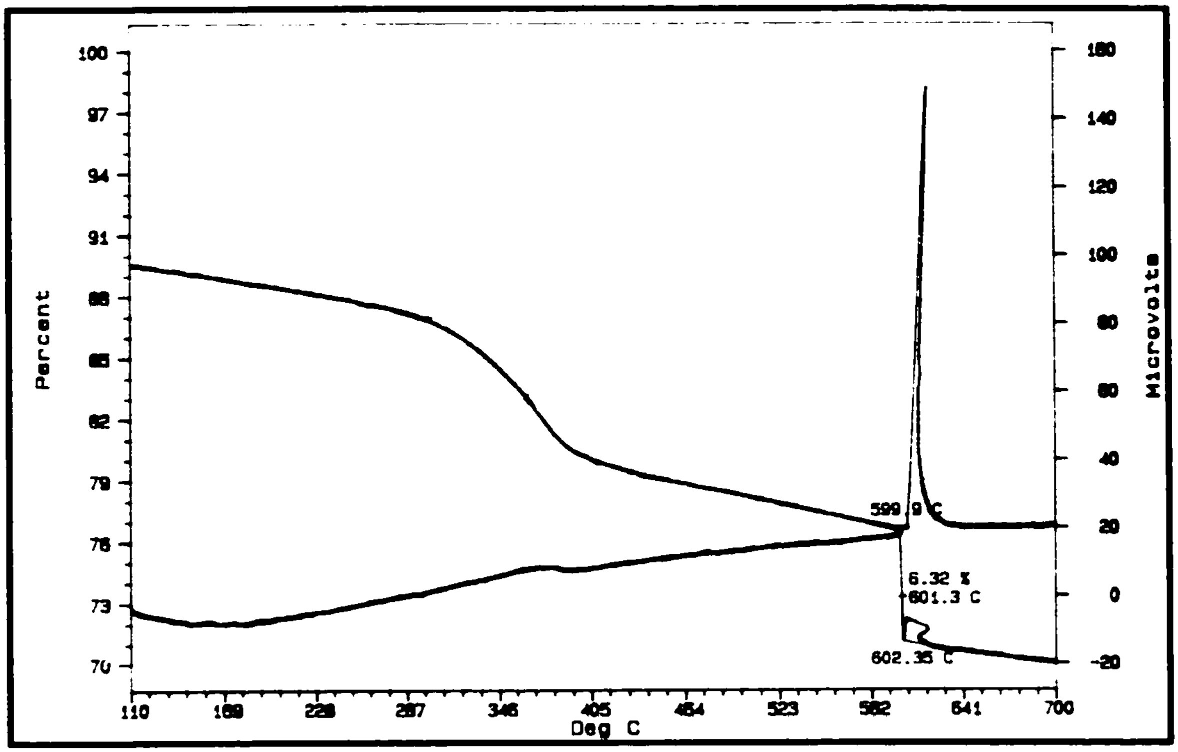


Figure 4.17

Thermal analysis on used catalyst at 200^{0}C

Below is a table summarizing the coke as weight percent of the catalyst and the DTA/TGA trace for the used catalyst for the maximum temperature reaction.

Reactor temperature (^{0}C)	Mass loss (wt%)
70	~0
110	1.09
140	1.15
160	1.28
180	1.45
200	6.30

Table 4.3

Mass loss due to coke by thermal analysis

There is certainly a temperature effect on the amount of coke deposited but a major increase is present when the reactor temperature reaches 200^{0}C. Such a large increase in coke deposits from a small temperature increase shows that the process by which the coking occurs most likely undergoes a change. This may be due to enough energy being available for certain side reaction to be favoured, namely oligomerization.

4.3.5 Catalyst evaluation and performance

Developing a catalyst for a process means that the operating conditions must be found for which the catalyst exhibits optimal performance. There are many variables in a typical reaction system but the ones of note that were looked at for this work are reactor temperature, contact time, isobutane/olefin ratio and the type of reactant use. In all tests, the contact time was 2 hr, the ratio of isobutene to olefin was 10/1 and the temperature in the reactor was 140^{0}C except when one of these quatities was varied for a series of tests. For example, the reactor temperature series are done at temperature besides 140^{0}C but at a contact time of 2 hr and a ratio of 10/1.

4.3.5.1 Reactor temperature and nature of olefin feedstock

The temperature at which an alkylation reaction is carried out is one of the most important factors for varying the conversion and selectivity for products in a reaction. This is due to the changes brought about by providing more energy for the reaction and will have a major impact on the types of reactions that occur. Most of the time it is better to use the lowest reaction temperature possible as high temperatures translate into higher costs to run the reactor, an important concern in industrial applications. This parameter was examined as it relates to alkylation reactions but another aspect of the reaction which will greatly affect the results is the nature of the olefin used as alkylating agent. Obviously a change in reactant will change the products and as we will see it can have major consequences in terms of conversion. These two critical factors have been considered in the alkylation tests and consist of a temperature variation for three different feedstocks. The feedstocks being 1-butene, a mixture of 2-butene cis/trans isomers and isobutene.

The results for an alkylation run are often represented in terms of conversion and selectivity. These quantities are the ones reported for the catalytic testing. The first graph shows how the conversion is dependent on temperature for each feedstock.

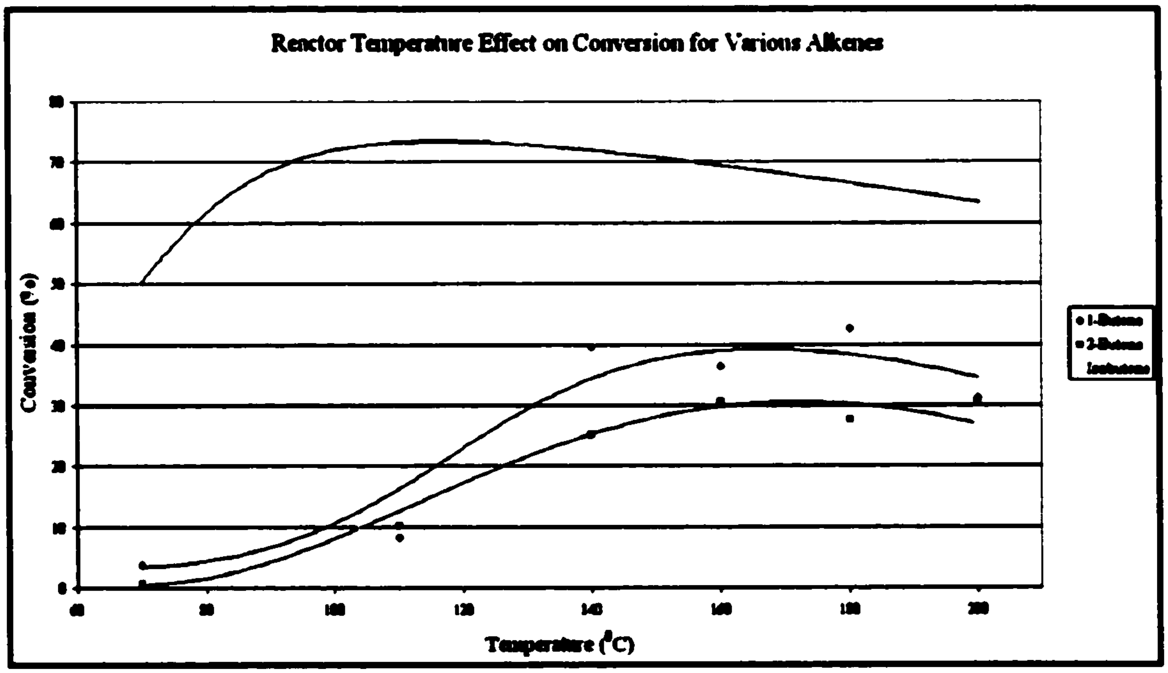


Figure 4.18

Conversion for various feedstocks

Normally an increase in temperature brings about an increase in conversion and the trend would be expected to be fairly regular. We can see in this graph though that there is a non linear appearance which will be explained using the state of the triflic acid as well as mechanistic considerations. At low temperatures, below 120^0C, we see the conversion level is relatively low for 1- and 2- butene. There is a small increase from 70^0C to 110^0C but at 120^0C the conversion level increases dramatically. Upon further temperature increase the conversion levels off and is no longer dependant on the temperature. This behaviour is thought to be related to the way in which triflic acid can enter the MCM-41 and the form it takes during this process. Triflic acid is added as an aqueous solution and it is known that the acid can form a monohydrate very readily. This monohydrate may cause hydrogen bonding to occur in the acid which prevents triflic acid in the protonic form from effectively catalyzing the reaction since it is locked into this solid state. Most likely there is a monohydrate layer that can form on the acid surface which blocks much of the reactants from reaching any actual acid sites. If we consider this scenario with respect to the conversion data we can postulate that the monohydrate lowers the activity of the catalyst but once a high enough temperature is reached the hydrogen bonding is disrupted and the triflic acid reverts to its protonic state. A rapid increase is seen between 120^0C and 140^0C which suggests that the monohydrate is unstable and easily removed with sufficient temperature needed to disrupt the hydrogen bonding. As the temperature exceeds 140^0C the conversion reaches a plateau. This is attributed to a maximum in the amount of acid available being reached and the more rapid deactivation of the catalyst as secondary reactions become more prevalent at higher temperatures. The next point to be addressed here is the slight difference in the curves for 1- and 2-butene. While they do have very similar values the 1-butene does have slightly better conversion over 2-butene. Carbocation stability of the alkylation intermediate alone will not explain this and in fact it suggests the opposite outcome where 2-butene would be better than 1-butene. There are several possible answers for this unexpected result. Two potential answers to this problem are that in the case of 2-butene an intermolecular hydride transfer takes place before the product can form. This extra step from a secondary to a tertiary cation will slow the production of alkylate.

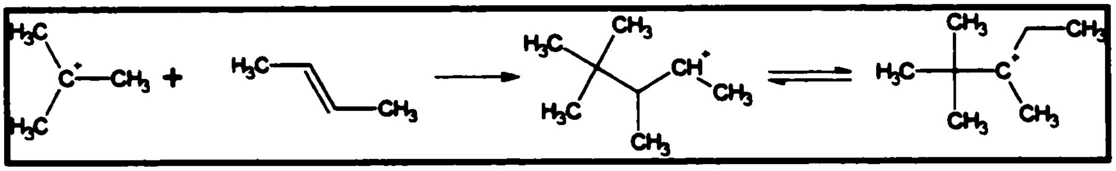


Figure 4.19

Hydride shift in secondary octyl cation

Also, once the octyl cation is formed after the intermolecular hydride shift the proton abstraction from an isobutane molecule may be sterically hindered compared to the 1-butene case. The additional methyl group at the carbocation from the 2-butene addition may be more difficult for isobutane to attain for the abstraction. In the carbocation derived from the 1-butene addition there is more space due to lack of a methyl group in addition to the cation being one carbon further from the bulky t-butyl group.

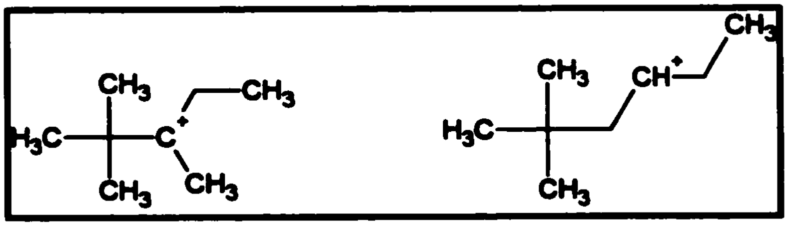


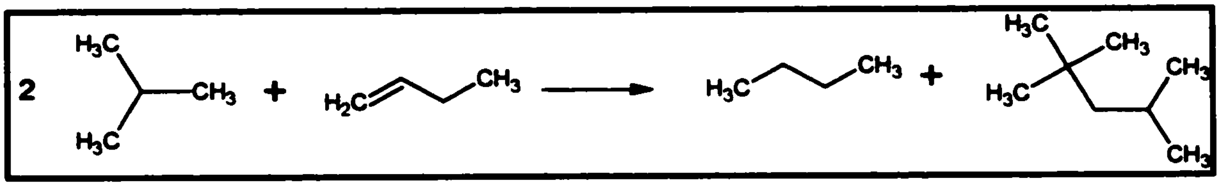
Figure 4.20

Comparison of steric hindrance in 1-butene and 2-butene derived octyl cations

There is a final explanation which is more involved than the previous 2 which relates to the mode in which isobutyl cations are formed in the reaction mechanism. The isobutyl cations are the most important component of the whole system in that they provide the highest octane products and are needed to complete the reaction cycle. For this discussion the various reaction mechanisms are grouped into four major categories. [33]

1) True or pure alkylation
2) Dimerization/cracking
3) Oligomerization
4) Self alkylation

The first three categories have been seen already but the fourth one, self-alkylation, is a new concept. This reaction is very useful in interpreting much of the selectivity and conversion data trends. In an alkylation reaction we know that isobutene reacts preferentially due to kinetic issues involving carbocation stability. Compared to the 1- and 2-butenes it reacts faster and forms more product. Isomerization of the feedstock occurs and most likely favors formation of isobutene from the 1- and 2-butenes during the reaction. It is important to point out here that for an isomerization of 1-butene to occur there must first be a double bond shift followed by a methyl shift but for 2-butene only the methyl shift is required. It turns out that when linear butenes are used in the reaction the self alkylation regime becomes operative. The linear butenes do not form as stable carbocations so the reaction takes care of this problem by using another source of tertiary carbocation, isobutane. Up until now the isobutane has served one purpose, formation of cations to add to the olefin double bond. However, when the olefin feedstock leads to slow kinetics the following mechanism will occur.



$2\ iC_4H_{10} + n\text{-}C_4H_8 \rightarrow n\text{-}C_4H_{10} + iC_8H_{18}$ [34]

Notice that from a linear olefin an iso paraffin is produced with a branching normally found only when isobutene is used as the olefin. This reaction creates isobutene from linear butenes to form the highly branched 2,2,4 TMP. This is a significant reaction. Rather than waiting for isomerization to produce isobutene, the isobutane assumes the role. To apply this to the fact that 1-butene outperforms 2-butene in terms of conversion is now quite simple. There is a competition with the above 4 categories of reactions for olefins but in the case of self alkylation the demand is lower. 2 isobutane molecules are needed for every one molecule of olefin whereas the others occur by a 1:1 ratio. Already the self alkylation is seen to be advantageous owing to lower relative olefin consumption. Now, 1-butene isomerises more slowly to the isobutene compared to the 2-butene yet it has high conversion. Self alkylation is a means of supplying isobutyl cations when the olefin can not do so effectively and 1-butene is the least effective so it is logical that it will engage in self alkylation more so than 2-butene. The formation of isobutyl cations from isobutane will occur more quickly for 1-butene because a primary carbocation will be converting to a tertiary whereas in the 2-butene case the change is only from a secondary to a primary.

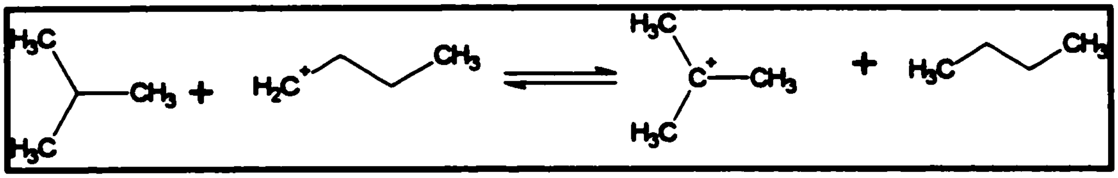


Figure 4.21

Formation of isobutyl cations from 1-butene primary carbocation

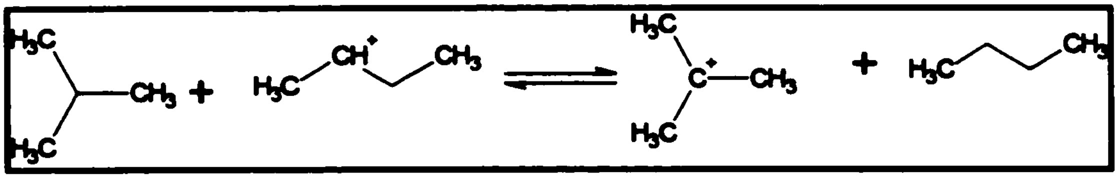


Figure 4.22

Formation of isobutyl cations from 2-butene secondary carbocation

This is a likely explanation for the difference between the two olefins. The equilibrium will lie more to the right for the case of 1-butene and so despite the formation of the primary carbocation for the formation of the isobutene, the equilibrium will result in more of the 1-butene generated isobutyl cations being used for the alkylation.

This explanation of the conversion data explains the observations for 1- and 2-butene but for isobutene the case is different. Here we see that the conversion is not very dependant on the temperature. In fact, at lower temperatures it is just as high as low temperatures. To rationalize this markedly different behaviour it is important to recall the simple carbocation based mechanism for alkylation. By invoking this mechanism we have 3 possibilities for forming a product molecule. Addition of an isobutyl cation to 1-butene will produce a secondary carbocation as the major product. A primary carbocation can also form but it will be the minor product according to Markovnikov's rule for addition to substituted alkenes. Addition of the same isobutyl cation to a molecule of 2-butene will also form a secondary carbocation exclusively since the molecule has a methyl group on both sides of the double bond. So far the stability of the carbocations for 1- and 2- butene are essentially similar and will yield the same products in roughly equal amounts. In the case of isobutene the only carbocation formed by the addition step is tertiary. Tertiary carbocations are much more stable than secondary carbocations and will result in product formation more quickly than secondary cations.

With this information the behaviour of isobutene can be interpreted when comparing conversion levels amongst butenes. At low temperatures the surface is mostly covered with a layer of monohydrate but there are some triflic acid molecules available at this point. Knowing that isobutene reacts via a tertiary carbocation the Hammond postulate can be applied. According to the postulate, the structure of a transition state resembles the structure of the nearest stable species. Addition reactions on an alkene are endothermic so the transition state should be structurally close to the carbocation. [35] If the carbocation is more stable due to tertiary substitution the transition state should be stabilized which leads to faster reaction rates. In short, the tertiary carbocation intermediate formed by isobutyl addition will have a faster rate of formation relative to the addition of the butyl ion of 1- and 2-butene. This information can now be correlated to the active surface of the catalyst.

When monohydrate resides on the majority of the catalyst surface with only a limited number of protonic triflic acid molecules available, the reaction using 1- and 2-butene gives less conversion. The rate of formation of the C8 carbocation intermediate is relatively slow and so is the formation of the final product. In tandem with limited acid sites the net effect is a suppression of conversion due to acid site coverage and slow kinetics. Isobutene is able to overcome the small number of acid sites because the tertiary carbocation intermediate forms much faster and consequently liberate the catalyst surface for further reaction. In this way we can understand the data concerning the various feedstocks and how they react. It is interesting to note that isobutene, if subjected to self alkylation, will not have any effect on the outcome of the reaction. Isobutene forms tertiary products so converting isobutane to isobutene will not offer any better stability.

4.3.5.2 Selectivity

The selectivity data for reactor temperature variation will show how the alkylation reaction proceeds along with the secondary reactions. It is clear that the myriad reactions all under way during a reaction will be influenced to varying degrees by temperature and studying this effect will demonstrate the trends in product distributions. The interpretation is done by dealing with 3 categories of products. The 3 categories are cracking products, alkylation products and oligomerization products. Taking an ideal alkylation reaction as the formation of a C8 molecule from two C4 molecules the cracking products are seen as molecules containing less than 8 carbon atoms and in fact this fraction is made of C5, C6 and C7 groups. Alkylation products are then any C8 molecule and oligomerization products are molecules containing more than 8 carbon atoms, specifically C9 molecules. This classification scheme is simple and will more easily show the tendency for the primary and secondary reactions as opposed to individually plotting each fraction. The graphs for each feedstock are presented separately.

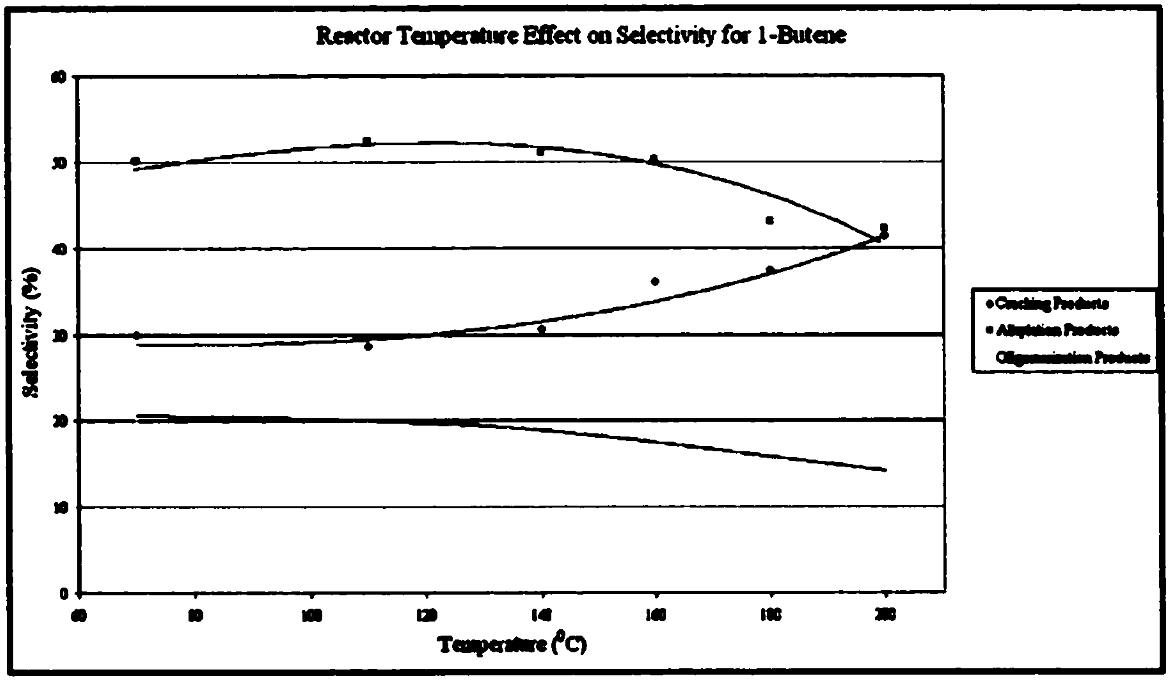


Figure 4.23

Selectivity for 1-Butene

The first graph displays the 1-butene selectivity data as a function of reactor temperature. The curves show that as temperature increases the selectivities for all categories change. The cracking fraction trend is to increase with temperature while the oligomerization and especially the alkylation fractions decrease with temperature. To explain this we must consider several things. There is a gain in cracking activity at the expense of alkylation mostly and to a lesser extent oligomerization. Cracking is an endothermic process while alkylation and oligomerization are exothermic.

When the temperature increases the cracking activity will increase at the expense of the exothermic processes. Based on thermodynamics alone we can understand why cracking would be preferred at higher temperatures. Self alkylation plays a role in the product distribution as well. The concept here is to minimize the occurrence of primary and also secondary carbocations during reactions in favour of tertiary cations. In a normal alkylation reaction the alkene feed is protonated as usual to produce a carbocation of varying degree. In the case of 1-butene, secondary and to a much lesser extent primary. Once this occurs the normal path is for this cation to do a hydride abstraction on isobutane yielding an isobutyl cation which is added to another 1-butene molecule. The product of this step then takes a hydride ion from isobutane and the cycle starts again. The self alkylation process departs from this scheme. Here, the isobutyl carbocation formed from a hydride transfer to the alkene has a proton abstracted by a new alkene molecule which yields isobutene and a carbocation. So far this has not shown any reason for being preferred in terms of stability but the important point is that the isobutene just formed will produce tertiary carbocations and the carbocation from the 1-butene molecule will be eliminated by a proton abstraction from a second isobutane molecule. This information allows a more detailed explanation of the behaviour observed in the selectivity for 1-butene. At low temperature the amount of 1-butene in the stream is relatively high so the extent of self alkylation will be higher in order to decrease the incidence of primary and secondary intermediates. The 1-butene is less capable of forming carbocations under normal alkylation mechanisms. As the temperature increases the isomerization of the feedstock will become more pronounced. 1-butene is the least stable of the C4 isomers and so we would expect it to readily form 2-butene and isobutene. By increasing the temperature the amount of self alkylation decreases and since this produces C8 products the alkylate selectivity will correspondingly drop as well. The bulk of this theory is that the 1-butene will attempt to isomerize to isobutene in order to follow the conventional alkylation reaction mechanism. This requires 2 steps and this will slow the reaction. In contrast to this, the self alkylation leads to formation of the cations from isobutane and the 1-butene is converted into a saturated paraffin. There may also be an effect from the disruption of the monohydrate layer where higher acid site density leads to more sites for secondary reactions to occur. This ties in quite well with the observation from conversion data. The fact that cracking reactions occur during the reaction is indicative that alkylation products can adsorb on the surface and further react through the secondary reaction mechanisms. At low temperatures when much of the acid is unavailable for reaction there are fewer sites for alkylation products to readsorb. They can thus exit the pore with lower probability of going through side reactions and this results in higher yields for larger molecules. Once the triflic acid reverts to the protonic form there are more sites on the surface for readsorption of products and more cracking to take place. These two factors are the most likely in contributing to the detrimental effect of higher reactor temperatures.

Having explained already the trends in 1-butene selectivity data the 2-butene case can be described along the same principles. Of course the increase in temperature will favour the cracking reactions which in turn lower the formation of larger molecules as in the previous case. Examining the extent of self alkylation will again point as to why the alkylate selectivity decreases as it does. In the 2-butene reactions we see a very large drop in alkylate selectivity from 100% at 70°C to levels below 60% at elevated temperatures. If we again consider the mechanism, 2-butene must first form secondary cations followed by isobutyl cation formation. As before this is a less desirable situation which must begin with a secondary cation. Instead, the isobutyl cation will form isobutene and the alkene molecule will abstract the proton to do so followed by a second hydride abstraction from isobutane. In the previous two examples involving 1- and 2-butene, the final octyl cations have been tertiary when self alkylation is invoked due to the process occurring via isobutene and an isobutyl cation. Without this process the octyl cations would be secondary. This is another reason that the self alkylation route is preferable when dealing with alkenes that will require primary and secondary cations to form.

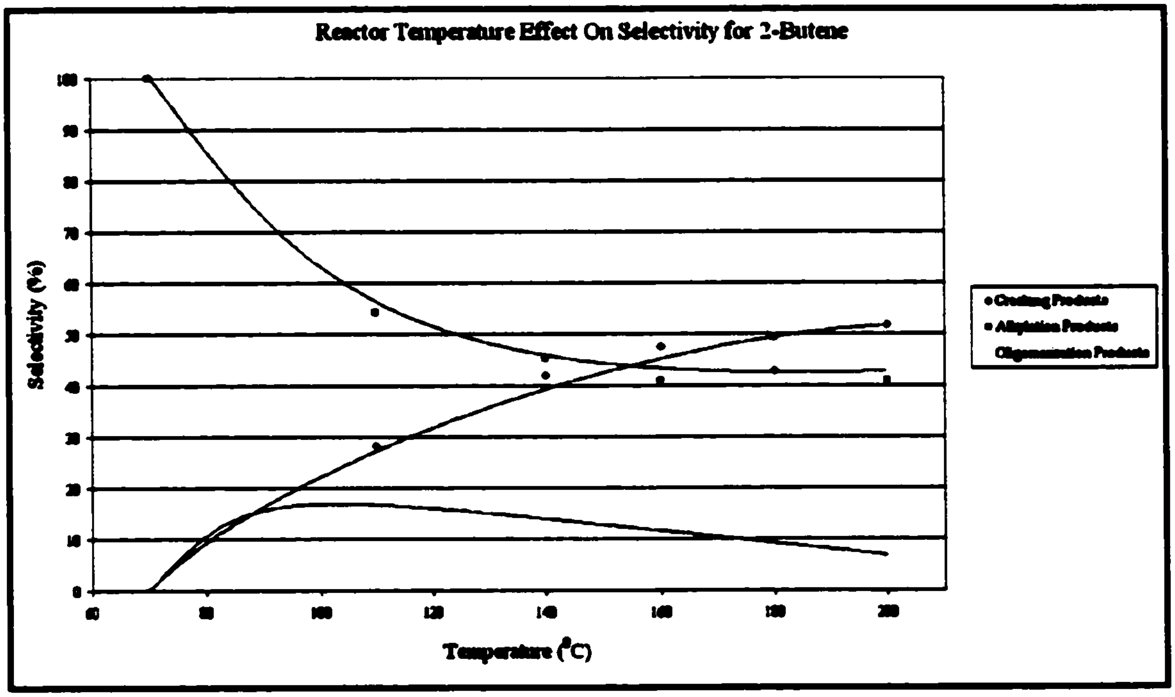


Figure 4.24

Selectivity for 2-Butene

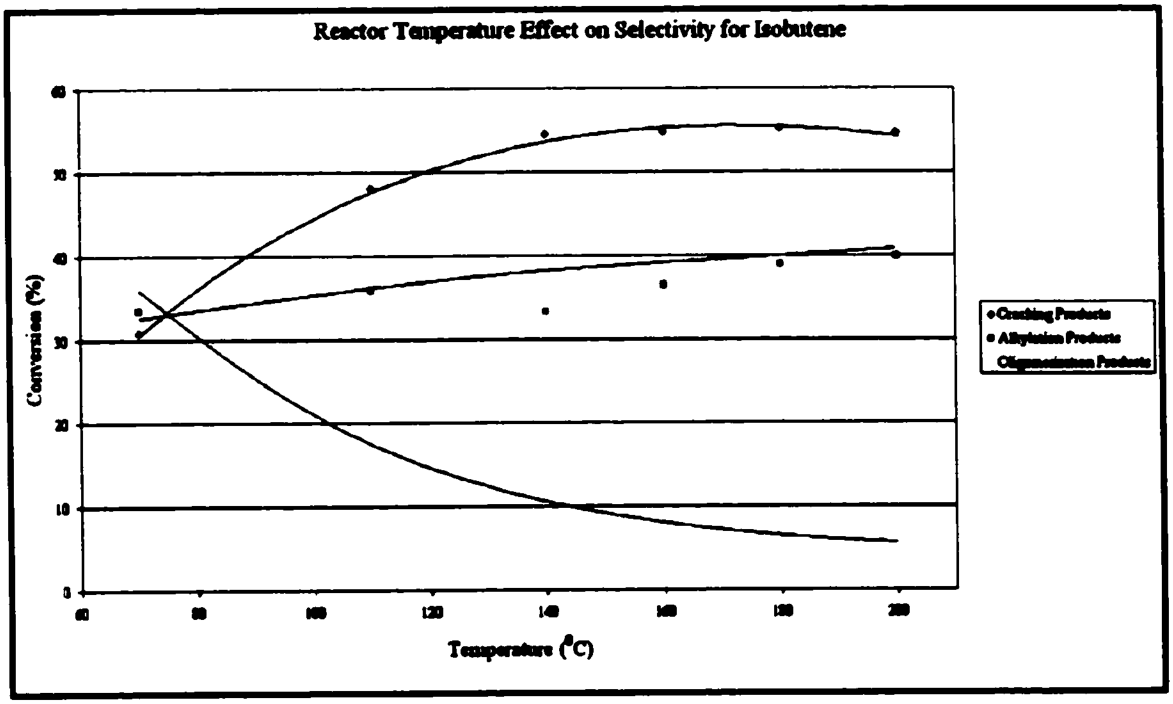


Figure 4.25

Selectivity as a function of temperature for isobutene

Moving on to the isobutene selectivity graph we see that cracking rises initially but eventually drops off and the alkylation actually increases with high temperatures. The cracking selectivity is significantly higher than the alkylation throughout most of the temperature range. The interesting aspect of this graph which distinguishes it from the previous two is that the alkylation selectivity is fairly indifferent to the reaction temperature. There are two reasons for this. Firstly, there is no reason for self alkylation to occur in this scenario due to the presence of tertiary carbocations only from isobutane or isobutene. There is no stability benefit to be had and even if it were to occur the product distribution would not be affected since the isobutene and isobutyl cations would be the only species present. For this reason we can understand that the alkylate selectivity will be more stable.

4.3.5.3 Contact time

The contact time is a value that represents the average amount of time reactants spend in contact with the catalyst in the reactor. Varying the contact time requires either a change in the mass of catalyst used or the flow rate of reactants through the reactor. Therefore, the contact time can be increased by adding catalyst or by decreasing the flow of reactants. The importance of studying the variation of this quantity stems from the fact that the contact time is essentially the amount of reactant passed through a unit amount of catalyst. Finding the optimum conversion and selectivity balance ensures the highest production of alkylate. However, the selectivities are also affected by changes in contact time due to the extent of secondary reactions which are allowed to occur once products are formed.

A plot showing the effect of contact time variation shows a linear trend in conversion as the contact time increases. The explanation for this is that the catalyst is governed by a diffusion regime where the reactants enter the front of the catalyst bed and work their way through. As this occurs, some reactions happen but conversion occurs throughout the whole length of the bed. So, the longer the molecules take to pass through, the more chance there is of adsorption occurring.

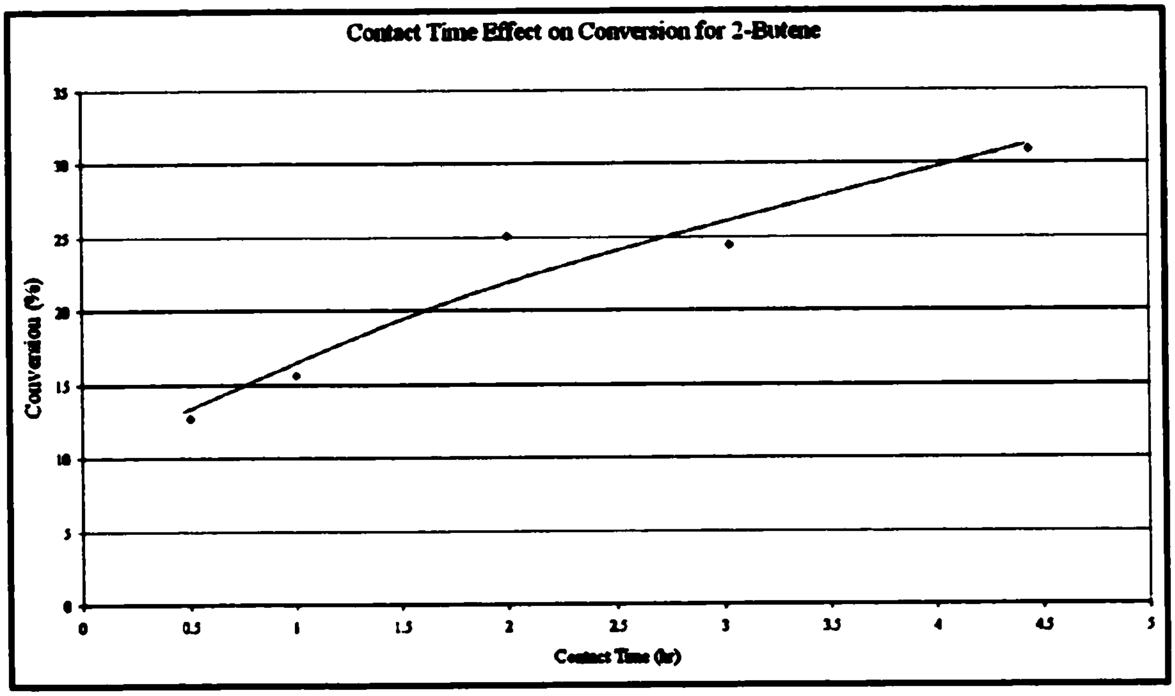


Figure 4.26

Conversion as a function of contact time

Logically, conversion must increase given the nature of the interactions of molecules with the catalyst but if this is the case there should also be a variation in the type of products formed. This idea is based on the notion that at longer contact times the amount of secondary reactions can increase. A certain amount of alkylate will form as the olefins and isobutane enter the catalyst but the more time allowed for all the molecules to remain in contact with the catalyst the more secondary reactions that will occur. In the next graph the alkylate selectivity does indeed suffer at the expense of the lighter C6 and C7 fractions which validates the idea that the product molecules can still adsorb for further reactions in the catalyst.

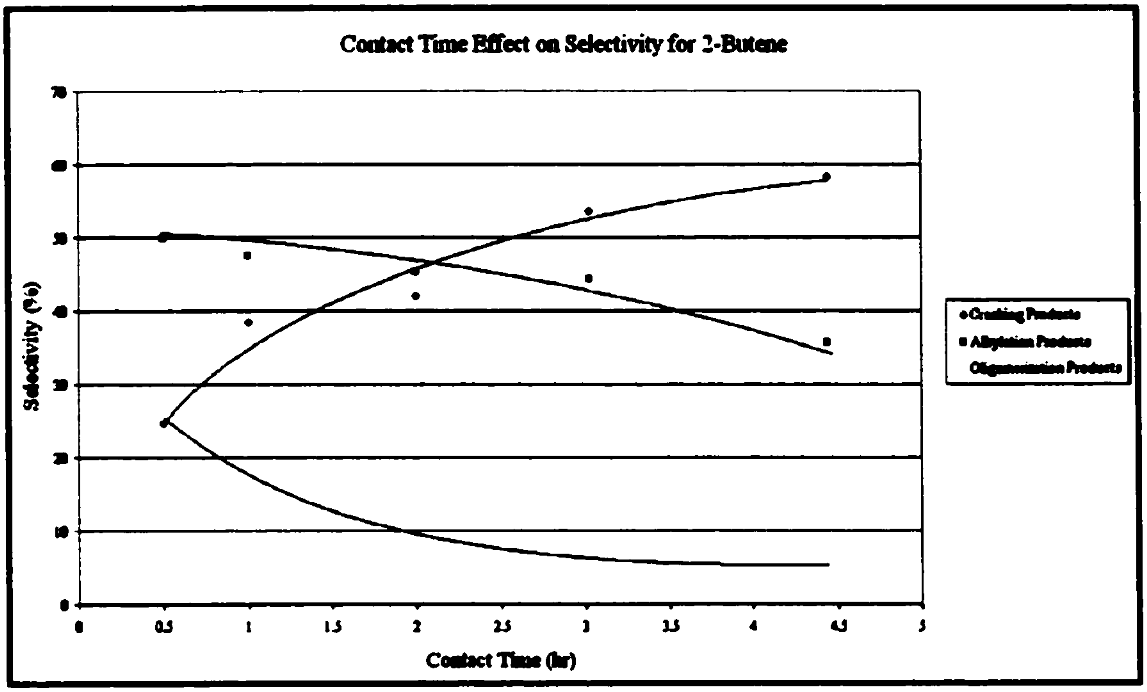


Figure 4.27

Selectivity as a function of contact time

The conclusion from this data is that despite improved conversion levels associated with longer contact times, the product distribution will be adversely affected by these higher contact times. A balance must be found where conversion and selectivity are both maximized. Plotting the yield for alkylate will take into account the conversion and the selectivity as temperature is varied.

4.3.5.4 Isobutane/olefin ratio

The ratio of the isobutane to the olefins in alkylation affects the extent of deactivation and the amount of isobutane used. Clearly, it is desirable to use as much isobutane as possible in the reaction because it produces highly branched products. At low ratios there is more olefin and eventually as the olefin content rises the olefins will react with each other preferentially due to their higher reactivity. The higher reactivity is due to the presence of the double bond pi electrons. Having olefins react with one another, a reaction capable of forming C8 products will only form linear products with poor octane numbers. Isobutane consumption will also drop and this defeats the whole purpose of alkylation which is to add isobutane which has limited use to olefins as a means of forming gasoline grade products. The range studied for the MCM-41/TFA catalyst was from 10/1 to 0.5/1. Liquid phase reactions typically run around 10/1 or 20/1 ratios and for studying zeolites much higher ratios are needed to ensure adequate olefin concentrations within the pores. In this case, the range was limited by the ability to bring olefin flow rates down to less than 0.5 ml/min. Therefore, extended ratio effects could not be seen.

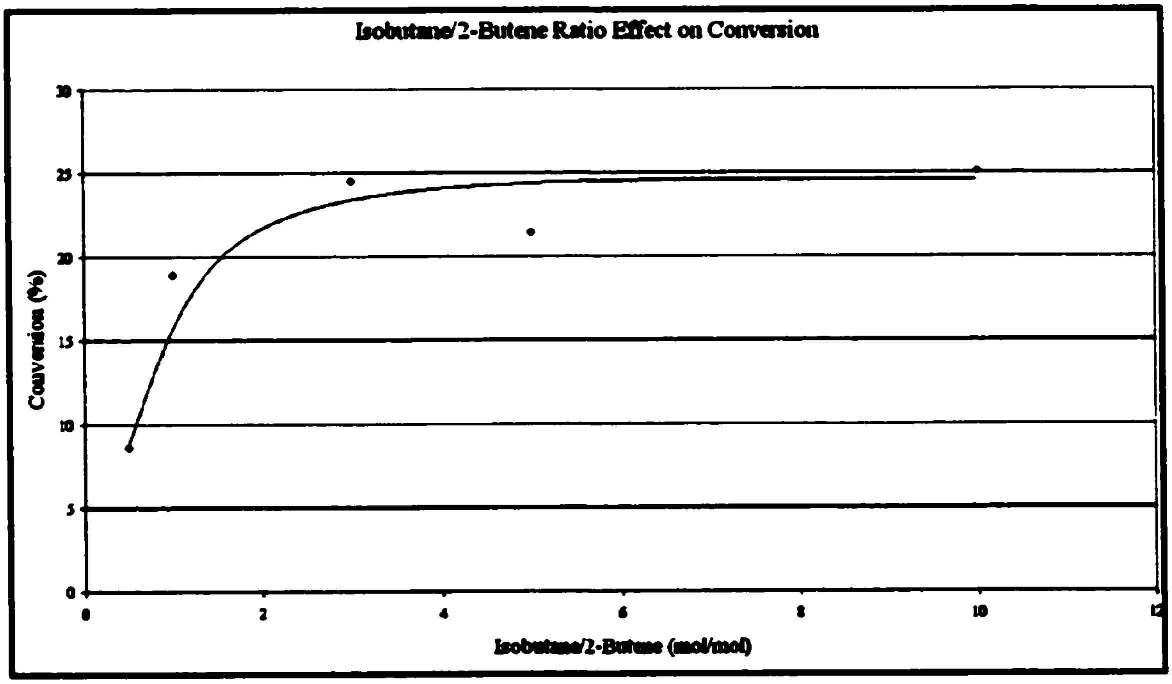


Figure 4.28

Conversion as a function of isobutane/2-butene ratio

The data shows a rapid deactivation as the ratio decreases which is indicative of more severe coking as a result of significant olefin dimerization as well as oligomerization. With ratios above 3 the conversion stabilizes. This stabilization may mean that at ratios higher than 3 there is no change in the ratio within the catalyst pores, such that additional isobutane may not change the rate of olefin dimerization significantly. The selectivities do not encounter the same trends as with conversion and are quite stable. The fact that conversion data proves the reaction is influenced by this ratio makes it difficult to think that the product spectrum would not be affected.

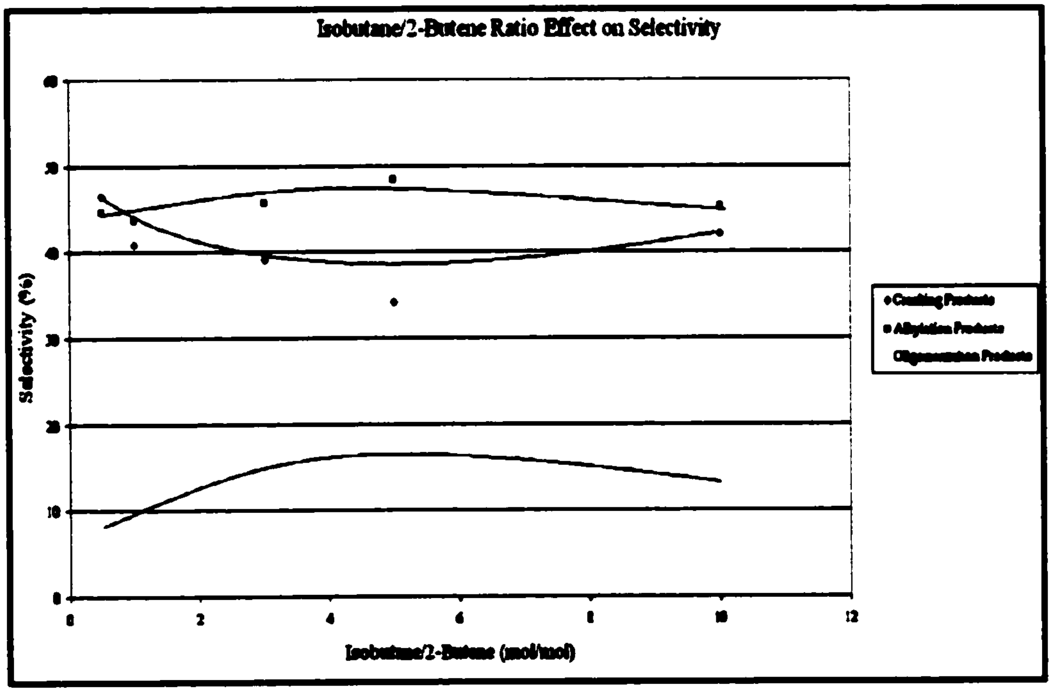


Figure 4.29

Selectivity as a function of isobutane/2-butene ratio

Although the summed product fractions do not experience variation under isobutane/2-butene ratio variation it is possible that specific products not yet identified do change. With increased dimerization at low ratio values there should definitely be a sharp increase in the amount of linear C8 products formed due to the linear nature of 2-butene compared to isobutane. This study will benefit from further investigation with a more detailed product spectrum identification. By understanding the exact type of products formed the reaction mechanisms could be further verified.

Conclusion

The use of mesoporous based catalyst has been found to have interesting results and improved performance over zeolite acid catalyst for the alkylation of isobutene with light olefins. The catalyst does not deactivate as quickly due to large pores and high surface areas which also provide elevated conversion values. The use of triflic acid has been found to lead to some structural collapse according to lower crystallinity from XRD analysis as well as surface area measurements. The acid also causes some pore occlusion but despite this still remains quite active due to the very large initial surface area of MCM-41.

The nature of the adsorbed acid is such that some of it is adsorbed on the MCM-41 surface through silicon atoms while the remainder is loosely held in the pores without any association to the surface. This loosely bound acid is removed from the MCM-41 pores at temperatures around 160^{0}C while the adsorbed triflic acid remains past 300^{0}C.

The use of isobutene as a feedstock will yield much higher conversion levels at lower temperatures which has been linked to the stability of the carbocations formed following the alkylation step. The conversion levels for 1-butene and 2-butene have been found to be lower due to lower carbocation stability and the 1-butene conversion level being higher than 2-butene is most likely due to the self alkylation process which attempts to reduce the occurrence of unstable primary and secondary carbocations.

Contact time is almost directly proportional to conversion levels and shows some effects on the selectivity of the catalyst during reactions while the isobutene/olefin ratio was not very influential on the outcome of reactions. Possibly due to insufficient range in the ratios tested.

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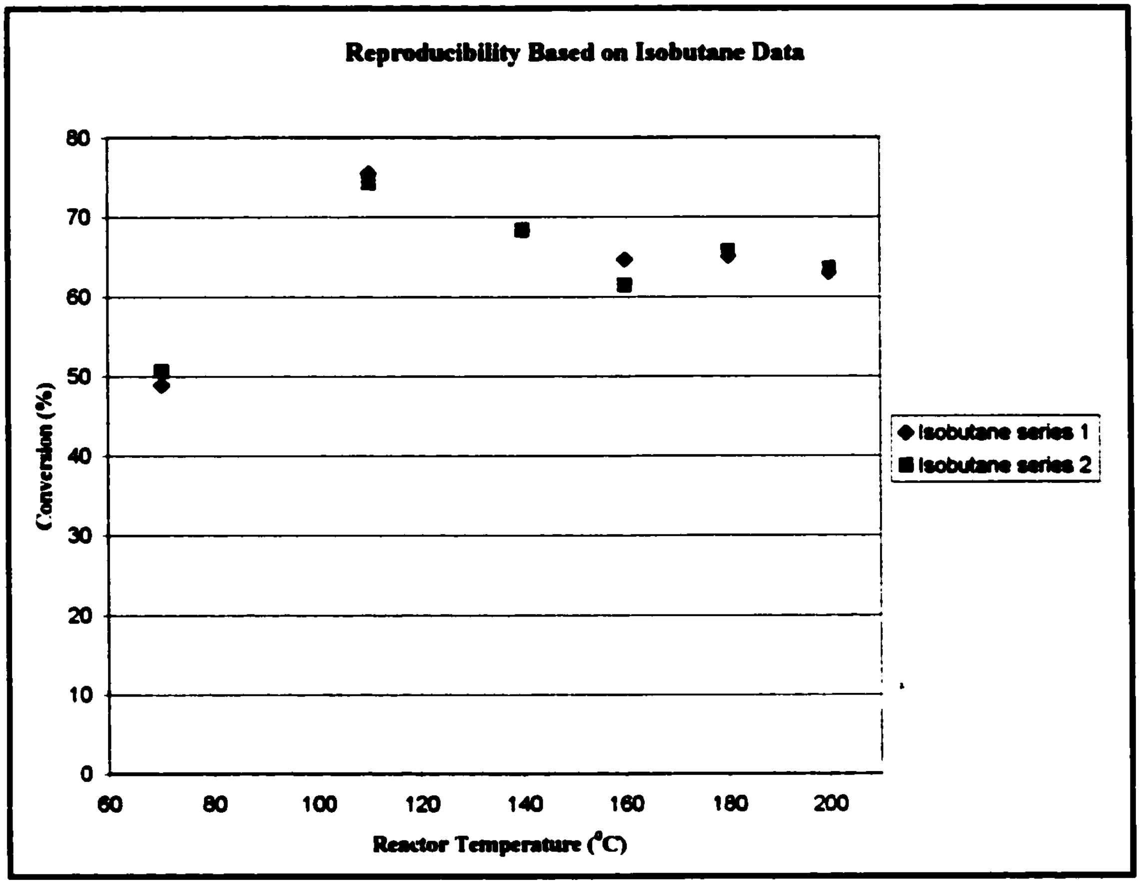
Appendix I: Reproducibility data

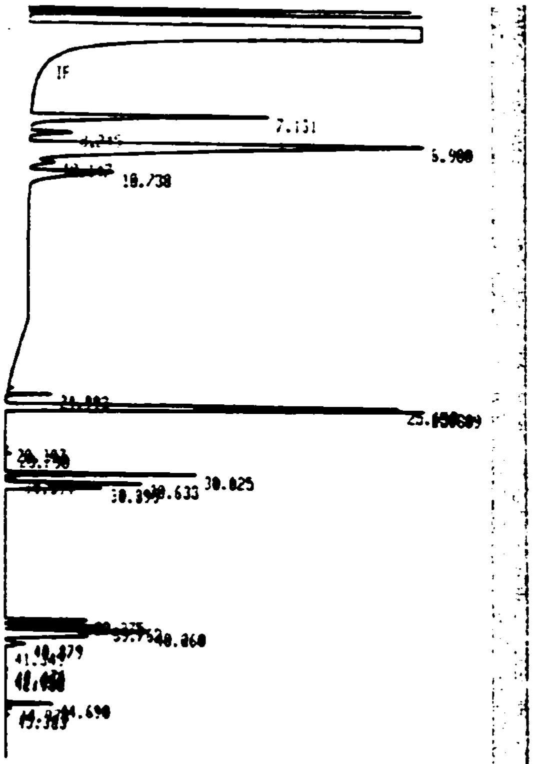


This graph shows two series of data point for identical reactions done for isobutene where reactor temperature was varied. The two series have very similar values from point to point.

Appendix II: Sample GC data

A sample GC chromtogram is shown for an alkylation reaction. The chromatogram shows the various compounds that elute from the column as a function of time. The olefin feedstock is observed 7 and 11 minutes. In this region the C5 fraction also appears. Following this, the separate clusters of C6, C7, C8 and C9 products are seen beginning at 24 minutes for C6. The elution times for these categories were determined by running known standard hydrocarbons in the GC to determine the elution time. In this way a general identification of the products is possible although not an exact identification of each individual compound.

The large peak at the start of the chromatogram is due to isobutene which is present in large excess.



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STOP


RUN0   120           FEB 25, 1901  09:16:08

AREA%
      RT          AREA TYPE  WIDTH        AREA%
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   8.245         35541   BB   .178      1.27418
   8.900        998116   BV   .472     35.78344
  10.147         32492   VV   .270      1.16487
  10.738        150401   VB   .372      5.39203
  24.993         16588   PB   .078       .59470
  25.650        186946   PV   .097      6.70220
  25.809        341510   VB   .156     12.24347
  28.397          3322   PB   .071       .11910
  28.790          6646   BB   .114       .23827
  30.025        117218   VV   .122      4.20238
  30.394         10822   VV   .133       .38798
  30.633         88247   VV   .128      3.16374
  30.895        100044   VB   .201      3.58668
  39.375         71920   BV   .160      2.57840
  39.762         75564   VV   .140      2.70904
  40.060        110316   VV   .147      3.95494
  40.879         44988   VV   .278      1.61286
  41.349          5308   VP   .102       .19030
  42.476         11421   VV   .127       .40945
  42.647          5678   VV   .089       .20356
  42.852          6783   VV   .087       .24318
  42.908          7924   VP   .111       .28408
  44.690         37437   VV   .123      1.34215
  44.973         17613   VV   .165       .63144
  45.383         23508   VV•  .250       .84279
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