The Alkylation of 2-Butene with Isobutane over Large-Pore Zeolites

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ABSTRACT

The growing demand for higher quality gasoline coupled with stringent environmental regulations necessitates the reduction in aromatics, sulfur and nitrogen compounds. The alkylation process utilises low value olefinic gases produced in the refinery with isobutane to produce high octane gasoline that is free from aromatics, sulfur, and nitrogen compounds. Current alkylation technologies utilise hydrofluoric or sulfuric acids as catalysts for the reaction. Both acids however present health and environmental concerns along with high operational and mitigation costs. Zeolites are an ideal alternative to both acids due to their benign nature and acidic properties. Catalyst deactivation remains a major challenge for a zeolite-based alkylation process.

Using a well-mixed reactor under ideal reaction conditions and relatively high flow rates, the alkylation of 2-butene with isobutane was studied over large pore zeolites. The effect of zeolite structure, of manipulating the acidity of the zeolite and of diluting the zeolite with additives on activity, stability and alkylate selectivity were examined.

Examining the effect of the zeolite structure indicated that a three-dimensional channel system was required for the reaction. Zeolites Beta and Y exhibited higher stability and selectivity while MOR deactivated rapidly. The rapid deactivation in MOR was attributed to the lack of intersecting side-channels which prevented the bulky molecules from escaping the pores thus causing faster pore blockages.

Varying the Si/Al ratio for zeolite Beta (12.5, 75, and 150) indicated that high aluminium content was required for the reaction. The siliceous Beta zeolites deactivated rapidly and mainly produced oligomerisation products. Lanthanum impregnation on the lowest Si/Al Beta zeolite reduced the Bronsted acidity and the impregnation procedure created Lewis acidity, both effects combined to reduce the activity and selectivity of the zeolite.

The Si/Al ratio was varied for zeolite Y ranging from 2.6 to 30. The optimum ratio was the lowest, 2.6. Increasing the Si/Al ratio decreased the acidic sites available for the reaction and reduced the alkylate selectivity. Lanthanum exchange was shown to significantly improve the catalytic stability due to the reduction in the strong Lewis acidity. The optimum number of exchanges was three followed by calcination. This procedure created the highest ratio of strong Bronsted/strong Lewis acidity and enhanced the stability of the catalyst.

Diluting the Y zeolite provided the most significant improvement on the catalytic stability. Silica additives, and particularly MCM-41, were shown to reduce the oligomerisation and enhance the alkylate production. The improvement was attributed to the separation of the zeolite clusters which reduced the olefin concentration and promoted alkylation. The optimum additive, MCM-41, had the highest surface area. Increasing the additive content did not provide additional improvements as the initial dilution seemed the most significant. Finally, the optimum catalysts from each section were compared for their stability and alkylate selectivity.
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LIST OF ABBREVIATIONS

BET Brunauer Emmett Teller
BEA Zeolite of the framework Beta
B/L Bronsted/Lewis
Bbl Barrel
C\textsubscript{4} Butane
i-C\textsubscript{4} Isobutane
C\textsubscript{4}\\textsuperscript{\textasciitilde} Butene
C\textsubscript{5-7} Hydrocarbons consisting of 5-7 carbon atoms
C\textsubscript{8} Hydrocarbons consisting of 8 carbon atoms
C\textsubscript{9+} Hydrocarbons consisting of 9 or more carbon atoms
C\textsubscript{9-12} Hydrocarbons with a boiling point range between n-Nonane and n-Dodecan
C\textsubscript{12+} Hydrocarbons with a boiling point range higher than n-Dodecan
Cat 8 Catalyst 8: 80 wt. % 3LaE Y(2.6) + 20 wt. % MCM-41
cm centimetre
CSTR Continuous stirred-tank reactor
DMH Dimethylhexane
EFAL Extra-framework aluminium
EMT Zeolite EMT
EDX Energy dispersive X-ray analysis
FAU Zeolites of the framework Faujasite
FCC Fluid catalytic cracking
FID Flame ionisation detector
F.S. Fumed silica
FTIR Fourier transform infrared spectroscopy
GC Gas chromatography
g gram
H-Beta Beta zeolite in the protonic form
H-EMT EMT zeolite in the protonic form
H-FAU Faujasite zeolite in the protonic form
1. Introduction and Literature Review
1.1 Introduction

The addition of isobutane to light olefins in the presence of acidic catalysts produces a mixture of highly branched paraffins called alkylates. Alkylates form approximately 12% of the gasoline pool and the total global production amounts to approximately 2.5 MM Bbl/day [1]. Alkylates are an excellent blendstock for the gasoline pool in the refinery due to their low vapour pressure, high octane number and the absence of aromatics, sulfur and nitrogen compounds [2]. A comparison between the gasoline produced from the various refinery processes is provided in Table 1-1.

Table 1-1: Typical gasoline components in the gasoline pool [3]

<table>
<thead>
<tr>
<th></th>
<th>Alkylate</th>
<th>FCC</th>
<th>Naphtha Reforming</th>
<th>Polygas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics (wt. %)</td>
<td>0</td>
<td>29</td>
<td>63</td>
<td>0</td>
</tr>
<tr>
<td>Olefins (wt. %)</td>
<td>0</td>
<td>29</td>
<td>&lt;1</td>
<td>95</td>
</tr>
<tr>
<td>Sulfur (ppm)</td>
<td>0</td>
<td>750</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MON</td>
<td>92-94</td>
<td>81</td>
<td>87</td>
<td>82</td>
</tr>
<tr>
<td>RON</td>
<td>94-98</td>
<td>92</td>
<td>98</td>
<td>94</td>
</tr>
</tbody>
</table>

Owing to the reduction and restriction on aromatics, olefins and sulfur molecules in the gasoline in the US and the EU, alkylate production is expected to increase [4]. The gasoline specifications for Euro Super 95 (Euro V) are provided in Table 1-2:

Table 1-2: Euro Super 95 gasoline specification [3]

<table>
<thead>
<tr>
<th></th>
<th>Max 35 vol. % (benzene max. 1 vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>Max 18 vol. %</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Max 10 ppm</td>
</tr>
<tr>
<td>RON/MON</td>
<td>Min 95/98</td>
</tr>
</tbody>
</table>

In a modern refinery, the Fluid Catalytic Cracking unit (FCC), along with other thermal cracking units such as visbreaking and delayed coking, produces a mixture of light olefins. The low value C4 and C5 olefins are typically converted in the alkylation unit to high quality gasoline that increases the refinery’s profit margin [5]. Furthermore, low value isobutane is produced in large quantities in the hydrocracking unit along with the isobutane available from the initial fractionation and isomerisation. The alkylation unit utilises these gases to produce high quality gasoline [6].
Octane ratings are a measured gasoline property representing standard knock intensity or the flammability of the fuel [7, 8]. Octane values are typically referred to as research octane (RON) and motor octane (MON). The research octane number (RON) represents normal road performances (600 rpm) at lower inlet temperatures (~65.5 °C) while the motor octane number (MON) represents to higher engine performance (900 rpm) and higher inlet temperatures (~150 °C) [8]. Higher octane values represent higher resistance of the gasoline to pre-ignite under higher pressures (knock) which causes significant damage to the engine and decreases its efficiency [8]. Table 1-3 provides the octane rating of some of the major components in the gasoline pool [8-10].

<table>
<thead>
<tr>
<th>Component</th>
<th>RON</th>
<th>Component</th>
<th>RON/MON</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C₄S</strong></td>
<td></td>
<td><strong>C₅S</strong></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>90.1</td>
<td>2-Methylheptane</td>
<td>21.7</td>
</tr>
<tr>
<td>Isobutane</td>
<td>97.6</td>
<td>3-Methylheptane</td>
<td>30.0</td>
</tr>
<tr>
<td><strong>C₅S</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>61.9</td>
<td>2,5-Dimethylhexane</td>
<td>55.5</td>
</tr>
<tr>
<td>Iso-pentane</td>
<td>93.0</td>
<td>3-Ethylhexane</td>
<td>52.4</td>
</tr>
<tr>
<td><strong>C₆S</strong></td>
<td></td>
<td>2,4-Dimethylhexane</td>
<td>65.2</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>24.8</td>
<td>2,2-Dimethylhexane</td>
<td>74.0</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>73.5</td>
<td>2,3-Dimethylhexane</td>
<td>78.9</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>74.5</td>
<td>3,4-Dimethylhexane</td>
<td>76.3</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>104.3</td>
<td>3-Ethyl-2-methylpentane</td>
<td>81.0</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>91.8</td>
<td>3,3-Dimethylhexane</td>
<td>83.4</td>
</tr>
<tr>
<td><strong>C₇S</strong></td>
<td></td>
<td>2,2,4-Trimethylpentane</td>
<td>100.0*</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0*</td>
<td>2,3,4-Trimethylpentane</td>
<td>102.7</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>42.4</td>
<td>3-Ethyl-3-methylpentane</td>
<td>87.0</td>
</tr>
<tr>
<td>3-Methylhexane</td>
<td>52.0</td>
<td>2,2,3-Trimethylpentane</td>
<td>109.6</td>
</tr>
<tr>
<td>2,4-Dimethylpentane</td>
<td>83.8</td>
<td>2,3,3-Trimethylpentane</td>
<td>106.1</td>
</tr>
<tr>
<td>3-Ethylpentane</td>
<td>65.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethylpentane</td>
<td>91.1</td>
<td>Cyclopentane</td>
<td>84.9</td>
</tr>
<tr>
<td>2,2-Dimethylpentane</td>
<td>95.6</td>
<td>Cyclohexane</td>
<td>77.2</td>
</tr>
<tr>
<td>3,3-Dimethylpentane</td>
<td>86.0</td>
<td>C₇ naphthenes</td>
<td>77.0</td>
</tr>
<tr>
<td>Trimethylbutane</td>
<td>112.1</td>
<td>C₈ naphthenes</td>
<td>50.0</td>
</tr>
</tbody>
</table>
1.2 History of Alkylation

The first experiments for the reaction of isoparaffins with olefins to produce alkylates were reported in 1935 by UOP using Friedel-Crafts catalysts, aluminium chloride (AlCl$_3$) with hydrochloric acid (HCl), and boron trifluoride (BF$_3$) with hydrofluoric acid (HF) [11]. Early alkylation units used sulfuric acid as a catalyst and the first commercial plant unit was built in 1938, using sulfuric acid at Baytown, Texas. The first HF alkylation unit was built in 1942 by Phillips at Phillips’s Borger, Texas refinery to provide high quality aviation gasoline during World War II [12]. During the 1950s, alkylation units were shifted from producing aviation fuel to producing alkylates as a blendstock in automotive motor fuels.

The regulations made by the United States Environmental Protection Agency (EPA) to phase out of lead in gasoline in the 1970s and 1980s caused an increase in the demand for alkylates [13]. Both H$_2$SO$_4$ and HF units enjoy a similar share of the worldwide production of alkylates although the current trend is to reduce new HF alkylation units [14]. Figure 1-1 shows the global alkylation capacity.

![Figure 1-1: Global alkylation capacity, adopted from [14]](image)

Both H$_2$SO$_4$ and HF have inherent disadvantages. H$_2$SO$_4$ is a corrosive liquid with substantial drawbacks [15]. High acid consumption in H$_2$SO$_4$ alkylation is a major operating cost associated with this process. Moreover, the spent acid has to be regenerated to remove any water or hydrocarbons. The typical cost of regeneration exceeds more than twofold the market value of fresh H$_2$SO$_4$ [16]. Acid consumption accounts for a significant portion of the operating costs of sulfuric acid alkylation units, about 30% [17]. The acid also needs to be transported to and from the refinery which adds to the operating costs.

HF is very toxic and corrosive. Coupled with its corrosive nature, leakage is a serious problem associated with HF due to its low boiling point (19 °C at atmospheric pressure). HF
release tests conducted in 1986 at Nevada’s desert showed that almost all of the HF released formed a dense, rolling cloud of gas; toxic concentrations were measured at a distance of 5-10 km of the release point [18]. Multiple accidents have also occurred in HF alkylation units. The most infamous occurred in 1987 at the Marathon Oil Company refinery in Texas, where HF leakages led to the evacuation of a 50 blocks area. Over 1000 people required medical treatment for HF exposure; fortunately there were no fatalities [19]. Refineries with HF alkylation units have to set up water stripping systems to reduce the hazards of HF release [20, 21].

To mitigate the corrosion and toxicity issues with the utilisation of liquid acids for the alkylation process, solid acids such as zeolites are of increasing research interest. In the 1960s, Garwood and Venuto [22] and Kirsch et al. [23], performed alkylation experiments on rare earth ion exchanged faujasites (REFAU) and documented that zeolites were active for alkylation and had a comparable product distribution to liquid acids. However, low stability and rapid deactivation prevented the wide-scale commercialisation of solid acid alkylation processes. To date, only one solid-acid process, based on the AlkylClean process, is under commercialisation [24]. Other acids explored in the literature include chlorinated alumina, sulfated zirconia, organic polymers and ionic liquids.

1.3 Reaction Mechanism

The mechanism of the alkylation reaction over liquid acids was extensively studied since the discovery of the reaction [25-27]. Detailed reaction mechanism studies were conducted by Corma and Martinez [28] and Feller and Lercher [29] over zeolites. The reaction mechanism established for liquid acid alkylation is very similar to that of solid acids. The main difference lies in the initiation step which is followed subsequently by alkene addition and hydride transfer. In addition, oligomerisation, cracking and self-alkylation can also occur. The simplified reaction mechanism is shown in Figure 1-2. The reaction is initiated by the protonation of the olefin from the acidic catalyst to produce a tertiary carbenium ion (reaction 1). The alkene is then added to the carbenium ion to produce a trimethylpentane alkyl-cation (reaction 2). The TMP alkyl-cation then undergoes a hydride transfer with isobutane to produce a trimethylpentane and a tertiary carbenium ion that propagates the reaction (reaction 3). A detailed representation of each step is discussed in the next section.
1.3.1 Initiation of the Olefin

The first step in the alkylation reaction is the olefin activation leading to a tertiary cation. The activation of the olefin occurs with the formation of carbenium ions in the case of liquid acids and surface alkoxides on zeolites. The carbenium ion then undergoes a methyl shift to yield a tertiary cation. The carbenium ion can also react with the isobutane to produce a tertiary cation. In liquid acids, the proton is added to the most substituted carbon as shown in Figure 1-3.

In zeolites, ab initio quantum-chemical calculations modelling the zeolite’s acidic site indicated that a π-complex would form between the zeolite’s acidic site and the olefin [30-32]. The alkene has been demonstrated to adsorb on the zeolite and produce an alkoxide instead of a carbenium ion. Figure 1-4 below shows the formation of the alkoxide on a zeolite’s acidic site [33].
More recently, Ren et al. modelled the protonation process of butene from the acidic sites of zeolite Y using quantum mechanical/molecular mechanical (QM/MM) modelling [34]. The authors simulated the protonation of 2-butene and isobutene on a 120 T-atom H-Y cluster. The formation energy of the π-complex in the case of isobutene was higher than that of the 2-butene and the authors attributed the increase in the formation energy to the steric hindrance between the double bond of isobutene and the hydrogen atom on the zeolite’s acidic site. Furthermore, the energy of the alkoxide formed from the isobutene was found to be higher than that of the alkoxide formed from the 2-butene because the C-O bond formed from the isobutene alkoxide (1.65 Å) was longer than that of the alkoxide formed from the 2-butene (1.55 Å). The energy required to protonate the isobutene alkoxide (36.8 kJ/mol) was significantly lower than that of the 2-butene alkoxide (67.8 kJ/mol), which demonstrated the ease of the protonation in the isobutene alkoxide. This result could explain the propensity of the isobutene to produce more oligomerisation products during the alkylation reaction than other butenes as was reported by Albright [35]. Figure 1-5 below shows a model of the alkoxides formed from the isobutene and the 2-butene.

![Figure 1-5: Alkoxides formed from Isobutene (A) and 2-Butene (B) on zeolite Y's acidic sites, adopted from [34]](image)

**1.3.2 Alkene Addition and Isomerisation to the TMPs**

Upon the formation of tertiary cations in step 1, alkene addition proceeds via electrophilic addition where the π bond in the butene is broken to form a σ bond in the alkyl-cation [29] as shown in Figure 1-6.

![Figure 1-6: Alkene addition to form a C₄ alkyl-cation](image)
This reaction is exothermic and the alkene addition constitutes most of the overall heat of reaction [29]. Multiple possibilities arise based on the type of the carbenium ion/alkoxide and the type of the alkene. Table 1-4 below provides the various possible reaction routes.

Table 1-4: Possible reaction routes depending on the carbenium-ion type and the feed alkene. Where MHP: Methylheptane, DMH: Dimethylhexane and TMP: Trimethylpentane, adopted from [29]

<table>
<thead>
<tr>
<th>Carbenium ion</th>
<th>Alkene</th>
<th>Resulting C8&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary</td>
<td>1-Butene</td>
<td>3-MHP&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
<tr>
<td>Secondary</td>
<td>2-Butene</td>
<td>3,4 DMH&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
<tr>
<td>Secondary</td>
<td>Isobutene</td>
<td>2,4 DMH&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
<tr>
<td>Tertiary</td>
<td>1-Butene</td>
<td>2,2 DMH&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
<tr>
<td>Tertiary</td>
<td>2-Butene</td>
<td>2,2,3 TMP&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
<tr>
<td>Tertiary</td>
<td>Isobutene</td>
<td>2,2,4 TMP&lt;sup&gt;+&lt;/sup&gt;</td>
<td><img src="image" alt="Reaction" /></td>
</tr>
</tbody>
</table>

Based on the information provided in Table 1-4 above, it is expected that 2-butene would produce mostly the 2,2,3 TMP. However, this particular TMP is usually observed in low quantities [36, 37]. The TMP-fraction usually consists of 2,3,3, 2,3,4, and 2,2,4 TMP. However, the skeletal isomerisation of the TMPs is unfeasible under typical alkylation reaction conditions. Nivarthy et al. pre-saturated zeolite Beta with n-octane after placing it in the reactor and isobutane was fed to the reactor at typical alkylation conditions (T = 75 °C, P = 25 bar). No isomerisation products were detected from the elution of the n-octane. It is therefore apparent that the selectivity of each TMP depends on the shape selectivity and steric conditions inside the used zeolite catalyst and the thermodynamics conditions of the reaction [38]. Figure 1-7 provides the thermodynamic distribution of the C<sub>8</sub> paraffins as a function of temperature.
Increasing the olefin space velocity can favour the production of the 2,2,3, TMP while reducing it usually increases the isomerisation activity since the alkyl-cation has more time to isomerise [40]. The isomerisation reaction proceeds via either a hydride transfer or a methyl shift. The isomers and the isomerisation pathways are summarised in Figure 1-8 below [29]:

Furthermore, Juzsakova et al. demonstrated through kinetic modelling of the reaction over zeolites Y and La-Y that the alkene addition is slowest reaction step and can thus be considered as the rate determining step [41].
1.3.3 Hydride Transfer

The hydride transfer reaction transfers the alkyl-carbenium ion, e.g. TMP+, to a saturated alkylate and regenerates the tertiary cation thus propagating the reaction as shown in Figure 1-9.

![Figure 1-9: The hydride transfer step](image)

This is the critical reaction step in the alkylation sequence since it can either lead to the formation of TMPs by the reaction of the C₈ alkyl-cation with an alkane or oligomerisation by the reaction with alkenes instead. The hydride transfer between an alkane and an alkyl-cation propagates the alkylation reaction and ensures the availability of tertiary cations necessary for alkene addition [42].

Hydride transfer in zeolites requires much higher activation energies in comparison to liquid acids. In liquid acids, the value was reported to span 15 kJ/mol [43], 18 kJ/mol [44] and 13 kJ/mol [45]. For zeolites, the value was measured by Boronat et al. to be around 118 kJ/mol for hydride transfer between isobutane and isobutene [46]. Kazansky reported the activation energy for hydride transfer between isobutane and a tertiary-alkoxide to be approximately 200 kJ/mol [30] while Yaluris reported it to be around 126 kJ/mol [47]. This difference between the activation energies in zeolite and liquid acids can be attributed to the higher acid strength of the liquid acids which allows for the direct protonation of the olefin to produce a carbenium ion in comparison to the zeolite where an alkoxide is formed instead. The activation energy is at its lowest value when the reaction occurs between a tertiary alkyl-cation and a tertiary carbon such as isobutane. This might also explain the low concentration of the 2,2,3 TMP in the product since the 2,2,3 TMP forms a secondary alkyl-cation while the remaining TMP alkyl-cations are tertiary alkyl-cations (Figure 1-8). Guisnet and Genp suggested that the hydride transfer reactions may require the presence of two adjacent acidic sites to stabilise the alkyl-cation while the dimerisation of butenes to produce C₈ olefins and oligomerisation to produce heavier molecules can proceed on a single site [48].

1.3.4 Side Reactions

There are three main side reactions occurring during the alkylation reaction: oligomerisation, cracking and self-alkylation. Oligomerisation and cracking are linked together; as the carbon chain propagates, it becomes easier to crack. The third side reaction is self-alkylation where linear alkanes are produced leading to the degradation of the overall product quality.
1.3.4.1 Oligomerisation and Cracking

The alkylation reaction produces a vast number of products. A typical alkylate can include up to 200 compounds in C\textsubscript{9+} fraction [49]. An example of a GC trace taken during the alkylation over zeolite Beta in this work is displayed in Figure 1-10 highlighting the large number of products observed in the C\textsubscript{9+} fraction.

![GC trace](image)

Figure 1-10: GC trace taken during the alkylation reaction over zeolite Beta, red lines are overlays of the normal-paraffins

The vast number products observed during the alkylation reaction can be attributed to the oligomerisation/cracking reactions. A typical alkylate contains C\textsubscript{5}-C\textsubscript{7} and C\textsubscript{9+} hydrocarbons along with the primary C\textsubscript{8} alkylates. Both fractions, however, are detrimental to the overall product since they exhibit lower octane values [17, 29].

Alkene addition occurs at a much higher rate than hydride transfer. This can lead to oligomerisation and a thin polymer starts to build up inside the pores of the zeolite. Pore blockage and accelerated deactivation then occurs due to the build-up of such compounds. In sulfuric acid-catalysed alkylation, oligomerisation has a reaction rate four times higher than the rate of hydride transfer [50]. While the oligomerisation reaction in zeolites has a reaction rate 2-3 times higher than hydride transfer [51, 52]. Also, the oligomerisation rate is considerably higher for iso-alkenes than linear alkenes in both liquid acids and zeolites [53, 54]. Figure 1-11 below summarises the oligomerisation reactions.
Higher paraffin/olefin ratios and the uniformity of the paraffin/olefin ratios in the reactor such as in a back-mixed reactor can reduce oligomerisation [51]. The oligomerised molecules are easier to crack due to the high acidity of the catalyst. It is expected that multiples of four carbon atoms are produced in the alkylation reaction, i.e. C₈, C₁₂ and C₁₆. However, typical alkylation products include a mixture of C₅-C₁₆ [49]. A combination of β-scission of the large alkyl-cations and hydride transfer from the resulting alkene contributes to the large number of products observed in the alkylation products (Figure 1-12).

Furthermore, isomerisation/oligomerisation of the alkene can also produce other higher alkenes or even di-alkenes which also can undergo β-scissions and other reactions contributing to the large number of products observed in the alkylation reactions. Figure 1-13 below shows the alkylation/isomerisation pathway of a C₅ alkene.
Moreover, Guisnet and Magnoux reported that USY zeolite with a Si/Al ratio of 5 has significant cracking activity of the 2,2,4 TMP at temperatures as low as 100 °C [55]. The products include isobutane and isobutene, the latter of which was reported to cause rapid oligomerisation [35].

1.3.4.2 Self-Alkylation

The self-alkylation reaction produces light, normal alkanes which are unfavourable to the overall product quality. Also, the yield of the desired C₈ products are reduced [17]. In HF propene alkylation, about 15 vol. % propane is produced [56]. In zeolites, this effect is reduced, depending on the zeolite type and the operating conditions (typically between 0.5-5 %) [57, 58].

In the reaction of 2-butene with isobutane, the tertiary cation can undergo a proton transfer to the zeolite to produce isobutylene. The isobutylene then reacts with another tertiary cation to produce a C₈⁺ cation. A feed butene will repeat the initiation step in parallel to form a secondary alkyl cation. Concomitantly, the cation undergoes a hydride transfer to produce a tertiary cation and a normal alkane. Figure 1-14 shows the self-alkylation mechanism.

![Figure 1-14: Self alkylation mechanism, adopted from [57]](image)

1.3.5 Summary of the Alkylation Mechanism

The alkane/alkene alkylation mechanism involves a complex set of reactions which are summarised in Figure 1-15 below. Side reactions including oligomerisation, cracking and self-alkylation are detrimental to the overall product quality and should be minimised.

![Figure 1-15: Simplified reaction mechanism of the alkylation reaction, adopted from [57]](image)
1.4 Zeolites as Alkylation Catalysts

Current alkylation technologies utilise liquid acids such as HF and H$_2$SO$_4$. Several other acids were explored in literature to mitigate the corrosion and health issues related to the current alkylation catalysts. These acids include sulfated zirconia [59-61], metal halides [62-64], ionic liquids [65-68] heteropolyacids [69-71], and supported acid resins [72-75]. The following section focuses on zeolite properties as a catalyst for the alkylation reaction.

1.4.1 Effect of the Type and Structure of the Zeolite

The type of the zeolite and its pore structure has a significant effect on its alkylation activity, selectivity and stability. In general, large pore zeolites show high activity for the alkylation reaction while medium and intermediate pore zeolites do not.

The product distribution of the large-pore zeolites exhibit significant resemblance to a typical alkylate with high C$_8$ selectivity and high TMP content. The acidity of large pore zeolites seems to have the largest influence on product quality and catalyst lifetime. Corma et al. compared three large pore zeolites, namely USY, Beta, and Mordenite. The zeolites had relatively close C$_8$ selectivity but different lifetimes, with Beta > USY, while Mordenite deactivated rapidly due to its one-directional pore structure. The differences between the performance of zeolite Beta and USY was attributed to the higher concentration of Brønsted acid sites in zeolite Beta [76]. Nivarthy et al. compared Beta, Y, and EMT. The zeolite's lifetime was shown to be correlated with the concentrations of the Brønsted sites. EMT, which had the highest Brønsted acid site concentration, showed the longest lifetime. While Beta, which had the lowest Brønsted acid site concentration, had the lowest lifetime [77]. Mota Salinas et al. compared the performance of H-Beta and H-USY and found that Beta outperformed USY in terms of selectivity to C$_8$s and catalyst lifetime due to the uniformity of the channels in zeolite Beta [78].

Medium and intermediate pore zeolites were found to be inactive under typical alkylation conditions. In the aforementioned study by Corma, the authors also compared ZSM-5 and MCM-22. The medium pore zeolites had significantly lower TMP selectivity and deactivated rapidly [76]. ZSM-5 and ZSM-11, medium pore zeolites, did not exhibit any significant activity below 150 °C; above that temperature, mostly cracking products were observed [79]. Chu and Chester compared ZSM-5 with zeolite Y and found that ZSM-5 was inactive for the alkylation reaction [80].

1.4.2 Acidity Effects

The acidity of the zeolite is directly correlated to its alkylation activity. Corma et al. proposed that the acid strength required for the alkylation reaction decreases in the order cracking > alkylation > dimerisation [81]. However this suggestion is in direct contradiction to the liquid
acid alkylation processes where the acid strength is maintained at very high levels. Feller and Lercher reported contrasting opinions on the acidity required regarding the alkylation reaction [29]. Mostad et al. compared the iso-structural SAPO-37 and Y zeolite under typical alkylation conditions. SAPO-37 only catalysed dimerisation and oligomerisation reactions while zeolite Y produced mostly TMPs. The authors concluded that the relative lack of strong acid sites in SAPO-37 in comparison to zeolite Y contributed to the lack of selectivity to TMPs [82].

1.4.2.1 Brønsted Acid Sites

During alkylation, the zeolite's lifetime is directly associated with the concentration of Brønsted sites as higher Brønsted acidity seems to improve the stability. Corma et al. compared Mordenite, Beta, USY, ZSM-5 and MCM-22 and observed that the deactivation rate and the deterioration of the product quality, in terms of TMP/DMH ratio, correlated directly with the concentration of Brønsted acid sites of the respective zeolite, with higher concentrations performing better than lower ones [76]. Stocker et al. compared EMT and FAU. EMT, which had a higher ratio of strong Brønsted / weak Brønsted sites showed improved performance in terms of lifetime and the products’ overall octane values [37]. Nivarthy et al. back-exchanged H-Beta with sodium ions to decrease the concentration of Brønsted acid sites which led to rapid deactivation of the zeolites with higher sodium content due to the decrease in the Brønsted acidity [83]. Diaz-Mendoza et al. compared REY, USY, and Beta zeolites. The authors found that the zeolites with intermediate Brønsted acid site strength performed better in terms of C₈ selectivity and stability with Beta (intermediate Brønsted acidity and lowest total acidity) > REY (strong Brønsted acidity and intermediate total acidity) > USY (strongest Brønsted acidity and total acidity). The high Brønsted and total acidity in the USY zeolite led to lower lifetimes and decreased the selectivity toward C₈s due to cracking and hence had the lowest lifetime [84]. Guzman et al. prepared a set of lanthanum-exchanged zeolite X; weak Brønsted acidity was shown to be detrimental to the catalyst lifetime while strong Brønsted acidity promoted alkylation [85].

1.4.2.2 Lewis Acid Sites

The presence of Lewis sites contributes to the degradation of the product quality and the deactivation of the zeolite. Diaz-Mendoza et al. observed that high concentrations of strong Lewis acidity increased the production of dimerisation products in zeolites Beta, USY and REY. Figure 1-16 below shows the IR spectra of adsorbed pyridine. Strong acidity was defined by the availability of peaks corresponding to an acid site after desorption of pyridine at 500 °C. The authors reasonably proposed that the strong Lewis sites in USY promoted the deactivation of the zeolite while the high concentration of intermediate Brønsted sites in REY promoted better lifetime and C₈ selectivity [84].
Nivarthy et al. proposed that Lewis acid sites increase the concentration of olefins inside the pores, due to the fact that olefins are polarisable, thus resulting in increased oligomerisation rate and limited hydride transfer which in turn would lead to shorter lifetimes [83]. Fiego et al. investigated the effect of activation temperature on the alkylation activity of La-H-Y and noted that as the activation temperature increased, the formation of mono- and di-olefins increased. This was attributed to the increase in the Lewis acid sites formed during the activation which might have increased the adsorption rate of the olefins inside the pores and thereby facilitated oligomerisation [86]. The presence of Lewis acid sites can strengthen the Brønsted acid sites as was observed by Corma et al. The authors also noted that the complete removal of Lewis acid sites from zeolite Y led to faster deactivation [87].

1.4.2.3 Si/Al Ratio
Silica to alumina ratios are a major factor affecting the alkylation performance. In general, lowering the value of the Si/Al ratio improves the alkylation performance depending on the zeolite type.

Faujasites show a clear pattern of improved performance with lower Si/Al ratios. This could be attributed to the increase in the number of Brønsted sites as the aluminium content increases. Multiple USY zeolites with varying Si/Al ratios were tested by Corma et al. Catalysts with the lowest Si/Al ratio (2.6), exhibited the best performance in terms of C₈ selectivity and lifetime [81]. In another study by the same cited group, dealumination of USY zeolites yielded differing results. Initial dealumination led to improved results while severe dealumination, despite the complete removal of extraframework aluminium (EFAL) species caused rapid deactivation. The authors attributed this finding to the interaction between the EFAL species and the Brønsted acid sites which increased the strength of such sites by enhanced polarisation [87]. Similar trends were also confirmed by de Jong who tested multiple USY zeolites in a slurry reactor with the lowest Si/Al ratio (3) performing better than higher Si/Al ratio USY zeolites [51]. Zeolite X, which has the lowest possible Si/Al ratio (~ 1), is unstable in the protonic form and metal ion-exchange has to be incorporated to generate
acidic sites without the collapse of the framework [88]. Weitkamp compared Ce-exchanged X and Y zeolites and found that zeolite X had almost twofold the lifetime of zeolite Y. The authors claimed that the higher Brønsted site density in zeolite X, due to its higher aluminium content and higher exchange capacity, was the main reason for its improved performance [54].

Zeolite Beta, a large pore zeolite, was explored by Yoo and Smirniotis. The authors synthesised zeolite Beta with a Si/Al ratio between 6 and 30. The optimum value for the Si/Al ratio was found to be between 8.5 and 15 [89]. Comparatively, Corma et al. synthesised zeolite Beta with a Si/Al ranging between 12 and 27. The optimum Si/Al ratio was found to be around 14 due to the differences in acidity and thermal stability of the used zeolite [90].

1.4.2.4 Effect of Metal Ion-Exchange
Rare-earth exchanged zeolites are extensively used in the refining industry [91, 92]. Brønsted acidity in zeolites is increased substantially with rare earth metal ion-exchange [93]. Polyvalent metals such as iron and rare earth metals such as cerium and lanthanum provide high Brønsted acidity and improved thermal stability [29]. Chu and Chester compared USY (Si/Al=5.6) and rare earth exchange Y (REHY) (Si/Al=5.2). REHY was shown to have the best performance in terms of product quality and catalyst lifetime. Further dealuminated REHY (Si/Al=8.8) zeolites did not, nevertheless, show any improvement in performance [80]. Rørvik et al. compared H-EMT, partially La-exchanged H-EMT (51% exchanged) and fully La-exchanged EMT. The partially exchanged zeolite had the best performance in terms of product quality and catalyst lifetime [94]. Sievers et al. compared the performance of fully La-exchanged zeolite X (LaX) with fully La-exchanged zeolite Y (LaY). The lifetime of LaX (15 hours) was more than twofold the lifetime of LaY (7 hours). Moreover, LaX had a higher concentration of strong Brønsted sites. The residual sodium in LaY contributed to its lower performance as it was difficult to fully exchange the sodium in zeolite Y [95]. Dalla Costa and Querini compared the performance of La-exchanged Beta (LaB) to HY and LaY zeolites. Surprisingly, LaB had worse performance than both LaY and HY. The authors attributed the lower performance of LaB to its high ratio of strong acid sites which enhanced cracking and led to pore blockage [96].

1.4.3 Adsorption Effects
Polar molecules are readily adsorbed in zeolites. Polarisable molecules, olefins for example, are attracted to the zeolite pores due to the electrostatic fields available in the pores, thus enhancing their adsorption [97]. Thus, olefin concentration inside the pores will be considerably higher than its bulk concentration [98]. This rise in the concentration of the olefins enhances the oligomerisation and cracking activity and hence reduces the rate of hydride transfer. It seems that the reduction of the olefin concentration near the acidic sites
is imperative to extending the lifetime of the zeolite. The adsorption of olefins varies significantly depending on the zeolite framework, Si/Al ratio and modification procedure even for the same framework type [99]. Reducing the olefin adsorption rate could possibly extend the catalyst lifetime. Moreover, the desorption of hydrocarbons from the zeolite also contributes to its alkylation activity. For instance, heat of adsorption measurements of H-FAU by Feller and Lercher at typical reaction temperatures (75 °C) revealed that the desorption rate of a C8 carbon molecule is four times faster than a C12 carbon molecule, eight times faster than a C16 carbon molecule and 12 times faster than a C20 carbon atom [29]. The large differences in desorption rates indicates the removal difficulty of large molecules once they are formed.

1.4.4 Summary of the Catalysis by Zeolites

Large-pore zeolites were shown to be active catalysts for the alkylation of isobutane with butene. Tailoring the acidity of the zeolite improves the selectivity toward the desired product (TMPs). Strong Brønsted sites seem to have the largest influence on the selectivity and lifetime of the zeolite. High density of Lewis sites appears to increase the adsorption of the olefins inside the pores leading to high oligomerisation, lower selectivity and shorter lifetime. Metal ion exchange and varying the Si/Al ratio can help manipulate the Brønsted/Lewis acidity of the zeolite, with stronger Brønsted/Lewis sites ratios favouring higher TMP selectivity and longer lifetime.

1.5 Effect of Operating Parameters

The most important operating parameters in the alkylation reaction are the temperature of the reaction, the olefin space velocity (OSV), the paraffin or isoparaffin / olefin (P/O) ratio and the reaction phase. The olefin feed type also impact the performance of the reaction. Furthermore, the internal P/O ratio can be affected by the reactor type. A summary of the range of operating conditions from industrial and literature sources is presented in Table 1-5 below.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temperature (°C)</th>
<th>P/O Ratio (mol/mol)</th>
<th>OSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>15 - 40</td>
<td>11 - 14</td>
<td>0.1 - 0.6</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>5 - 15</td>
<td>7 - 10</td>
<td>0.03 - 0.2</td>
</tr>
<tr>
<td>Zeolites</td>
<td>50 - 120</td>
<td>6 - 150</td>
<td>0.01 - 1.0</td>
</tr>
</tbody>
</table>
1.5.1 Effect of Temperature

The strength of liquid acids in comparison to the acidity of zeolites allows for lower operating temperatures. The need for higher operating temperatures in zeolites is not only attributed to its lower acid strength, but also to its lack of solvation ability [29].

In general, the accepted operating temperature range for zeolites is between 50 to 100 °C. Taylor and Sherwood tested the effect of temperature on the performance of USY (Si/Al ~3). The experiment, conducted at 38, 66, and 94 °C, showed that increasing the temperature decreased TMP selectivity; the longest lifetime was achieved at 66 °C [100]. Kirsch et al. compared multiple REY zeolites at a temperature range of 25-100 °C. The residual sodium had a significant impact on the operating temperature. A 0.2 wt. % sodium sample had an optimum operating temperature of 40 °C while a 1.0 wt. % sodium sample had an optimum temperature of 80 °C. This can be explained by the varying acid strength of the zeolites as higher sodium contents significantly reduced the acidity [23]. Feller et al. compared the performance of LaX zeolites in the range of 40-130 °C; increasing the temperature decreased the TMP/DMH ratio and the longest lifetime of the catalyst was achieved at 75 °C [57].

The effect of temperature on the alkylation performance of Beta zeolites shows a similar trend to FAU zeolites. Corma et al. tested the performance of H-Beta at a temperature range of 50-80 °C. Higher operating temperatures produced an increase in the catalytic activity and conversion of the olefins. However the cracking performance also increased and the TMP selectivity decreased [90]. Further, Nivarthy et al. reported that the optimum operating temperatures in terms of product quality is 75 °C. Lower temperatures enhanced oligomerisation while higher temperatures facilitated cracking, both of which were detrimental to the overall product quality [38].

1.5.2 Effect of the Reaction Phase (Gas, Liquid and Supercritical)

The reaction phase contributes significantly to the alkylation performance. The alkylation reaction over solid acids is usually carried out in the liquid phase to enable the dissolution of coke precursors. Zeolite catalysts have also shown higher stability and improved selectivity in liquid phase alkylation [52]. A study by Nivarthy et al. [38] on the effect of the operating parameters on the alkylation activity of zeolite Beta showed that the reaction pressure has no effect once the reactants were in liquid-phase. Increasing the pressure beyond that point did not improve the results. Dalla Costa and Querini [101] tested the alkylation performance of the zeolites LaY and LaB in the gaseous phase. At liquid-like operating temperatures, i.e. 80 °C, the catalyst performed worse than its performance in the liquid phase. Yet surprisingly, as the researchers increased the reaction temperatures, the product quality substantially increased. The optimum temperature was found to be 110 °C. At the beginning
of the reaction, the catalyst was very active for cracking yet after an induction period the TMP selectivity improved. The authors attributed this behaviour to the initial coking of the strong acid sites and subsequent dissolution of large molecules from the pores of the catalyst due to cracking at higher temperatures.

Supercritical conditions were also examined in order to enhance the removal of the coke precursors. The critical point of isobutane is at 135 °C and 36.5 bar. Under this high temperature, the reaction yielded high amounts of cracked products however the lifetime of the catalyst is improved as reported by Fan et al. [102]. Moreover, the cracked products were highly olefinic in nature. Mota Salinas et al. compared the performance of H-Beta and H-Y zeolites under supercritical conditions. The authors concluded that the better performance of H-Beta can be attributed to its higher surface acid sites. The authors also noted that there are no significant benefits of supercritical conditions as the product quality diminished whilst the catalyst lifetime was improved [78]. Clark and Subramaniam tried to overcome the excessive cracking under the supercritical conditions of isobutane by using supercritical carbon dioxide (CO₂) as a diluent (50 °C and 155 bar CO₂ pressure). The catalyst was stable but the conversion of butenes was low (<20 %) and the selectivity for TMPs was also very low [103]. Moreover, comparing a variety of supercritical solvents, Ginosar et al. concluded that supercritical conditions were not beneficial to the alkylation performance [104].

1.5.3 Effect of Paraffin/Olefin Ratio, Space Velocity and Reactor Type

High paraffin (isobutane) concentrations are crucial to maintaining and propagating the alkylation and minimising side reactions. Internal P/O ratios are highly dependent on the reactor type. Back-mixed reactors have very high internal P/O ratio due to instantaneous mixing. Olefin space velocity (OSV) determines the alkylate rate of production. Unfortunately, the effects of P/O ratio, the OSV and the reactor type are not mutually exclusive.

Corma et al. tested the effect of operating conditions on the alkylation performance of zeolite Beta. The authors observed that high P/O ratios did improve the product quality [90]. When de Jong et al. used a back-mixed slurry reactor to examine the alkylation activity of zeolite H-Beta the catalyst lifetime was considerably improved from 5-60 minutes in plug flow reactors to 20-30 hours in a back-mixed reactor. Moreover, the authors concluded that increasing the P/O ratio increased the catalyst lifetime while increasing the OSV decreased the catalyst lifetime [51]. Similar trends were observed on the effect of P/O ratios on the catalyst lifetime when a back-mixed stationary Berty reactor was used by Taylor and Sherwood to examine the alkylation performance of USY. [100]. Additionally, Feller et al. tested LaX zeolites in a slurry reactor. The authors found that the total catalyst productivity
was nearly independent of the OSV. The catalyst had a shorter lifetime at higher OSVs but the total amount of alkylate produced was thereby equal to the total amount produced at lower OSVs and longer reaction times [57]. Nivarthy et al. also found that the butene turnover remained constant after changing the space velocity over zeolite Beta [38].

1.5.4 Effect of Olefin Feed Type

A mixture of propene, butenes, and pentenes is usually used as a feedstock for alkylation units [5]. Zeolites were examined with a variety of olefin feeds. Guisnet and Gnep compared the performance of USY zeolite with propene and 2-butene as an olefin feed. The conversion of the olefin was considerably lower in the propene/isobutane alkylation, 57% vs 82% [48]. Nivarthy et al. compared the effect of the feed olefin on the performance of zeolite H-Beta. The best performance, in terms of catalyst lifetime, corresponded to 2-butene followed by propene while ethylene caused rapid deactivation of the catalyst [58]. Amongst the butenes, isobutene was shown to cause more oligomerisation products than the other butenes [35]. This can be explained by the lower energy required to protonate the isobutene from the Brønsted acid sites [34].

1.5.5 A Summary of the Effect of the Operating Parameters

The variation in the operating parameters was shown to have a significant impact on the alkylation reaction. The optimum reaction temperature has been shown to be around 75 °C. Increasing the temperature beyond 75 °C resulted in increased cracking while operating at lower temperatures reduced the catalyst activity and promoted oligomerisation. Liquid-phase alkylation is preferred to gaseous alkylation due to the dissolution of the coke precursors in the liquid phase while supercritical conditions were shown to be detrimental due mainly to the increased temperature. The olefin turnover seems to be independent of the space-velocity (OSV). A certain number of acid sites are available for the reaction and the turnover will always be the same over such sites. Selection of the reactor (CSTR or PFR) plays a significant role in prolonging the catalyst lifetime with back-mixed reactors providing significant improvement in the catalyst lifetime due to the reduced internal P/O ratios. Table 1-6 summarizes the effect of the operating parameters on the alkylation activity.
Table 1-6: Summary of the effect of the operating parameters on the alkylation activity over zeolites

<table>
<thead>
<tr>
<th>Operating Parameter</th>
<th>Range</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>50 - 100 °C</td>
<td>Increasing temperature increases the cracking activity while operating at lower temperatures promotes oligomerisation. The optimum reported temperature is around 75 °C.</td>
</tr>
<tr>
<td>Reaction Phase and Pressure</td>
<td>1 - 155 bar</td>
<td>Operating at liquid phase seems to increase the catalyst lifetime and promote better alkylate selectivity. Increasing the pressure beyond that point had no effect. Gas and supercritical conditions are detrimental to the catalyst stability.</td>
</tr>
<tr>
<td>Paraffin/Olefin Ratio and Olefin Space Velocity</td>
<td>P/O = 1000 - 5, OSV = 0.001 - 0.50 h⁻¹</td>
<td>Multiple studies confirmed that the P/O ratio and the OSV have no effect on the catalytic behaviour as the amount of alkylate produced will be always the same. There are a certain number of acidic sites available for the reaction and the catalyst turnover will always remain constant.</td>
</tr>
<tr>
<td>Reactor Type</td>
<td>Tubular/CSTR</td>
<td>CSTR-like reactors show significantly improved catalytic stability while tubular reactors suffer from rapid deactivation. The improved mixing in the CSTRs reduces the olefin concentration and improves the stability of the catalyst.</td>
</tr>
<tr>
<td>Olefin Type</td>
<td>C₃, C₄, C₅ olefins</td>
<td>C₄ olefins outperform other types due to the higher octane rating of the product. Amongst the C₄ olefins, isobutene seems to promote oligomerisation.</td>
</tr>
</tbody>
</table>

1.6 Commercial Alkylation Technologies

Paraffin alkylation to produce high quality gasoline blend stock is a very economical way to improve the quality of the gasoline pool. The alkylation unit utilises low value off gases produced from cracking units such as the Fluid Catalytic Cracking unit (FCC), the Visbreaking unit and the Coking unit to produce high quality gasoline [5]. Current alkylation technologies employ either sulfuric acid or hydrofluoric acid as catalysts for the reaction. Although not fully commercialised, some technology licensors are proposing the use of solid catalysts for the alkylation units.

1.6.1 Liquid Acid Technologies

The use of liquid acids requires the formation of stable emulsions between the feed and the acid. The formation of such emulsions requires intensive mixing inside the reactor. The stability of the emulsion phase has to be balanced to ensure proper product separation.
Typically, either hydrofluoric (HF) or sulfuric (H₂SO₄) acid is used in the alkylation unit. HF has a low viscosity and blends well with the reactants. Conversely, H₂SO₄ has a higher viscosity and requires the use of impellers to improve the emulsion. Operating temperatures for HF units are between 15-40 °C, while H₂SO₄ operates at lower temperatures, typically between 5-18 °C, thus requiring significant cooling and complex heat exchange systems [5].

1.6.1.1 **Sulfuric Acid Processes**

There are two licensors offering sulfuric acid alkylation technologies: Stratco’s Effluent Refrigerated Sulfuric Acid Alkylation Process and ExxonMobil’s Auto-Refrigerated Alkylation Process.

1.6.1.1.1 Stratco’s Effluent Refrigerated Sulfuric Acid Alkylation Process [105, 106]:

The ERSA process employs a horizontal reactor called the contactor reactor (Figure 1-17). The feed is cooled prior to entering the reactor. The contactor is an intricately designed reactor/heat exchanger. It houses a heat exchange tube to control the reaction temperature and remove the excess heat of reaction. The contactor also employs an impeller to maintain an adequate level of mixing and stable emulsions. High recirculation rates have to be maintained to ensure the temperature and concentration uniformity of the reactor (Figure 1-18).

![Figure 1-17: Stratco's Effluent Refrigerated Sulfuric Acid Alkylation Process, adopted from [107]](image)

Fresh acid is pumped to maintain the acid strength at about 90%. Propane, an inert at the reaction conditions, is mixed with the feed to increase the efficiency of the cooling process.
Acid is usually passed to a bank of 2-4 contactor reactors in a series to maximise the product's octane rating and minimise acid utilisation. Typical feed P/O ratios are 7-10. The olefin space velocity is usually 0.06-0.19 h⁻¹ and the temperature of the reaction is maintained between 5-18 °C.

1.6.1.1.2 ExxonMobil’s Stirred Auto-Refrigerated Process [5, 105]:
The Stirred Auto Refrigerated Process by ExxonMobil consists of a horizontal, sectioned reactor vessel. Each section of the reactor is stirred (Figure 1-19). The olefin feed is premixed with propane and subsequently mixed with the recycle isobutane before being fed in parallel into the reactor. The acid only enters the first zone of the reactor and then cascades to the other zones.

Figure 1-18: Stratco’s Contactor reactor, adopted from [107]

The temperature is controlled by the evaporation of isobutane and the added propane. To minimise any temperature increase along the reactor, the reactor operates at a pressure...
differential. A slipstream of propane is withdrawn to prevent build-up in the system and a settler is used to separate the liquid products. The operating temperature is typically kept at 5 °C to minimise side reactions while the olefin space velocity is about 0.1 h⁻¹ while the acid strength is usually kept at 90-92 wt. %.

1.6.1.2 Hydrofluoric Acid Processes

There are mainly two hydrofluoric alkylation technology licensors, namely ConocoPhillips and UOP.

1.6.1.2.1 ConocoPhillips Reduced Volatility Alkylation Process [5, 105]:

The ConocoPhillips alkylation technology utilises a non-cooled riser reactor. The feed olefins are dried to remove any excess water prior to entering the reactor. The olefins are premixed with the isoparaffins and feed nozzles are used to introduce the reactant mixture from the bottom of the reactor as well as to introduce the mixture along the reactor's length. The overall process flow diagram is shown in Figure 1-20.

![Figure 1-20: ConocoPhillips' HF Alkylation process, adopted from [107]](image)

To maintain a high acid dispersion rate, the reactor is fitted with perforated trays. Products enter the settler to separate hydrocarbons. The acid is withdrawn and cooled at the bottom of the reactor and fed back to the reactor control the temperature. Figure 1-21 shows the reactor used in the process. Typical process temperature is ~ 24 °C. The P/O ratio is about 14-15 while the acid strength is typically kept at 89-92 %. 
1.6.1.2.2 UOP’s Alkyplus HF Alkylation [5, 105]
UOP’s Alkyplus HF alkylation process employs a similar concept to Stratco’s contactor reactor. The main difference is in the reactor orientation. UOP utilises a vertical reactor-heat exchanger setup. The process flow diagram for the Alkyplus process is shown in Figure 1-22.

The olefins and isobutane are mixed and the mixture enters a drying bed to remove excess water. The reactants enter the reactor shell through feed nozzles. The acid is introduced
from the reactor’s bottom. Cooling water flows through coils inside the reactor to control the temperature and remove any excess heat. The reactor schematic is shown in Figure 1-23.

![Reactor Schematic](image)

**Figure 1-23: UOP’s Alkyplus HF Alkylation reactor, adopted from [105]**

The reactor effluent then enters a settler where the emulsion is broken. Acid is withdrawn from the settler and recycled back to the reactor. Afterwards, hydrocarbons are sent to the main fractionator (isostripper) where alkylates are withdrawn at the bottom. A side stream, containing isobutane and HF, is withdrawn from the fractionator and recycled back to the reactor. No external regeneration is required for the acid. The acid is distilled with the product during normal operations.

HF alkylation process requires the installation of expensive mitigation systems. These systems include complex acid leak detection systems and water spray towers. Some technology licensors are proposing process modifiers such as UOP/Chevron’s ALKAD process that utilises an additive based on the amine salts of HF to produce complexes, while Phillips/ExxonMobil propose the use of sulfones to reduce the formation of HF aerosols during leaks.

### 1.6.2 Solid Acid Processes

Although not operational thus far, some technology licensors are suggesting the use of solid acid catalysts for alkylation units. The rapid deactivation of the catalysts requires continuous regeneration. There are four main technologies for solid acid alkylation. Two of these processes use a Y zeolite-based catalyst, one use chlorinated alumina and the fourth uses triflic acid.

#### 1.6.2.1 Akzo Nobel/CBI AlkyClean Process [108]

The AlkyClean process utilises multiple reactors and a solid catalyst. The catalyst does not contain any halogens. Figure 1-24 below describes the AlkyClean process.
Olefin feed is mixed with recycle isobutane prior to entering the reactor. The reactor is operated in the liquid phase at a temperature range of 50 to 90°C. Several reactors are used to facilitate a continuous operation. Reactors are cycled between on-line alkylation and rejuvenation (low temperature regeneration), and are regularly regenerated at elevated temperatures. The regeneration is conducted either by hydrogen at elevated temperatures or by isobutane at low temperatures [29]. The reaction section is shown in Figure 1-25.
According to a process patent, a catalyst consisting of Pt/USY zeolite with an alumina binder is used. The patent also discloses that the addition of the inert binder improves the overall product RON. Furthermore, the patent also provides information about the optimum binder content, namely 20 wt.% [9]. The molar P/O feed ratio is kept between 8 and 10. This process was the first solid acid alkylation process to be commercialised. It was constructed at Shandong Wonfull Petrochemical Group’s refinery in China and is estimated to produce 100,000 ton/year of alkylates [24].

1.6.2.2 UOP’s Alkylene Process [70]
UOP’s Alkylene process utilises a riser reactor similar to an FCC unit. The olefin feed is passed on a feed pre-treatment section. The olefins are then mixed with the recycled isobutane. The reaction section is shown in Figure 1-26.

![Figure 1-26: UOP’s Alkylene reaction section, adopted from [107]](image)

The feed, along with the reactivated catalyst, is injected into the reactor. The catalyst particles are separated from hydrocarbons at the top of the reactor and then dropped to the reactivation zone. The hydrocarbons are then passed on to the fractionation section where the products are separated. Isobutane is cooled and recycled back to the reactor.

Catalyst reactivation is done via a counter-flow of isobutane and hydrogen. After disengagement, the catalyst flows down the reactor. Isobutane and hydrogen are fed into counter-current to reactivate the catalyst. Catalyst reactivation is not enough for full
regeneration and a slipstream has to be withdrawn to a reactivation vessel. The reactivation is done at high temperatures in a semi-batch mode with hydrogen.

The catalyst used in the process is not disclosed. Patents from UOP indicate that the catalyst used is an alumina-supported metal halide, most probably chloride, modified with alkali metals for hydrogenation. Moreover, the presence of a feed pre-treatment section indicates that the presence of halogens in the catalysts thus requiring continuous halogen addition [109]. The operating temperature is between 10 and 40 °C while the P/O ratio is between 6 and 15.

1.6.2.3 LURGI’s EUROFUEL Process [110]
LURGI and Sud-Chemie’s EUROFUEL process is a reactive distillation process. The catalyst is suspended in isobutane and enters the tower at the top. The olefins are introduced at the stages of the tower. The process flow diagram is shown in Figure 1-27.

![Figure 1-27: The EUROFUEL process, adopted from [110]](image)

Catalyst separation is done at the bottom of the reactor. Recycled isobutane is mixed with the catalyst and fed to the reactor. The isobutane/catalyst mixture enters at the top of the reactor. Hydrogen is introduced intermittently to the catalyst to reduce deactivation. Regeneration is done in a proprietary section at high temperatures. A faujasite-based catalyst containing a hydrogenation function is used in this process. The process temperature is between 50 and 100 °C and the P/O ratio is between 6 and 12 [29].
1.6.2.4 Haldor Topsøe FBA Process [111]

The FBA process employs a supported catalyst in a fixed bed. The catalyst is triflic acid supported on a porous surface. The catalytic zone contains a high concentration of the acid. The process is described in Figure 1-28 below.

![Diagram of the FBA process](image)

Figure 1- 28: The FBA process, adopted from [109]

Ester intermediates are formed upstream of the catalyst zone and these esters, which are soluble in the hydrocarbon feed, enter the acid zone of the reactor. The esters react producing alkylates and regenerating acid. Products must be treated to remove any trace amount of acids. Reaction temperatures are between 0 and 20 °C.

1.6.3 Summary of the Commercial Alkylation Technologies

Although liquid acid alkylation continues to dominate the commercial alkylation technologies, the health and safety issues along with increasing mitigation costs necessitates the use of other catalysts. Table 1-7 below summarizes the main properties of the commercial technologies listed above.
Table 1-7: Summary of Commercial Alkylation Technologies

<table>
<thead>
<tr>
<th>Process</th>
<th>Licensor</th>
<th>Catalyst</th>
<th>Reactor Type</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluent Refrigerated Sulfuric Acid Alkylation (ERSAA)</td>
<td>Stratco</td>
<td>H₂SO₄</td>
<td>Proprietary (Contactor)</td>
<td>Acid strength = 90% P/O ratio = 7 - 10 OSV = 0.06 - 0.19 h⁻¹</td>
</tr>
<tr>
<td>Stirred Auto-Refrigerated Alkylation</td>
<td>ExxonMobil</td>
<td>H₂SO₄</td>
<td>Large, segmented vessel with each segment acting as a CSTR</td>
<td>Acid strength = 90-92% OSV = 0.1 h⁻¹</td>
</tr>
<tr>
<td>Reduced Volatility Alkylation</td>
<td>ConocoPhillips</td>
<td>HF</td>
<td>Up-flow reactor with perforated trays and multiple feed nozzles</td>
<td>Acid strength = 89-92% Temperature = 24 °C P/O ratio = 15</td>
</tr>
<tr>
<td>Alkyplus HF Alkylation</td>
<td>UOP</td>
<td>HF</td>
<td>Up-flow reactor with multiple feed nozzles</td>
<td>Not disclosed</td>
</tr>
<tr>
<td>AlkyClean</td>
<td>Akzo Nobel/CBI</td>
<td>Pt/USY catalyst</td>
<td>Multiple fixed-bed reactors in parallel for continuous regeneration</td>
<td>Temperature = 50 - 90 °C</td>
</tr>
<tr>
<td>Alkylene</td>
<td>UOP</td>
<td>Not disclosed, most probably AlCl₃</td>
<td>FCC-like reactor for continuous regeneration</td>
<td>Temperature = 10 - 40 °C P/O = 6 - 15</td>
</tr>
<tr>
<td>EUROFUEL</td>
<td>Lurgi</td>
<td>FAU-based catalyst</td>
<td>Reactive distillation</td>
<td>Temperature = 50 -100 °C P/O = 6 - 12</td>
</tr>
<tr>
<td>Fixed Bed Alkylation (FBA)</td>
<td>Haldor Topsøe</td>
<td>Triflic acid supported on porous material</td>
<td>Fixed-bed</td>
<td>Temperature= 0-20°C</td>
</tr>
</tbody>
</table>

1.7 Aim and Objectives

The aim of this research was to develop an improved zeolite-based alkylation catalyst. Various zeolites were characterised, modified and tested to maximise the catalyst lifetime and improve the TMP selectivity. The study also aimed to re-evaluate some of the literature data using a well-mixed reactor under ideal reaction conditions. Large-pore zeolites Beta, Y and Mordenite were selected as the starting point of this thesis to examine the effect of the zeolite’s structure. Furthermore, the study also evaluated the acidity effects of selected zeolites by varying the Si/Al ratio and incorporating rare-earth metals into the zeolites. The effect of the catalyst dilution by inerts was also investigated and indeed provided the most significant improvement.
1.8 References


changes at high butene conversion in a slurry reactor, Applied Catalysis A: General, 156 (1997) 267-283.


2. Experimental Methods and Catalyst Characterisation Techniques
2.1 Introduction

The general steps used to prepare the respective catalysts are listed in this section and a detailed description of the catalytic testing procedures, along with the catalytic setup is provided. A specific catalyst preparation section is available where applicable in following chapters of this work. The theoretical background of the catalyst characterisation techniques used in this work along with the methods used to characterise the catalysts is also discussed in this section.

2.2 Catalyst Preparation and Testing

2.2.1 Catalyst Preparation and Experimental Setup

The catalyst powder (between 15-20 g, 40 mL by volume) was pressed in a hydraulic press, crushed and sieved to a particle size of approximately 3 mm. The apparatus used to prepare the catalysts are presented in Figure 2-1.

The alkylation reaction was conducted in a top-driven stainless steel 300 mL autoclave reactor fitted with an annular catalyst basket (40 mL) shown in Figure 2-2.
The pressed catalyst was placed inside the basket and nitrogen (99.99%, BOC) was introduced into the reactor at 2.0 MPa to check for leaks. The pressurised vessel was left for 2 hours and the pressure was monitored. Once the leak testing was complete, the reactor was connected to the catalytic rig, shown in Figure 2-3, and the rig was tested for leaks using pressurised nitrogen at 1.7 MPa for 1 hour. The system was then depressurised.

![Simplified process flow diagram of the alkylation unit](image)

Figure 2-3: Simplified process flow diagram of the alkylation unit

The reactor was heated using a heating jacket and the temperatures of the wall and the reactor were monitored using a k-type thermocouple placed inside the heating jacket and the reactor respectively. The catalyst was dried *in-situ* under flowing nitrogen (150 mL/min) by heating from ambient at a ramp rate of ~1.5 °C/min to 200 °C and held for 16 hours. The reaction conditions used in this work are summarised in Table 2-1. A relatively high olefin space velocity was chosen to enable the investigation of the deactivation behaviour within a manageable timeframe.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>75.0</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>1.70</td>
</tr>
<tr>
<td>Olefin Space Velocity (h⁻¹)</td>
<td>0.30</td>
</tr>
<tr>
<td>Paraffin/Olefin Ratio (mol/mol)</td>
<td>15/1</td>
</tr>
<tr>
<td>Catalyst Weight (g)</td>
<td>15-20</td>
</tr>
<tr>
<td>Feed Flow Rate (g h⁻¹)</td>
<td>70-100</td>
</tr>
<tr>
<td>Test Duration (h)</td>
<td>4-10</td>
</tr>
</tbody>
</table>
Prior to the experiment, the nitrogen flow was stopped and the reactor was pressurised with liquefied isobutane (99%, BOC) to 1.7 MPa using a Brooks Flowmega mass flow controller. The feed was liquefied under nitrogen pressure (30 bar) and a nitrogen cylinder (99.99%, BOC) was used to maintain the liquefied gases under constant pressure. The temperature was then dropped to 75 °C. An example of a temperature profile taken during the alkylation reaction is shown in Figure 2-8. Once the reaction temperature was achieved and the reactor’s internal temperature was stabilised, the flow of isobutane was stopped and the feed (93.75 mol % isobutane/6.25 mol % cis-2-butene, BOC) was introduced using the same mass flow controller. The flow of the feed was adjusted to achieve an olefin space velocity of 0.30 h⁻¹. The mass flow controller measurements are available in section 2.2.3. Agitation was achieved by using an electric motor attached to an impeller that operated at 1200 rpm.

Products exited the reactor and passed through a filter to collect any catalyst fines. A back pressure regulator was used to maintain the system pressure at 1.7 MPa. A continuous distillation unit, with wall-circulating chilled water (3.0 °C), was used to separate the gas and liquid products. Gas from the separator was passed through a gas flow meter and was analysed online while the liquid samples were weighed and stored in a freezer for offline analysis. At the end of the experiment, the flow of the feed was stopped, the system depressurised and nitrogen was introduced (100 mL/min) at the reaction temperature (75 °C) for 16 hours to flush the reactor and dry the catalyst.

The butene conversion fractional selectivity and the weighted hourly space velocity based on the olefin (OSV) were obtained using the equations (2-1, 2-2 and 2-3) below:

\[
\text{Butene Conversion (X)} = \frac{C_F - C_P}{C_F} \times 100 \% \quad (2-1)
\]

\[
\text{Fraction Selectivity (S)} = \frac{m_{\text{fraction}}}{m_{\text{products}}} \times 100 \% \quad (2-2)
\]

\[
\text{OSV (h}^{-1}) = \frac{\text{Flow rate of butene in the feed (}g/\text{h})}{\text{Catalyst weight (g)}} \quad (2-3)
\]

where \( C_F \) is the concentration of the butene in the feed, \( C_P \) is the concentration of the butene in the product stream and \( m \) is the mass of the fraction/product. An example of the conversion and selectivity calculations is available in appendix (A). It should be noted that as the space velocity was based on the weight of the catalyst and the mass flow rate of the olefin, the product volume expansion or contraction could not be deduced.

### 2.2.2 Product Analysis

Feed and gaseous products from the reactor were analysed by a Varian CP-3800 GC-FID fitted with a 100 m fused silica HP-1 PONA column (0.2 µm x 0.5 µm film thickness) while
liquid samples were analysed using HP 6890 GC-FID fitted with the aforementioned column. The major liquid products were identified using a SUPELCO ASTM D5134 standard. The major product identification is available in appendix (B).

Two methods were applied for the analysis. The method applied to separate the gas products and the feed starts with a temperature hold of 15 minutes at 35 °C for reactant separation. The temperature was then increased in two steps; a ramp rate of 9 °C/min to 110 °C and a final ramp of 15 °C/min to 245 °C with a 20-minute hold to ensure that no products were left in the column prior to the next run. Figure 2-4 below shows an example of the feed’s GC-trace.

![Figure 2-4: GC trace taken from the feed](image)

The GC was calibrated by measuring the response factors ($R_F$) for a volumetric gas standard containing 1 vol% of C₁, C₂, C₃, i-C₄, n-C₅ and i-C₅ provided by BOC. The peak area counts were acquired and the response factor was calculated for each component. Table 2-2 shows the typical response factor calculation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Carbon Number (C)</th>
<th>log (C)</th>
<th>Area (µV.min)</th>
<th>$R_F$</th>
<th>Log (R_F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1</td>
<td>0.00</td>
<td>1011</td>
<td>9.89E-04</td>
<td>-3.00</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>0.30</td>
<td>1913</td>
<td>5.23E-04</td>
<td>-3.28</td>
</tr>
<tr>
<td>Propane</td>
<td>3</td>
<td>0.48</td>
<td>2808</td>
<td>3.56E-04</td>
<td>-3.45</td>
</tr>
<tr>
<td>Isobutane</td>
<td>4</td>
<td>0.60</td>
<td>3616</td>
<td>2.77E-04</td>
<td>-3.56</td>
</tr>
<tr>
<td>Isopentane</td>
<td>5</td>
<td>0.69</td>
<td>4435</td>
<td>2.25E-04</td>
<td>-3.65</td>
</tr>
<tr>
<td>Pentane</td>
<td>5</td>
<td>0.69</td>
<td>4378</td>
<td>2.28E-04</td>
<td>-3.64</td>
</tr>
</tbody>
</table>

The plot of Log ($R_F$) vs Log (C) showed a linear relationship as expected over the carbon number range of the gas as shown in Figure 2-5. The response factors were then used to calculate the concentration of the gaseous products. The response factors of heavier
molecules observed in the gaseous products, namely (C₆, C₇ and C₈), was extrapolated utilising the trend line generated in Figure 2-5.

![Figure 2-5: Typical plot of log (C) vs log (R_f)](image)

The liquid products were analysed using an offline HP 6890 GC-FID fitted with an auto sampler. The method used for liquid analysis was developed in order to separate the SUPELCO ASTM D5134 standard for peak identification. The method started with a temperature hold of 35 °C for 65 minutes. The temperature was then increased at a ramp rate of 2.5 °C/min to 245 °C and then held for 40 minutes to ensure that high boiling point molecules were eluted from the column. The GC trace of the SUPELCO ASTM D5134 standard is provided in Figure 2-6 highlighting the TMPs.

![Figure 2-6: GC trace of the SUPELCO ASTM D5134 standard highlighting the TMPs](image)

2.2.3 Mass Flow Controller Measurements

The flow rate of the isobutane and the feed mixture was controlled using a Brooks Flowmega liquid mass flow controller. The flow rate was set in the controller at a range of values between 25 – 250 gh⁻¹. For each value, measurements were taken using a gas flow...
meter and analysed using the GC to convert the results to \( \text{gh}^{-1} \) and the measured flow rates were in good agreement with the set point values for both isobutane the feed as shown in Figure 2-7. The operating flow rate was usually between 50-150 \( \text{gh}^{-1} \) which was within the calibration curve.

![Graph showing mass flow controller measurement results](image)

**Figure 2-7**: Mass flow controller measurement results

### 2.2.4 Reactor Furnace Controller and Reaction Temperature

The temperature of the reaction was maintained at 75 °C using the reactor furnace. Typically, the furnace temperature was set to ~ 110 °C to achieve the reaction temperature. Figure 2-8 shows the temperature profile taken during the alkylation reaction over zeolite Y. The average temperature during the reaction was 75.2 °C.

![Graph showing temperature profile during the alkylation reaction over zeolite Y](image)

**Figure 2-8**: Temperature profile during the alkylation reaction over zeolite Y

A typical temperature profile, using nitrogen flow of 150 ml/min during the catalyst activation, is presented in Figure 2-9. The furnace temperature was set to 290 °C and temperature readings were collected every 10 minutes. The activation temperature selected for this work was 200 °C. It should be noted that the PTFE seal used to seal the reactor had a maximum
operating temperature of 300 °C which limited the maximum activation temperature to ~ 220 °C. Furthermore, Guzman et al. demonstrated that the optimum activation temperature for La-X was around 180 °C and that increasing the activation temperature above 220 °C caused faster deactivation. The cited authors attributed the decrease in the catalyst lifetime at higher activation temperatures to the dehydroxylation of the bridging-OH groups that mainly decreased the Brønsted acidity and slightly increased Lewis acidity [1]. Based on the technical limitations and literature evidence, an activation temperature of 200 °C was selected and maintained for this dissertation.

![Temperature profile during the activation of the catalyst](image)

**Figure 2-9: Temperature profile during the activation of the catalyst**

### 2.2.5 Reproducibility

Various factors can affect the reproducibility of the experiments such as operator errors, variations in the used catalyst and instrumental errors (e.g. variation in reaction conditions, variation in analysis). To establish the error tolerance, reproducibility experiments were conducted on zeolite Beta with a Si/Al ratio of 12.5 provided by Zeolyst (CP814E). The conditions for the experiments were: temperature of 75 °C, olefin space velocity of 0.30 h⁻¹ and 1.7 MPa of pressure. The experiments were conducted by loading approximately 16 g of the catalyst in the reactor. Fresh catalyst powder was calcined, pressed and loaded in the reactor. The experiments were conducted over three separate days and the samples were taken at similar time-on-stream. The conversion and C₈ selectivity results are presented in Figure 2-10.
The results provided in Figure 2-10 show that both the conversion and C₈ selectivity results for each experiment were close. The results, along with the average and standard deviation (σ) are presented in Table 2-4. The standard deviation (σ) was calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}}$$  \hspace{1cm} (2-4)

where, σ: sample standard deviation, \(\bar{X}\) = sample mean, and n = number of repeated experiments. The results showed a slight difference between the experiments however the variation was found to be within tolerance (σ ≤ 1.04).

Table 2-3: Reproducibility data using zeolite Beta (12.5)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Ex 1</th>
<th>Ex 2</th>
<th>Ex 3</th>
<th>Average</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.00</td>
<td>99.28</td>
<td>99.70</td>
<td>99.66</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>99.25</td>
<td>98.87</td>
<td>98.45</td>
<td>98.86</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>97.60</td>
<td>97.21</td>
<td>98.10</td>
<td>97.64</td>
<td>0.36</td>
</tr>
<tr>
<td>4.5</td>
<td>93.58</td>
<td>92.56</td>
<td>94.21</td>
<td>93.45</td>
<td>0.68</td>
</tr>
<tr>
<td>5.5</td>
<td>90.76</td>
<td>90.24</td>
<td>92.24</td>
<td>91.08</td>
<td>0.85</td>
</tr>
<tr>
<td>6.5</td>
<td>89.23</td>
<td>87.36</td>
<td>87.83</td>
<td>88.14</td>
<td>0.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Ex 1</th>
<th>Ex 2</th>
<th>Ex 3</th>
<th>Average</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.11</td>
<td>51.11</td>
<td>52.44</td>
<td>52.22</td>
<td>0.83</td>
</tr>
<tr>
<td>2</td>
<td>47.00</td>
<td>46.05</td>
<td>45.36</td>
<td>46.14</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>40.93</td>
<td>41.77</td>
<td>40.19</td>
<td>40.96</td>
<td>0.65</td>
</tr>
<tr>
<td>4.5</td>
<td>34.46</td>
<td>32.16</td>
<td>34.23</td>
<td>33.62</td>
<td>1.04</td>
</tr>
<tr>
<td>5.5</td>
<td>29.28</td>
<td>26.89</td>
<td>28.38</td>
<td>28.18</td>
<td>0.99</td>
</tr>
<tr>
<td>6.5</td>
<td>25.26</td>
<td>23.11</td>
<td>24.55</td>
<td>24.31</td>
<td>0.89</td>
</tr>
</tbody>
</table>
2.3 Catalyst Characterisation

The characterisation techniques used to study the structural and chemical properties in this dissertation were: x-ray diffraction (XRD), scanning electron microscopy (SEM)/ energy dispersive x-ray analysis (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES), nitrogen adsorption measurements (N2-BET) and Fourier transform infrared spectroscopy (FTIR) coupled with pyridine adsorption/desorption. This section describes the basic principles for each technique along with the experimental methods used to characterise the catalysts.

2.3.1 X-Ray Diffraction (XRD)

XRD is an analytical technique used to identify crystalline solids. A crystalline material has its own ‘fingerprint’ pattern which can be used to distinguish it from different materials [2]. Zeolites are crystalline aluminosilicates and each zeolite framework (e.g. FAU, BEA and MOR) has its own unique pattern which is recognised by the International Zeolite Association (IZA) [3]. The ideal diffraction patterns for each zeolite are published on the IZA website [4]. Furthermore, the changes in the crystallinity of each material can be compared and calculated based on the reference pattern.

The principal equation used in powder XRD is Bragg’s law (eq 2-5) [5]:

\[ n\lambda = 2d \sin \theta \]  

(2-5)

where n is an order of diffraction, a positive integer (1, 2, 3...), \( \lambda \) is the wavelength of the incident X-ray (\( \lambda = 1.54178 \) Å for CuKα), d is the space between the planes in the atomic lattice and \( \theta \) is the angle between the X-ray and the scattering planes. Figure 2-11 shows the parameters in the powder XRD experiment.

![Figure 2-11: Illustration of Bragg’s law in a solid crystal][6]
Approximately 0.5 g of the catalyst powder sample was pressed into a glass stick and packed tightly to a 2 mm wafer disk. The sample was then loaded into the diffraction chamber where the XRD patterns of the samples were collected using Rigaku MiniFlex X-ray powder diffractometer equipped with nickel-filtered copper K alpha (CuKα) radiation and generator settings of 30 mA and 40 kV. The sample was scanned from the interval of $2\theta = 5^\circ$ to $70^\circ$. The step size of 0.05° and a step time of 6 s were used, while the divergent slit and scatter slit used were 1/8" and 1/4" respectively.

The XRD patterns of zeolites used in this dissertation were compared with patterns available in literature to confirm the zeolite’s structure. An example XRD pattern for zeolite Y is provided in Figure 2-12.

![XRD pattern of zeolite Y](image)

Figure 2-12: XRD pattern of zeolite Y

The relative crystallinity of modified zeolites was calculated using equation 2-6 [7]:

$$Crystallinity(\%) = \frac{\sum_{i=1}^{n} \text{Peak intensity of the modified sample}}{\sum_{i=1}^{n} \text{Peak intensity of the reference sample}}$$  \hspace{1cm} (2-6)

where i is the peak number.

### 2.3.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX)

Scanning electron microscopy (SEM) is a characterisation technique used to observe the size, morphology and topology of crystalline and amorphous materials between micrometre and nanometre in size [8]. Typical SEM components are illustrated in Figure 2-13. Two SEMs were used; a Philips XL30 FEGSEM fitted with a Bruker energy dispersive spectrometer and an FEI Quanta 200 Environmental SEM.
Energy dispersive X-ray spectroscopy (EDX) was used to obtain the elemental composition of the catalysts. The EDX technique allows the detection of elements with an atomic number ranging from 4 to 92 [10]. Prior to the SEM experiment, a small amount of powder, typically 100 mg, was suspended in acetone in an ultrasonic bath and then, using a micropipette, few drops of the mixture were dropped on the sample holder and left to evaporate the acetone. The sample was then coated with an ultrathin layer of electronically-conducting material to eliminate electrostatic charges upon scanning. For EDX analysis, the zeolite powder was scattered over a carbon tape and pressed lightly. The sample holder was then coated with an ultrathin layer of gold by a sputtering coater under vacuum to eliminate electrostatic charges when scanned. Figure 2-14 shows an example of an SEM image of zeolite Y along with its EDX spectrum while Figure 2-15 shows SEM images of MCM-41 at different magnifications.
2.3.3 Pyridine Adsorption-Fourier Transform Infrared (Py-FTIR)

Fourier transform infrared (FTIR) spectroscopy was used to characterise the acidic sites of the catalysts. The IR spectra were recorded before and after the adsorption of the base (Pyridine). The changes in the IR bands can be used to investigate the effect of the catalyst modification on the acidic properties. Figure 2-16 shows the FTIR spectra of zeolite Y(30) in the region of 3800-3400 cm\(^{-1}\) before and after the pyridine adsorption.

The band located at 3743 cm\(^{-1}\) was attributed to the terminal silanol groups (Si-O-H) while the bands located at 3624 and 3564 cm\(^{-1}\) were attributed to bridging-OH groups (Si-OH-Al).
inside large cavities and small cavities of zeolite Y respectively [11-14]. The acidic bridging-OH groups disappeared after the base adsorption while the non-acidic Si-O-H remained.

Pyridine adsorption experiments can also determine the Brønsted and Lewis acidity of the catalyst. Pyridine interacts with both sites to generate IR bands located at 1545 and 1455 cm\(^{-1}\) which are attributed to Bronsted and Lewis acid sites respectively [15-17]. Figure 2-17 shows the spectra collected after pyridine adsorption on zeolite Y(30).

![FTIR spectrum of zeolite Y(30)](image)

Figure 2-17: FTIR spectrum of zeolite Y(30) in the region of 1400-1600 cm\(^{-1}\) after pyridine adsorption and desorption at 150 °C

To conduct the experiments, approximately 10 mg of the sample was pressed into self-supporting discs using a hydraulic press. The discs were then placed into an in-situ infra-red cell (Figure 2-18) and heated to 450 °C at a rate of 1°C/min under vacuum (1.33 x 10\(^{-3}\) MPa) for 6 hours to remove moisture. The samples were then cooled to 150 °C and held for 30 minutes. An excess of pyridine (~1-2 µl) was then injected into the cell using a syringe and the spectra was monitored until no changes were observed. The cell was evacuated for 20 minutes to remove physically adsorbed pyridine. The spectra were recorded using a Nicolet Protege 460 or Thermo iS10 spectrometer at 2 or 4 cm\(^{-1}\) resolution. The spectra were analysed and presented (including integration and determination of peak positions) using specialised Nicolet software Omnic and Origin. Accuracy of the maximum positions is estimated to be ±1 cm\(^{-1}\) for \(v_{0-\rightarrow 1}\) lines. Pyridine adsorption/desorption experiments were kindly carried out in cooperation with Dr. Vladimir Zholobenko at Keele University.
2.3.4 BET Surface Area and Pore Volume Measurements

The surface area of the catalyst along with the pore volume, pore size and pore size distribution contributes towards its catalytic activity. The physical adsorption (physisorption) of nitrogen is a method widely used to study the catalyst porosity [19].

The surface area of the materials used in this work was determined via nitrogen adsorption analysis using the Brunauer, Emmett and Teller (BET) technique. Nitrogen (N\textsubscript{2}) gas was used as a probe molecule for adsorption on the zeolite sample [20]. The BET surface area of the zeolite sample was calculated using equation (2-7):

\[
\frac{P / P_0}{V\alpha (1 - P / P_0)} = \frac{P}{V\alpha(P_0 - P)} = \frac{1}{V_m \times C} + \left[ \frac{C - 1}{V_m \times C} \right] \times P / P_0
\]  

(2-7)

where \(P\): Vapour pressure, \(P_0\): Saturated pressure of adsorbate, \(V\alpha\): Volume of gas adsorbed at the equilibrium adsorbate pressure and the temperature of adsorption (-196.15 °C for nitrogen), \(V_m\): Volume of adsorbed gas in the monolayer (cm\textsuperscript{3}/g) and C: BET constant, representing the interaction between the adsorbent (solid) and adsorbate (gas).

The monolayer volume \((V_m)\) and the BET constant (C) can be calculated by plotting \(\frac{P}{V_m(P_0 - P)}\) against \(P / P_0\) which gives a linear plot where the slope is \(\frac{C - 1}{V_m \times C}\) and the intercept is \(\frac{1}{V_m \times C}\). The surface area \((S_A)\) can be then obtained using equation (2-8):

\[
S_A = V_m \times N \times \sigma
\]  

(2-8)
where \( N \) is Avogadro’s number and \( \sigma \) is the average area occupied by every molecule in the entire monolayer \((16.2 \times 10^{-20} \text{ m}^2 \text{ for } \text{N}_2)\).

The adsorption isotherms vary amongst different materials. The majority of the isotherms can be classified into five categories (type I to V) \([21]\). Zeolites used in this work exhibit Type I, II, and III isotherms since the filling of the micro-pores occurs at considerably low partial pressures and the adsorption process being mostly complete at \( P/P_0 \sim 0.5 \) \([22, 23]\).

The BET surface area and pore volume was determined using a Micromeritics Gemini 2365 surface area analyser. Approximately 0.2 g of the sample powder was loaded into a bulb-ended tube, and then degassed for 18h at >100 °C to remove contaminants and moisture under a constant flow of He using a Micromeritics Flowprep 060. Afterwards, samples were adsorbed at -196 °C. Sample vials were finally weighed, and the mass of the empty vial was subtracted to give the mass of the purged samples within. The BET plot for zeolite Beta (12.5) is shown in Figure 2-19. BET experiments were kindly conducted with Dr. John Waters in the School of Earth and Environmental Sciences at the University of Manchester. Unfortunately, the Micromeritics Gemini 2365 surface area analyser did not record desorption isotherms and hence the pore size distribution was not obtained.

![BET plot for zeolite Beta (12.5)](image)

**Figure 2-19: BET plot for zeolite Beta (12.5)**

### 2.3.5 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used to determine the chemical composition of solid aluminosilicates. The technique can also detect trace elements and metals in the zeolite \([24]\). The technique
involves the digestion of 10 mg of the zeolite sample in a concentrated solution of hydrofluoric and nitric acids. The digested sample was then analysed using a Varian Vista MPX ICP-OES. The estimated error was ±0.3 wt. % for aluminium and silicon and ±10 ppm for metals. The ICP-OES analysis was conducted by MEDAC LTD since the use of concentrated hydrofluoric acid was restricted in CEAS.

2.4 Conclusions
The experimental methods used to conduct the catalytic testing along with the catalyst characterization techniques used in this work were presented. Repeating the catalytic experiment using the same protocols showed that the experiments were reproducible with negligible variances. The characterization techniques along with their key features used in this work are summarized in Table 2-4.

<table>
<thead>
<tr>
<th>Characterisation Technique</th>
<th>Key Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>Crystal structure and phase purity</td>
</tr>
<tr>
<td>Electron microscopy (e.g. SEM, EDX)</td>
<td>Morphology, structure and elemental analysis</td>
</tr>
<tr>
<td>Infrared spectroscopy (IR)</td>
<td>Functional groups (silanol, bridgin-OH), acidity</td>
</tr>
<tr>
<td></td>
<td>(Bronsted, Lewis) and acid strength</td>
</tr>
<tr>
<td>BET surface area</td>
<td>Surface area, pore volume</td>
</tr>
<tr>
<td>Inductively coupled plasma optical emission</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>spectrometry (ICP-OES)</td>
<td></td>
</tr>
</tbody>
</table>

2.5 References


3. Reactor Optimisation and the Effect of Zeolite Structure on the Alkylation Activity
3.1 Introduction

The reaction of isobutane with butene over zeolite-based catalysts was broadly studied in the literature. Initially, the reaction of isobutane with butenes was conducted by using liquid acid catalysts. Ipatieff and Grosse used boron fluoride (BF₃) as a catalyst for the reaction of isobutane with light olefins. The reaction was carried in a glass-lined batch rotating autoclave at a temperature of 10-50 °C and 5-20 atm. of pressure. Figure 3-1 below shows the reported experimental setup [1]

![Figure 3-1: The Ipatieff and Grosse experiment, adopted from [1]](image)

3.1.1 Effect of the Reactor Type

In the alkylation reaction of 2-butene with isobutane, the localised olefin concentration must be minimised to reduce the oligomerisation and extend the catalyst lifetime. This can either be done by using excessively high P/O ratios (i.e. between 100 – 1000) or by improving the mixing patterns inside the reactor. As shown earlier, liquid-acid alkylation technologies utilise intricate reactor designs to ensure the mixing of the feed and the catalyst to promote the formation of TMPs. Although not economically favoured, CSTR-type reactors are preferred in the commercial alkylation processes. Solid acids, and particularly zeolites, suffer from rapid catalyst deactivation due to the oligomerisation of butenes that produces bulky molecules that block the catalyst pores.

The reaction of isobutane with butene over zeolite-based catalysts has been extensively examined in the literature. Various reactor configurations, feedstock options and experimental protocols were examined. Variations in terms of product quality and useful catalyst lifetime were observed and can be attributed to the variations in the experimental
setup. Packed bed reactors usually suffer from rapid catalyst deactivation. The deactivation occurs once the oligomerisation takes place on the first layer of catalysts in the packed bed. The catalyst in the first layer deactivates which lowers the butene conversion around it. The high butene concentration around the adjacent layer then promotes oligomerisation in that layer. The process continues rapidly across the catalyst bed until the entire bed is deactivated [2]. Typical catalyst lifetimes in a packed-bed reactor are between 10 and 100 minutes depending on the olefin space velocity and the paraffin/olefin ratio of the feed.

CSTR reactors were used to overcome the rapid deactivation in tubular reactors. de Jong et al. were able to extend the catalyst lifetime significantly, up to 20 hours, in a slurry-type autoclave reactor. The improved mixing of the catalyst and the feed reduced the olefin concentration around the catalyst and reduced the oligomerisation leading to a significant improvement in the catalyst lifetime. However, the cited authors used a semi-batch protocol to conduct the experiments [3]. Various CSTR reactors have been used in the literature. For instance, slurry type reactors were used by de Jong and initially, the Lercher group [4-8]. The use of slurry reactors can lead to catalyst attrition which could perhaps lead to the catalyst escaping the reactor with the product effluent thus affecting the space-velocity of the reaction, especially in long time on stream operations. Additionally, the non-uniformity of the catalyst's particle size due to the attrition from the impeller blades can lead to variations in the intra-particle diffusion behaviour of the products which can impact the understanding of the reaction trajectories and outcome. Also, the suspension of the catalyst must be ensured to assume true, gradient-free CSTR behaviour.

Gradientless reactors were introduced to overcome the issues associated with slurry reactors. A variety of gradient-less reactors were developed such as Robinson-Mahoney, Carberry, Harshaw and Berty reactors. Taylor and Sherwood used a stationary Berty reactor in continuous operation to study the alkylation of 2-butene with isobutane over zeolite USY. The authors were able to extend the catalyst lifetime for more than 20 hours [9].

The reactor and system setup used in this dissertation was based on the Taylor-Sherwood setup due to the similarity of the vessel size. A 300 mL Parr autoclave was transformed to a top-driven stationary Berty reactor by using a manufacturer-designed catalyst basket and impeller setup. The volume of the empty basket was 40 mL. The use of a catalyst basket in such a reactor ensured that the catalyst was not affected by the impeller blades and enabled the catalyst to be fully preserved. Zeolite Beta with a Si/Al ratio of 12.5 was selected to optimise the reactor used in this work.
3.1.2 Effect of the Zeolite Structure

The industrial applications of zeolites vary from the petroleum refining and petrochemical industries to the production of intermediate and fine chemicals. The wide-range of zeolite structures and pore dimensions enables tailoring the zeolite catalyst to a specific reaction based on the shape of the pore system and the concentration of active sites inside the system [10, 11]. Unfortunately, the pore structure and catalytic site densities are not mutually exclusive. Furthermore, minute differences in the nature of the acidic site can significantly alter the catalyst lifetime and product selectivity during the alkylation reaction as reported by Guzman et al. [12]. Comparing different zeolite structures with varying acidity profiles has created a few discrepancies in the literature data. Furthermore, using different reactor types in literature also contributes to the state of ambiguity of some results reported by different research groups. In general, only large-pore zeolites exhibit significant activity regarding the alkylation reaction while medium and small pore zeolites usually catalyse oligomerisation and cracking.

Medium and intermediate pore zeolites were found to be inactive under typical alkylation conditions. Weitkamp and Jacobs studied the alkylation of 2-butene with isobutane over medium pore zeolites ZSM-5 and ZSM-11. However, the pentasil-type zeolites exhibited significant activity only at elevated temperatures, above 150 °C. The products however were mostly methylheptanes and no TMPs were observed in the product stream [13]. Corma et al. compared MCM-22 and ZSM-5, both medium-pore zeolites, with USY, Beta and MOR. Large-pore USY, Beta and MOR had significantly higher TMP selectivity while the MCM-22 and the ZSM-5 had lower TMP content with the MCM-22 producing slightly higher TMPs than the ZSM-5. The improved activity of MCM-22 when compared to ZSM-5 was attributed in the cited work to the higher acidity of MCM-22. Within the large pore zeolites, zeolite Beta showed the highest catalytic lifetime followed by USY while MOR deactivated rapidly due to its single-channel system. The difference in lifetimes between Beta and USY was attributed to the differences in the acidities of the zeolites with zeolite Beta having higher number of Brensted acid sites [14]. Chu and Chester compared ZSM-5, a medium-pore zeolite, with a variety of Y zeolites. ZSM-5 was found to be inactive for the alkylation process since it did not produce significant alkylates unlike zeolite Y that produced significantly higher alkylates. Furthermore, mixing ZSM-5 with the Y zeolite did not improve the alkylation activity of zeolite Y [15].

The high C8 selectivity and high TMP/C8 ratios produced from the alkylation over large-pore zeolites is very similar to a typical alkylate produced in the liquid acid processes. The acidity of large pore zeolites seems to have the largest influence on the product quality and catalyst lifetime. Nivarthy et al. compared the alkylation activity and catalytic stability of three large-pore zeolites; namely Beta, Y, and EMT and the authors indicated that the catalyst lifetime
was directly associated with the concentration of the Brønsted sites in the zeolite. The high concentration of Brønsted acid sites in the EMT zeolite led to improved lifetimes. Zeolite Beta, which had the lowest number of Brønsted acid sites, had the lowest lifetime [16]. Mota Salinas et al. compared the performance of Beta and USY in supercritical isobutane conditions. Zeolite Beta, which lacked channel expansion, outperformed USY in terms of selectivity to C\textsubscript{8}s and catalyst lifetime. The authors attributed the improved lifetime of zeolite Beta to its lack of channel expansion which prevented the formation of large molecules [16]. Yoo et al. studied the effect of the pore structures of zeolites USY, Beta, ZSM-12, MOR and LTL-20 with varying Si/Al ratios. ZSM-12, MOR, and Beta were shown to outperform the other zeolites in terms of catalyst lifetime and selectivity. The authors concluded that the uniform nature of the channels in zeolites Beta, MOR and ZSM-12, which lacks a significant channel expansion, prevented the formation of large carbonaceous molecules; whereas in zeolites USY and LTL-22, the large channel expansions led to the formation of the bulky molecules that led to faster deactivation. The authors concluded that the channel homogeneousness is the most important factor in the zeolite’s alkylation activity and selectivity [18]. This finding was in contrast to the aforementioned study by Corma et al [14].

The contradictory nature of some literature data arises from the differences in the acidity profiles of the tested catalysts, variation in the experimental protocols, differences in the reaction conditions and the varying reactor types used in the catalytic experiments. The following section will also explore the effect of the zeolite structure on the alkylation performance using a CSTR-like reactor and optimal reaction conditions.

3.2 Experimental

3.2.1 Catalyst Selection and Preparation

Zeolite Beta (12.5) was used in the catalytic reactor optimisation study. The effect of the zeolite’s structure was studied by selecting three large-pore zeolites based on their dimensionality and total acidity. Zeolites Beta and Y have a 3-dimensional structure with zeolite Beta lacking channel expansions while zeolite MOR is a one-dimensional zeolite without channel expansions. The Si/Al ratio of the zeolites was selected to provide a relatively close acidity value. The major properties of the selected zeolites are presented in Table 3-1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Channel Dimension</th>
<th>Si/Al</th>
<th>Channel Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta (12.5)</td>
<td>3-D</td>
<td>12.5</td>
<td>N</td>
</tr>
<tr>
<td>Y (6)</td>
<td>3-D</td>
<td>6</td>
<td>Y</td>
</tr>
<tr>
<td>MOR (10)</td>
<td>1-D</td>
<td>10</td>
<td>N</td>
</tr>
</tbody>
</table>
The zeolites were transformed into the protonic form by calcination in a muffle furnace at 450 °C for 6 hours. The zeolites were then pressed once and sieved to a particle size of ~ 3 mm and placed inside the catalyst basket. The catalysts were subsequently dried in-situ under flowing nitrogen (150 mL/min) at 200 °C for 16 hours to remove moisture.

3.3 Results and Discussion

3.3.1 Catalyst Characterisation

The physical properties of the three tested zeolites are presented in Table 3-2. The Si/Al ratio of the catalysts was shown to be in good agreement with the values quoted by the manufacturer. The surface area of the zeolite decreased in the order of Y (6) > Beta (12.5) > MOR (10) whilst the pore volume decreased in the order of Y (6) > MOR (10) > Beta (12.5).

Table 3-2: Physical properties of the zeolites used in this study

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Reported Si/Al</th>
<th>Si/Al (ICP-OES)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta (12.5)</td>
<td>12.5</td>
<td>12.6</td>
<td>534</td>
<td>0.18</td>
</tr>
<tr>
<td>Y (6)</td>
<td>6</td>
<td>6.7</td>
<td>571</td>
<td>0.25</td>
</tr>
<tr>
<td>MOR (10)</td>
<td>10</td>
<td>12</td>
<td>459</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The zeolite aggregate size was measured by SEM (Figure 3-2). The aggregate size for Beta (12.5) was about 0.2-0.4 μm, 0.5-1.0 μm for Y (6) and 0.25-1.0 μm for MOR (10).

Figure 3-2: SEM images of zeolites Beta (a), Y (b) and MOR (c)

The XRD results were also in good agreement with the XRD patterns of the zeolites documented in the literature. Figure 3-3 shows the XRD pattern of the three zeolites.
The acidity of the catalysts was measured by Pyridine-FTIR. Figure 3-4 shows the spectra recorded after the pyridine desorption at 150 °C. The peak intensity at 1545 cm\(^{-1}\) was attributed to the Brønsted acid sites while the peak intensity at 1455 cm\(^{-1}\) was attributed to Lewis acid sites. The summary of the acidity measurements is provided in Table 3-3.

All the tested zeolites had relatively similar acidity; MOR had the highest overall acidity. The Brønsted acidity decreased in the order of MOR > Beta > Y while the Lewis acidity decreased in the order of Y > Beta > MOR.
Table 3- 3: Acidity measurements for the tested catalysts

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Py-B (mmol/g)</th>
<th>Py-L (mmol/g)</th>
<th>B/L</th>
<th>B+L (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta (12.5)</td>
<td>0.43</td>
<td>0.42</td>
<td>1.02</td>
<td>0.85</td>
</tr>
<tr>
<td>Y (6)</td>
<td>0.37</td>
<td>0.56</td>
<td>0.66</td>
<td>0.93</td>
</tr>
<tr>
<td>MOR (10)</td>
<td>0.98</td>
<td>0.17</td>
<td>5.76</td>
<td>1.15</td>
</tr>
</tbody>
</table>

3.3.2 Catalytic Results

3.3.2.1 Unit Optimisation

3.3.2.1.1 Effect of Agitation Speed

Higher mixing correlates directly with improved catalyst lifetime and product quality due the improved dispersion of olefins. Rørvik et al. compared the performance of Ce-Y, H-EMT and H-Y in a semi-batch 300 mL autoclave. The authors noted that increasing the agitation speed to 1200 rpm greatly improved the product distribution and improved the alkylate selectivity [19]. Taylor and Sherwood conducted the alkylation experiments on H-USY in a 300mL stationary-Berty autoclave with a bottom-driven impeller operated at 1250 rpm [9]. In the aforementioned work by de Jong et al. on the alkylation activity of zeolites Beta and Y in a slurry autoclave reactor (250 mL), the authors noted that an agitation speed of 1000 rpm was not enough for catalyst suspension [3].

The initial impeller setup used by the author of this dissertation had a maximum rotation of 600 rpm. A new pulley set was installed to increase the rotation speed to 1200 rpm. The effect of the agitation on the butene conversion is shown in Figure 3-5.

![Figure 3-5: Effect of agitator speed on the alkylation stability of zeolite Beta (12.5), 40 mL catalyst basket & with feed dip-tube](image-url)
Despite the initial high conversion, the catalyst deactivated rapidly when the impeller was at 600 rpm. When the impeller was at 1200 rpm, the variation in conversion levels were significant starting from the first hour on-stream. Moreover, the catalyst deactivation occurred more rapidly at lower agitation speeds with the conversion at 4 hours dropping below 80%. By contrast, operating at higher agitation speeds reduced the conversion at 4 hours by ~ 6%. The results demonstrate the need for high agitation rates to minimise the olefin concentration around the catalyst pellets and hence extend the catalyst lifetime.

3.3.2.1.2 Effect of Catalyst Loading

Catalysts weights used to fill the catalyst basket varied with the catalyst density. For example, zeolite Beta (12.5) required ~16 g to fill the entire basket while zeolite Y (6) required ~20 g. The amount of catalyst placed inside the basket also affected the performance of the reactor. Taylor and Sherwood compared the catalyst loading effect on the performance of USY zeolites in a 300 mL stationary Berty reactor. While maintaining similar olefin space velocities, temperature and P/O ratios, the cited authors compared the effect of three loading values: 10 g, 20 g and 30 g on the conversion of 2-butene. Altering the amount from 30 g to 20 g had little effect on the butene conversion whereas the catalytic stability was significantly affected when the catalyst weight was reduced to 10 g (Figure 3-6). The cited authors concluded that lowering the catalyst loading led to higher unreacted olefin concentration which in turn produced more oligomerisation products and thus caused further deactivation [9].

![Figure 3-6: Effect of catalyst loading on the conversion of 2-butene (adapted from[9])](image-url)
To study the effect of catalyst loading, the catalyst loading was varied at three levels, 16.1 g (100 vol. %), 12.8 g (~80 vol. %) and 6.4 g (~40 vol. %) while maintaining a constant OSV of 0.30 h\(^{-1}\). The results are presented in Figure 3-7.

![figure 3-7](image)

**Figure 3-7**: Effect of catalyst loading on the alkylation stability of zeolite Beta (12.5), 1200 rpm agitation and with feed dip tube.

The results indicated that reducing the catalyst amount significantly altered the catalytic stability. Reducing the amount from 100 vol% to 40 vol% reduced the olefin conversion at 4 hours by more than 10% while at 80 vol%, the conversion dropped by about 3%. Moreover, repeating the 40 vol% experiment by mixing the same amount of zeolite with an inert (glass beads) to fill the remaining volume did not improve the results. This indicated that due to the design of the catalyst basket, the entire volume must be filled with active catalyst pellets.

Reducing the catalyst amount significantly affected the mixing patterns inside the reactor which led to faster deactivation.

### 3.3.2.1.3 Feed Entry Location

Another factor that was considered to improve the mixing inside the reactor is the use of a dip-tube to disperse the feed. The only reported use of a dip-tube was by Mostad et al. who studied the alkylation of 2-butene over H-SAPO-37 and H-Y in a 250 mL semi-batch slurry autoclave and a dip-tube was used to remove the liquid products from the reactor [20]. Initially, the entry and exit points of the reactor used in this dissertation were at the same height which could have led to the feed bypassing the catalyst. A 5 cm long by 1/8” wide stainless steel dip tube was installed to introduce the feed. Figure 3-8 shows the improved catalytic performance.
Despite being minor, it was evident that the use of a dip-tube to disperse the feed helped to reduce the feed bypassing and improved the mixing patterns and that led to improved catalytic stability.

3.3.2.2 Effect of the Zeolite Structure

3.3.2.2.1 Initial Catalytic Behaviour
The initial 2-butene conversion and product distribution were compared in Table 3-4. Although all the studied zeolites showed high initial butene conversion ($X \approx 90\%$), the selectivity towards the primary alkylate product ($C_8$) was clearly dependent on the zeolite structure. Zeolites Y and Beta showed the highest $C_8$ selectivity compared to Mordenite that showed much lower selectivity to the primary alkylates. It is therefore noted that even at high conversion; a three-dimensional channel system was required for the production of the $C_8$s. Moreover, the oligomerisation products ($C_{12+}$) were the highest in Mordenite while zeolites Beta and Y produced much lower amounts of oligomerisation products. The lack of large-intersecting channels in Mordenite means that once the oligomerisation occurred, the entire channel was effectively blocked which decreased the conversion.
Table 3-4: Initial product distribution at t = 1 h

<table>
<thead>
<tr>
<th>Initial Alkylation Activity</th>
<th>Catalyst Beta (12.5)</th>
<th>Catalyst Y(6)</th>
<th>Catalyst MOR (10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>100</td>
<td>95.64</td>
<td>89.98</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>3.6</td>
<td>3.79</td>
<td>0.94</td>
</tr>
<tr>
<td>C₈</td>
<td>53.11</td>
<td>53.64</td>
<td>30.33</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>29.44</td>
<td>32.96</td>
<td>35.44</td>
</tr>
<tr>
<td>C₁₂+</td>
<td>13.85</td>
<td>9.61</td>
<td>33.29</td>
</tr>
<tr>
<td>Composition of C₈ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>77.11</td>
<td>79.04</td>
<td>68.15</td>
</tr>
<tr>
<td>DMHs</td>
<td>19.87</td>
<td>16.02</td>
<td>13.52</td>
</tr>
<tr>
<td>MHs</td>
<td>3.02</td>
<td>4.04</td>
<td>13.73</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>46.74</td>
<td>29.24</td>
<td>33.25</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.45</td>
<td>9.6</td>
<td>5.32</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>27.1</td>
<td>29.18</td>
<td>44.5</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>13.71</td>
<td>31.98</td>
<td>16.93</td>
</tr>
</tbody>
</table>

Within the C₈ fraction, Mordenite showed the highest selectivity to the methylheptanes indicating that, due to steric limitations, the C₈ alkyl-cation underwent isomerisation to the smaller methylheptanes and the thermodynamically favoured dimethylhexanes in order to desorb from the zeolite pores. Figure 3-9 shows the accessibility of different C₈ isomers in the channels of zeolites Beta and Mordenite highlighting the steric hindrance facing highly branched molecules in Mordenite.

![Figure 3-9: Channels in MOR (1) and Beta (2) accessible to n-C₈ (a), 2,5 DMH (b) and 2,2,4 TMP (c), adopted from [21]](image)

Moreover, the TMP distribution varied significantly across the examined zeolites. Zeolite Beta and Y showed higher content of the primary product of the alkylation reaction (2,2,3 TMP) indicating higher hydride transfer rates [16] while in Mordenite, the low content of this
isomer indicated that the hydride transfer step was slower which forced the 2,2,3 alkyl-cation to isomerise mostly to the 2,3,4 TMP, which has the smallest kinetic diameter amongst the TMPs [18] in order to desorb from the zeolite pores.

3.3.2.2 Catalytic Stability

The catalytic stability results are presented in Figure 3-10. All the catalysts lose their activity as the reaction time progressed. The deactivation occurred more rapidly in Mordenite followed by Y while zeolite Beta showed the highest catalytic stability.

![Figure 3-10: Effect of the zeolite structure on the catalytic stability during the alkylation reaction](image)

Zeolite Beta with its uniform three-dimensional pore structure showed higher activity and catalytic stability while zeolite Y, due the presence of large super-cages and the high Lewis acidity deactivated more rapidly. Mordenite, despite it having the highest concentration of Brønsted acid sites and its uniform channel system which lacks channel expansion, displayed the highest deactivation behaviour amongst the tested zeolites.

The deactivation behaviour is inherently tied to the product distribution. The formation of large molecules inside the zeolite pores led to pore-blockage which was the main cause of deactivation. Moreover, as the deactivation occurred, the olefin concentration increased inside the catalyst pores promoting further oligomerisation instead of hydride transfer. The C₈ selectivity suffered as a result of the deactivation of the catalyst. As the catalyst deactivated, the C₈ selectivity dropped. Thus, maintaining high conversion levels is essential for the C₈ selectivity. Figure 3-11 shows how the C₈ selectivity degrades with time.
Zeolites Beta and Y showed the highest C₈ selectivity due to the high conversion levels which kept the olefin concentration low and thus delayed the oligomerisation. Mordenite produced less C₈ due to its low conversion levels.

The distribution of the TMPs also varied with time. Although the primary product of the reaction of 2-butene with isobutane should be the 2,2,3 TMP, the production of other TMPs indicated that the C₈ alkyl-cation must have undergone isomerisation based on both the thermodynamic and steric conditions of the reaction as shown in Figure 3-12.

Zeolite Beta showed a TMP distribution where the thermodynamically favoured 2,2,4 TMP predominated. Here, the value of the 2,2,4 TMP was very close to the thermodynamic value which, coupled with the relatively high 2,2,3 TMP concentration level indicated that in zeolite Beta, the C₈ alkyl-cation faced the least steric hindrance amongst the tested zeolites. The stable time-on-stream behaviour of the TMP distribution indicated that the zeolite’s pore structure was not affected by the build-up of hydrocarbons inside the pores. The decreasing value of the total TMP fraction indicated that the deactivation probably caused entire set of channels to be effectively blocked. As the number of channels available for the alkylation reaction decreased, the conversion, and the TMP selectivity also decreased.

In zeolite Y, the observed differences in the TMP distribution were attributed to the narrowing of the zeolite’s super cage. The build-up of larger molecules inside the super cage caused the 2,2,3 TMP alkyl-cation to isomerise either to the smaller 2,3,4 TMP or to the 2,3,3 TMP, which has a smaller transition-state intermediate [18]. The isomerisation seemed to favour the 2,3,3 TMP as its concentration increased with time. This was indicative of the
variation in the zeolite pore systems with time due to the build-up of large hydrocarbons inside the supercages as that forced the 2,2,3 TMP alkyl-cation to isomerise to the 2,3,3 TMP due to low steric conditions.

The TMP distribution in Mordenite showed that the production of the smallest TMP, the 2,3,4 TMP was favoured. The high production rate of the 2,3,4 TMP, despite it having the lowest thermodynamic value amongst the TMPs, indicated that the C₈ alkyl-cation faced significant steric hindrance and therefore must have undergone isomerisation from 2,2,3 TMP⁺ to produce the smaller 2,3,4 TMP.

The content of 2,2,3 TMP, the primary product of the alkylation reaction, in Mordenite was the lowest amongst the tested zeolites which indicated that due to its low conversion levels, Mordenite seems to have the lowest hydride transfer activity. High 2,2,3 TMP content is indicative of high hydride transfer rates as was in the case of the three-dimensional zeolites Y and Beta despite the fact that Mordenite had the highest number of Bronsted acid sites and the highest B/L ratio.

The oligomerised and cracked products can be split into two main fractions; namely the C₅⁻C₇/C₉⁻C₁₂ fractions, that are typically included in the gasoline pool and the C₁₂⁺ fraction which cannot be included in the gasoline pool and is the main cause of the catalyst
deactivation. Cracking and oligomerisation are inherently tied. The C$_8$ alkyl-cation could react with an olefin instead of a paraffin, especially under low conversion conditions, leading to the formation of a C$_{12+}$ alkyl cation which can further react to form a C$_{16+}$, C$_{20+}$, ... etc. alkyl-cations. These larger alkyl-cations then underwent hydride transfer to produce a large iso-paraffin that might desorb from the catalyst pores or be cracked to produce smaller compounds. The larger molecules were easily cracked due to the high acidity of the zeolites used in this work. The cracked fraction is shown in Figure 3-13.

![Figure 3-13: Cracking selectivity (C$_{5-7}$ + C$_{9-12}$)](image)

In zeolites Beta and Y, the cracked products selectivity increased with time. This increase was tied to the deactivation. As the conversion dropped, the formation of large molecules increased which were then cracked due to the acidity of the zeolite. Mordenite however reached a maximum cracking capacity at 4 hours and subsequently started to decrease indicating that the strong acidic sites of the catalyst were deactivated and only weaker acid-sites remained.

As aforementioned, the formation of the C$_{12+}$ fraction inside the zeolite pores leads to the deactivation of the catalyst. Figure 3-14 shows the C$_{12+}$ selectivity of the tested zeolites. For all the zeolites tested in this work, the production of oligomerised products increased with time due to the deactivation of the catalyst. Low conversion levels led to an increase in the olefin concentration which in turn promoted oligomerisation instead of hydride transfer. Mordenite produced higher oligomerisation products which indicated that due to the blockage of its single-channels, the reaction occurred mostly on the outer surface of the zeolite.
Zeolites Y and Beta also followed this trend albeit being at lower values. The availability of side channels in zeolites Y and Beta meant that once a large molecule was produced, the availability of large-side channels helped to remove such molecules from the zeolite's system and the alkylation activity remained in the channel. In Mordenite, the lack of large intersecting side–channels prevented the bulky molecules from escaping the zeolite and such molecules blocked the entire channel.

![Figure 3-14: Effect of the zeolite structure on the C_{12}+ selectivity](image)

3.4 Conclusions

Development and optimisation of a continuous catalytic rig based on a stationary Berty reactor was completed. The catalytic experiments were based on the Taylor and Sherwood setup due to the similarity in the size of the autoclave. High impeller speeds were shown to significantly improve the catalytic stability of zeolite Beta. The catalyst loading was also shown to affect the mixing patterns inside the reactor with low loadings leading to higher catalyst deactivation. The use of a dip-tube for feed entry was demonstrated to slightly improve the catalytic stability of the catalyst at hand.

The effect of the zeolite structure on the alkylation activity was also examined. Three-dimensional, large-pore zeolites were shown to be active for the alkylation reaction while the one-dimensional Mordenite was shown to be less active due to the lack of intersecting side-channels. The three-dimensional nature of zeolites Beta and Y allowed the large molecules, once formed, to desorb from the catalyst instead of blocking the pores although the deactivation seemed to increase with time. Zeolites Beta and Y will be further investigated in the next chapters while Mordenite was excluded from further investigation.
3.5 References


4. The Effect of Si/Al and Lanthanum Loading on the Alkylation Activity of Zeolite Beta
4.1 Introduction

Three dimensional large-pore zeolites were shown to be active for the alkylation reaction with a product distribution similar to liquid acid processes. Zeolite Beta, a 12 member-ring three-dimensional zeolite has been explored in literature as an alkylation catalyst due to its high acidity and its three-dimensional nature which allows large molecules to desorb from the zeolite pores without causing blockages. The zeolite, first discovered in 1967 by Mobil [1], has been extensively used in the petrochemical industry [2]. Figure 4-1 shows the pore structure of zeolite Beta.

![Figure 4-1: The pore structure of zeolite Beta, adopted from [3]](image)

The Si/Al ratio of zeolite Beta plays a major role in its alkylation activity. Corma et al. dealuminated zeolite Beta with a starting Si/Al ratio of 12 utilising various dealumination techniques. The cited authors concluded that dealuminating zeolite Beta did not improve the results. Acid leaching decreased the acidity of the catalyst and generated extraframework aluminium which decreased the catalyst lifetime. The mildly acid-leached zeolites had better activity and selectivity than their severely acid-leached and steamed counterparts; both however were inferior to the original zeolite [4]. Yoo and Smirniotis synthesised zeolite Beta with a variety of Si/Al ratios; namely; 6, 8.5, 15 and 30 and the optimum Si/Al ratio was reported to be between 8.5 - 15. The higher Si/Al ratio Beta zeolites performed worse due to the lack of acidity which decreased the catalyst lifetime and selectivity. The low Si/Al ratio Beta zeolite (Si/Al = 6) suffered from low crystallinity, about 85%, which could have contributed to the formation of Lewis acid sites during calcination hence decreasing the activity and selectivity. Moreover, the lower Si/Al zeolite had lower pore volume which also contributed to its inferior performance [5].

The acidity of zeolite Beta seems to play the major role in its alkylation activity. Nivarthy et al. back-exchanged zeolite H-Beta (Si/Al ratio = 15) with sodium to examine the effect on
acidity. Increasing the sodium content significantly decreased the acidity of the zeolite as sodium ions selectively poisoned the Brønsted acid sites. Moreover, sodium acted as a weak Lewis site which also increased the adsorption of the olefins inside the pores. Therefore, increasing the sodium exchange decreased the total acidity of the catalyst and the B/L ratio. The cited authors concluded that in zeolite Beta, maximising the Brønsted acidity was essential for the alkylation reaction and sodium ions were detrimental to the catalyst’s activity due to the selective poisoning of the Brønsted acid sites [6]. Another study by the same cited group examined the effect of the operating parameters on the alkylation activity of zeolite Beta with a Si/Al ratio of 15. The catalyst turnover was shown to be independent of the olefin space velocity. A certain number of acid sites were available for the reaction and increasing the olefin space velocity (OSV) reduced the catalyst lifetime while reducing the OSV increased the lifetime. However, the catalyst turnover always remained constant [7]. Loenders et al. examined the effect of zeolite Beta’s Si/Al ratio between 10 and 75 and the authors concluded that the catalyst turnover was only a function of the Brønsted acid sites [8].

Metal ion-exchange of zeolite Beta was also reported in literature. Dall-Costa and Querini studied lanthanum-exchanged zeolite Beta with a Si/Al of 15. The authors performed the reaction in a tubular reactor. The authors concluded that the lanthanum-exchanged Beta zeolites were active for the alkylation reaction. Unfortunately, the cited authors only performed pyridine-TPD experiments to measure the catalyst acidity and thus no information can be inferred about the nature of the acidic sites created by the lanthanum ions, the total acidity however decreased slightly with the introduction of lanthanum [9]. Mostad et al. compared lanthanum exchanged zeolites Y, Beta and EMT. The lanthanum exchanged EMT had a higher conversion and C₈ selectivity. Unfortunately, no information was provided about the acidity of the lanthanum exchanged Beta zeolite. Furthermore, the ion-exchange degree was different between the tested zeolites which could have also influence the acidity [10].

Examining the effect of Si/Al and lanthanum loading on the alkylation activity of zeolite Beta in a continuous CSTR under optimum reaction conditions can provide better insight on the effect of such variables on the catalytic activity and selectivity.

4.2 Experimental

4.2.1 Materials
Zeolite Beta with varying Si/Al ratios, between 12.5 and 150, was supplied by the vendors listed in Table 4-1. Lanthanum was supplied by Sigma Aldrich as Lanthanum (III) nitrate hexahydrate.
Table 4-1: Parent zeolite materials (as supplied by manufacturer)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product Number</th>
<th>Reported Si/Al</th>
<th>Form</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta 12.5</td>
<td>CP814E</td>
<td>12.5</td>
<td>Ammonium</td>
<td>Zeolyst Int.</td>
</tr>
<tr>
<td>Beta 75</td>
<td>MSZB0202</td>
<td>75</td>
<td>Hydrogen</td>
<td>ACS Material</td>
</tr>
<tr>
<td>Beta 150</td>
<td>CP811C-300</td>
<td>150</td>
<td>Hydrogen</td>
<td>Zeolyst Int.</td>
</tr>
</tbody>
</table>

4.2.2 Catalyst Preparation and Testing
Ammonium zeolites were calcined in a muffle furnace at 450 °C for 6 hours to transform the zeolite into their protonic forms. Lanthanum was added to zeolite Beta 12.5 via wet-impregnation in deionised water at 100 °C for 12 hours under intense stirring using the required amount of the salt. Wet-impregnation was chosen over ion-exchange due to the tendency of the latter method to dealuminate the sample. The lanthanum-containing zeolites were denoted by their respective lanthanum content: 1La-B, 5La-B and 10La-B. After impregnation, the zeolites were dried for 16 hours at 110 °C. The zeolites were then calcined at 450 °C in a muffle furnace for 6 hours.

4.3 Results and Discussion

4.3.1 Catalyst Characterisation

4.3.1.1 Effect of Si/Al

4.3.1.1.1 Physicochemical Properties
The BET surface area and pore volume values are reported in Table 4-2. A variation between the reported Si/Al ratios and the elemental results was observed. The acidity results used further in this work were based on the elemental analysis of the zeolites results and not the reported Si/Al.
Table 4-2: Elemental analysis and BET surface area and pore volume results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Reported Si/Al</th>
<th>Si/Al (ICP-OES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta 12.5</td>
<td>534</td>
<td>0.18</td>
<td>12.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Beta 75</td>
<td>477</td>
<td>0.15</td>
<td>75</td>
<td>82.8</td>
</tr>
<tr>
<td>Beta 150</td>
<td>475</td>
<td>0.18</td>
<td>150</td>
<td>113</td>
</tr>
</tbody>
</table>

The acidity of the zeolite is inherently related to the aluminium content. For a similar zeolite structure, high aluminium zeolites usually exhibit higher acidity than high silica zeolites. Zeolite Beta 12.5 exhibited higher total acidity than zeolites Beta 75 and Beta 150. Figure 4-2 shows the pyridine FTIR spectra of the zeolites in the region of 1400 – 1600 cm⁻¹.

Figure 4-2: Py-FTIR spectra of zeolites Beta 12.5, 75 and 150 after pyridine adsorption and desorption at 150 °C

The acidity measurement results are provided in Table 4-3. The total acidity significantly decreased with increasing the Si/Al ratio. Zeolite Beta 12.5 exhibited the highest acidity followed by Beta 75 and finally Beta 150. The B/L ratio however was in reverse order with Beta 150 having the highest B/L ratio followed by Beta 75 and finally Beta 12.5

Table 4-3: Acidity measurements of zeolites Beta 12.5, 75 and 150

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Py-B (mmol/g)</th>
<th>Py-L (mmol/g)</th>
<th>B+L (mmol/g)</th>
<th>B/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta 12.5</td>
<td>0.43</td>
<td>0.42</td>
<td>0.85</td>
<td>1.02</td>
</tr>
<tr>
<td>Beta 75</td>
<td>0.09</td>
<td>0.09</td>
<td>0.18</td>
<td>1.07</td>
</tr>
<tr>
<td>Beta 150</td>
<td>0.08</td>
<td>0.02</td>
<td>0.10</td>
<td>4.23</td>
</tr>
</tbody>
</table>
Figure 4-3 shows the relation between the Si/Al and the zeolite’s total acidity. A direct relation was observed between the zeolite’s aluminium content and its acidity.

![Graph showing the relation between Si/Al and acidity](image)

Figure 4-3: Dependence of the zeolite Beta’s acidity on the aluminium content

### 4.3.1.2 Effect of La³⁺ Levels

#### 4.3.1.2.1 Physical Properties

The surface area and pore volume results are reported in Table 4-4. Both the surface area and the pore volume decreased with increasing the lanthanum content in the zeolite. The elemental analysis of the catalysts showed that the lanthanum levels were in good agreement with the amount of salt used in the preparation. The degree of ion-exchange (La-EX) was calculated based on the calculations provided in appendix (C).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (m³/g)</th>
<th>La Content (wt.%) (ICP-OES)</th>
<th>Si/Al (ICP-OES)</th>
<th>La-EX %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta 12.5</td>
<td>534</td>
<td>0.18</td>
<td>n.a.</td>
<td>12.6</td>
<td>0</td>
</tr>
<tr>
<td>1 La-B</td>
<td>416</td>
<td>0.15</td>
<td>1.01</td>
<td>12.5</td>
<td>20.57</td>
</tr>
<tr>
<td>5 La-B</td>
<td>396</td>
<td>0.13</td>
<td>4.9</td>
<td>12.7</td>
<td>96.97</td>
</tr>
<tr>
<td>10 La-B</td>
<td>354</td>
<td>0.10</td>
<td>9.7</td>
<td>12.6</td>
<td>197.56</td>
</tr>
</tbody>
</table>

Table 4-4: Effect of La³⁺ on the physical properties of zeolite Beta

Figure 4-4 shows the decrease in the surface area and pore volume of the catalysts. The initial introduction of the lanthanum ions had the highest impact on the surface area and pore volume of the catalysts. Further increments in the lanthanum content seemed to marginally decrease both the even after exceeding the ion-exchange capacity.
4.3.1.2.2 Location of lanthanum ions

The parent zeolite Beta (12.5) exhibited high Si-OH band intensities both at 3730 and 3745 cm\(^{-1}\) attributed to internal and external silanols respectively [11]. The silanol groups were affected by the interdiction of lanthanum. Figure 4-5 shows the IR spectra of the zeolites in the region of 3800-3650 cm\(^{-1}\). The band associated with internal silanols decreased rapidly with the introduction of lanthanum and continued to decrease as the lanthanum content increased as shown in Figure 4-6. The decrease in band intensity of the internal silanols indicated an interaction between the lanthanum species and the silanol groups inside the zeolite’s pores.

![Figure 4-4: Effect of La\(^{3+}\) on the surface area and the pore volume of the catalysts](image)

![Figure 4-5: Effect of La\(^{3+}\) on the Si-OH groups in the region of 3800-3650 cm\(^{-1}\)](image)
The external silanols meanwhile remained relatively constant indicating that most of the lanthanum species were located inside the pores of the zeolite apart from 10La-B, where the lanthanum content exceeded the ion-exchange capacity, external silanols decreased significantly. This decrease in the external silanols in 10La-B might indicate the presence of lanthanum in significant amounts on the surface of the zeolite.

![Figure 4-6: Effect of La$^{3+}$ levels on the intensity of the Si-OH band](image)

4.3.1.2.3 Effect of lanthanum on the acidity of zeolite Beta
The parent zeolite Beta (12.5) exhibited relatively high band intensity located at 1545 cm$^{-1}$ which is associated to the creation of a pyridinium ion after its interaction with a Brønsted acid site. The band intensity associated with the pyridinium ion (1545 cm$^{-1}$) decreased with increasing the lanthanum content due mainly to the lanthanum species replacing up to 3 bridging-OH groups (Figure 4-7). Interestingly, the band intensity associated with Lewis acid sites (1455 cm$^{-1}$) also increased with increasing the lanthanum content. The total acidity of the zeolite did not change significantly by the introduction of lanthanum due to the increase in the Lewis acidity apart from 10La-B which decreased significantly due to exceeding the ion-exchange capacity.

Each lanthanum cation can replace up to 3 bridging-OH groups [12]. The band in the 1455 cm$^{-1}$ region was attributed to the Lewis acid sites associated with pyridine accessible to extra framework aluminium. The intensity of the 1455 cm$^{-1}$ band increased with increasing the lanthanum content.
This can possibly be from the EFAL species generated during the impregnation procedure. The pH of the solution was approximately 5.2 during the impregnation of the 1La-B and 4.9 with 5La-B. The acidity of the solution can induce the removal of aluminium from the zeolite's framework. The removed aluminium could then agglomerate and generate EFAL species as it was not washed out from the sample. Furthermore, the remaining nitrates from the solution could possibly generate nitric acid during the calcination procedure from the moisture trapped in the catalyst which would further remove the aluminium from the framework and generate EFAL species. Figure 4-8 shows the effect of the lanthanum content on the acidity of zeolite Beta.

Figure 4- 7: FTIR spectra of the La$^{3+}$ containing zeolites in the 1600 – 1400 cm$^{-1}$ region after Pyridine adsorption

Figure 4- 8: Effect of La$^{3+}$ on the acidity of zeolite Beta
The decrease in Brønsted acidity was accompanied by an increase in Lewis acidity which reached a maximum in 5La-B and dropped afterwards (Figure 4-9). The total acidity therefore remained relatively constant due to the increase in Lewis acid sites.

The FTIR spectra of the zeolites in the bridging OH region (3609 cm\(^{-1}\)) indicated that the bridging OH groups were significantly reduced after the introduction of lanthanum. A significant initial reduction in the bridging OH band intensity was observed. Further increments in the lanthanum content decreased the bridging OH band intensity albeit at a lower rate than the initial addition of lanthanum (Figure 4-10).

![Figure 4-9: Effect of \(\text{La}^{3+}\) on the Brønsted acidity (A) and Lewis acidity (B)](image)

![Figure 4-10: Effect of \(\text{La}^{3+}\) on the 3609 cm\(^{-1}\) band intensities](image)
Initially, the lanthanum species could have replaced up to 3 bridging-OH groups in the zeolite’s framework hence the initial sharp decline of the band intensity while further additions of lanthanum replaced 1 or 2 bridging-OH groups.

4.3.2 Catalytic Results

4.3.2.1 Effect of Si/Al Ratio

4.3.2.1.1 Initial Catalytic Behaviour

The initial 2-butene conversion and product distribution at $t = 2$ h. are compared in Table 4-5. Even though the conversion levels were relatively high ($X > 80\%$), the $C_8$ selectivity was clearly dependent on the Si/Al ratio. The high aluminium zeolite Beta (12.5) showed the highest $C_8$ selectivity while reducing the aluminium content significantly reduced both the conversion and the $C_8$ selectivity while increasing the oligomerisation activity. This illustrates that even at high conversions; a high aluminium content and thus high acidity was required for the alkylation activity while the oligomerisation of butenes can occur even on a lower acidity catalyst. Moreover, the oligomerisation products ($C_{12+}$) were higher in the high silica Beta zeolites while Beta (12.5) produced lower quantities of oligomerised products. The low number of acid sites available for the reaction in the more siliceous zeolites led to a drop in the conversion levels which promoted oligomerisation due to the increase in the olefin concentrations inside the pores.

<table>
<thead>
<tr>
<th>Initial Alkylation Activity</th>
<th>Catalyst Beta (12.5)</th>
<th>Catalyst Beta (75)</th>
<th>Catalyst Beta (150)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>99.30</td>
<td>88.28</td>
<td>83.47</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_5$-$C_7$</td>
<td>2.83</td>
<td>0.53</td>
<td>0.25</td>
</tr>
<tr>
<td>$C_8$</td>
<td>47.00</td>
<td>11.88</td>
<td>10.52</td>
</tr>
<tr>
<td>$C_9$-$C_{12}$</td>
<td>38.17</td>
<td>49.02</td>
<td>47.79</td>
</tr>
<tr>
<td>$C_{12+}$</td>
<td>12.00</td>
<td>38.57</td>
<td>41.44</td>
</tr>
<tr>
<td>Composition of $C_8$ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>69.93</td>
<td>28.17</td>
<td>13.71</td>
</tr>
<tr>
<td>DMHs</td>
<td>21.38</td>
<td>19.70</td>
<td>9.20</td>
</tr>
<tr>
<td>MHs</td>
<td>5.22</td>
<td>13.97</td>
<td>11.44</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>45.51</td>
<td>34.42</td>
<td>33.11</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>11.65</td>
<td>7.13</td>
<td>5.44</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>29.00</td>
<td>39.89</td>
<td>42.30</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>13.84</td>
<td>18.56</td>
<td>19.15</td>
</tr>
</tbody>
</table>

Table 4-5: Initial product distribution at $t = 2$ h
Within the C₈ fraction, the high aluminium Beta zeolite, Beta (12.5), exhibited the highest selectivity towards TMPs while the TMP content significantly dropped with increasing Si/Al ratios due to the reduction in acidity. Moreover, the TMP distribution varied significantly between the zeolites. The high aluminium Beta (12.5) showed the highest content of the primary product of the alkylation reaction (2,2,3 TMP) indicating higher hydride transfer rates [6]. In the more siliceous zeolites, the low content of this isomer indicated that the hydride transfer step was slower. Furthermore, the content of the 2,3,4 TMP, which has the lowest kinetic diameter, increased with increasing Si/Al which indicated steric hindrance facing the 2,2,3 alkyl-cation because of the build-up of large molecules around the remaining acidic sites of the catalyst.

4.3.2.1.2 Catalytic Stability

The catalytic stability of the Beta zeolites with varying Si/Al ratio is presented in Figure 4-11. The high aluminium zeolite showed the highest catalytic activity and stability while the more siliceous zeolites deactivated rapidly. The Beta (12.5) catalyst reached a final conversion level of 85% while Beta (75) and Beta (150) reached a final conversion level of 65% and 59% respectively.

![Figure 4-11: Effect of Si/Al on the catalytic stability of zeolite Beta](image)

The lack of acid sites available for hydride transfer in the more siliceous zeolites caused the conversion to drop. Once the conversion dropped, the increase in the olefin concentration
inside the pores promoted additional oligomerisation which blocked the channels and caused further deactivation. This negatively impacted the C₈ selectivity. Figure 4-12 shows the change in the C₈ selectivity with time. The aluminium-rich zeolite Beta (12.5) displayed a decrease in the C₈ content with time due to the deactivation of the catalyst while surprisingly, the more siliceous zeolites showed an increase. However, the low TMP/DMH ratio coupled with the low conversion indicated that the major components in the C₈ fraction were C₈ olefins originating from the dimerisation of the butene.

![Figure 4-12: Effect of Si/Al on the time-on-stream on the C₈ selectivity of zeolite Beta](image)

The TMP/DMH ratio in the more siliceous Beta zeolites approached the thermodynamic value at 75 °C (Figure 4-13). This might have indicated that surface reactions were beginning to dominate. The blockage of the pores, besides the high reactivity of the butenes, forced the reaction to occur on the surface acidic sites instead. Surface reactions do not usually abide by the shape selectivity of the zeolite. The aluminium-rich Beta zeolite, due to its high number of acidic sites available for the reaction, maintained the butene conversions levels high enough as to not block the pores which favoured the production of TMPs instead of the thermodynamically-favoured DMHs, although the ratio was decreasing with time due to the catalyst deactivation. A similar trend was also observed by Nivarthy et al. [7].
The C_{12+} fraction increased with time for all the catalysts (Figure 4-14). The build-up of bulky molecules in the catalyst led to the oligomerisation and dimerisation of butenes since coke itself may act as a hydride transfer medium for the oligomerisation and dimerisation of butenes [14].

4.3.2.1.3 Effect of the Turnover

The varying acidity of the tested zeolites means that the butene turnover over the acidic sites was not equivalent. At high Si/Al ratios, the turnover of butenes over the acidic sites of
the zeolite was much higher than at lower Si/Al ratios. Assuming that only the acidic sites accessible to pyridine contributed to the reaction, the butene turnover can be calculated from equation 4-1:

\[
\text{Turnover} = \frac{1000 \times \text{Molar flow rate of butene (mol/h)}}{\frac{\text{Catalyst acidity (mmol-Py/g-cat)}}{\text{Catalyst weight (g)}} \times \text{Time-on-stream (h)}}
\] (4-1)

Figure 4-15 shows the effect of the butene turnover on the conversion. The turnover behaviour indicated that the catalytic stability of the zeolites was slightly improved with decreasing acidity. The amount converted per acidic site improved with increasing the Si/Al ratio which can be explained by the significant decrease in the Lewis acid sites (Table 4-3). The decrease in the Lewis acid sites reduced the concentration of the butenes around the remaining sites which decreased the deactivation activity. However, the TMP selectivity did not follow the same trend (Figure 4-16).

Figure 4-15: Effect of the turnover on the conversion behaviour of zeolite Beta with varying Si/Al ratios

Increasing the Si/Al ratio led to a decrease in TMP selectivity indicating that TMP production probably required the presence of two adjacent acidic sites. Decreasing the aluminium content of the zeolite reduced the number of adjacent sites. The butenes could be converted on a lone acidic site however the TMPs seemed to require two adjacent acidic sites to be produced as was suggested Guisnet and Gnep [14].
4.3.2.1.4 Overall Product Distribution

The overall product distribution is shown in Table 4-6. The conversion levels were dependent on the acidity of the zeolite with the conversion decreasing in the order of Beta 12.5 > Beta 75 > Beta 150. Although the conversion levels were relatively high, the acidity of the catalyst played a major role in maintaining high butene conversions.

Table 4-6: Effect of Si/Al Ratio on the overall product distribution during the alkylation reaction

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
<th>Beta (12.5)</th>
<th>Beta (75)</th>
<th>Beta (150)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time-on-stream (h)</td>
<td></td>
<td>10</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Butene Conversion (%)</td>
<td></td>
<td>91.14</td>
<td>78.30</td>
<td>74.11</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_5$-$C_7$</td>
<td></td>
<td>1.72</td>
<td>0.27</td>
<td>0.15</td>
</tr>
<tr>
<td>$C_8$</td>
<td></td>
<td>32.86</td>
<td>15.94</td>
<td>16.98</td>
</tr>
<tr>
<td>$C_9$-$C_{12}$</td>
<td></td>
<td>46.33</td>
<td>38.91</td>
<td>36.27</td>
</tr>
<tr>
<td>$C_{12+}$</td>
<td></td>
<td>19.09</td>
<td>44.88</td>
<td>46.60</td>
</tr>
<tr>
<td>Composition of $C_8$ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td></td>
<td>59.71</td>
<td>11.60</td>
<td>5.41</td>
</tr>
<tr>
<td>DMHs</td>
<td></td>
<td>23.16</td>
<td>19.33</td>
<td>10.68</td>
</tr>
<tr>
<td>MHS</td>
<td></td>
<td>9.55</td>
<td>6.98</td>
<td>3.75</td>
</tr>
<tr>
<td>Other $C_8$</td>
<td></td>
<td>7.58</td>
<td>62.09</td>
<td>80.16</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td></td>
<td>42.97</td>
<td>29.66</td>
<td>28.21</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td></td>
<td>12.59</td>
<td>6.02</td>
<td>5.01</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td></td>
<td>30.21</td>
<td>40.69</td>
<td>44.23</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td></td>
<td>14.23</td>
<td>23.63</td>
<td>22.55</td>
</tr>
</tbody>
</table>
Figure 4-17 describes the dependence of the butene conversion on the acidity of the zeolite. The availability of the acidic sites in the catalyst maintained the olefin conversion levels high thus reducing the olefin concentration near the acidic sites. Once the conversion level dropped, the butene concentration increased in the vicinity of the remaining sites which promoted oligomerisation and blocked the pores leading to further deactivation.

The acidity also contributed towards the formation of C₈s (Figure 4-18). Beta (12.5) showed the highest affinity to the production of C₈s due to its high acidity. The high C₈ selectivity in zeolite Beta (12.5), coupled with the low C₁₂⁺ selectivity indicates that the acidity required for the alkylation reaction seemed to be higher than the acidity required for both the oligomerisation and cracking. The increase in the C₁₂⁺ selectivity can be attributed to the lack of acidic sites available for the alkylation which increased the oligomerisation activity as shown in Figure 4-18 B.
Also, the composition of the \( C_8 \)s was significantly affected by the zeolite’s acidity. Zeolite Beta (12.5), due to its high acidity favoured the production of TMPs while zeolites Beta 75 and 150 produced less TMPs.

The TMP distribution was also affected by the acidity of the catalyst. The primary product of the alkylation reaction, the 2,2,3 TMP was the highest in Beta (12.5) indicating faster hydride transfer while it decreased with decreasing acidity [6]. Moreover, Beta 75 and 150 favoured the production of the 2,3,4 TMP, which has the smallest kinetic diameter among the TMPs [5], indicating the steric limitation facing the TMP alkyl-cation due the build-up of coke inside the pores.

### 4.3.2.2 Effect of La\(^{3+}\) Loading

#### 4.3.2.2.1 Initial Catalytic Behaviour

To further understand the acidity effects, lanthanum was introduced to manipulate the Bronsted and Lewis acidity on zeolite Beta (12.5). Table 4-7 shows the initial activity and selectivity of the catalysts. The butene conversion level was initially 100% for all the catalysts apart from 10La-B. The significant reduction in the acidity of the 10La-B catalyst caused the conversion to drop. The product distribution of the 10La-B also showed significant differences. The 10La-B catalyst, due to its lower acidity, produced the lowest \( C_8 \) content while all the other catalysts produced similar \( C_8 \)s.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Beta (12.5)</th>
<th>1La-B</th>
<th>5La-B</th>
<th>10-LaB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>95.90</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_5)–( C_7 )</td>
<td>3.60</td>
<td>3.12</td>
<td>3.35</td>
<td>1.22</td>
</tr>
<tr>
<td>( C_8 )</td>
<td>53.11</td>
<td>50.33</td>
<td>51.20</td>
<td>18.68</td>
</tr>
<tr>
<td>( C_9)–( C_{12} )</td>
<td>29.44</td>
<td>38.32</td>
<td>35.81</td>
<td>32.76</td>
</tr>
<tr>
<td>( C_{12+} )</td>
<td>13.85</td>
<td>8.23</td>
<td>9.64</td>
<td>47.34</td>
</tr>
<tr>
<td>Composition of ( C_8 ) Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>77.11</td>
<td>76.44</td>
<td>78.07</td>
<td>58.32</td>
</tr>
<tr>
<td>DMHs</td>
<td>19.87</td>
<td>19.16</td>
<td>20.12</td>
<td>26.15</td>
</tr>
<tr>
<td>MHs</td>
<td>3.02</td>
<td>4.40</td>
<td>1.79</td>
<td>11.61</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>46.74</td>
<td>44.67</td>
<td>45.80</td>
<td>36.75</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.45</td>
<td>12.96</td>
<td>11.61</td>
<td>10.58</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>27.10</td>
<td>28.64</td>
<td>26.29</td>
<td>36.67</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>13.71</td>
<td>13.73</td>
<td>16.30</td>
<td>16.00</td>
</tr>
</tbody>
</table>

Table 4-7: Effect of La\(^{3+}\) loading on the initial alkylation activity of zeolite Beta (12.5) at t = 1 h
Also, the 10La-B catalyst had the highest C_{12+} selectivity due to the decrease in its acidity which also reduced the TMP selectivity. Moreover, the TMP/DMH ratio in the 10La-B catalyst was approximately 2.2 while the in the other catalysts, the TMP/DMH ratio was significantly higher indicating the diffusion limitations in 10La-B. Another indication of the diffusion limitations in 10La-B was the high selectivity towards MHs which was much higher than the other zeolites. The TMP distribution also confirms the steric hindrance in zeolite 10La-B which had the highest 2,3,4 TMP content.

4.3.2.2.2 Catalytic Stability
The catalytic stability of the zeolites is presented in Figure 4-19. All the catalysts showed high butene conversion levels and maintained high stability apart from 10La-B which deactivated more rapidly due to its lower acidity. Zeolites Beta (12.5), 1La-B and 5La-B showed similar conversion levels due to their similar acidity.

![Figure 4-19: Effect of La^{3+} loading on the catalytic stability of zeolite Beta](image)

The C_8 selectivity, presented in Figure 4-20, showed a similar trend to the conversion. The 10La-B catalyst showed the lowest C_8 selectivity due to its low acidity while zeolite Beta (12.5) showed the highest C_8 selectivity due to the higher number of Brønsted acid sites available for hydride transfer. The decrease in the C_8 selectivity in zeolites 1La-B and 5La-B can be attributed to the decrease in the Brønsted acid sites and the increase in the Lewis acid sites.
Moreover, the TMP/DMH ratio continued to decrease with time in all the catalyst signifying that the C₈ alkyl-cation underwent isomerisation to the thermodynamically favoured and smaller in-size DMHs due to steric limitations inside the catalyst pores and due to the reaction occurring on the surface of the zeolite (Figure 4-21). It should be noted also that the TMP/DMH ratio approached its thermodynamic value indicating that, as the reaction progressed, surface reactions were beginning to dominate. Zeolite 10La-B reached the thermodynamic limit ahead of all the zeolites due to a combination of low porosity and reduced Brønsted acidity. Zeolites Beta (12.5) and 1La-B favoured the production of TMPs over DMHs while the decrease in the Børnsted acidity in 5La-B caused the ratio to rapidly approach the thermodynamic value.
The C\textsubscript{12}+ fraction, which is the main cause of the catalyst deactivation due to its propensity to block the catalyst pores, originated from the oligomerisation of the C\textsubscript{8} alkyl-cation with butenes to resulting in larger molecules. As the deactivation occurred, the butene concentration increased around the acidic sites of the catalyst promoting further oligomerisation. The low number of acidic sites in 10La-B led to an increase in the butene concentration inside and around the zeolite pores promoting further oligomerisation (Figure 4-22). High acidity seemed to have supressed the formation of the C\textsubscript{12}+ fraction.

Figure 4-21: Effect of La\textsuperscript{3+} loading on the TMP/DMH ratio of zeolite Beta

Figure 4-22: Effect of La\textsuperscript{3+} loading on the C\textsubscript{12}+ fraction of zeolite Beta
4.3.2.2.3 Overall Product Distribution

The overall product distribution is presented in Table 4-8. After 10 hours on stream, all the catalysts maintained high butene conversion levels, X >80 %. Zeolite 10La-B had the lowest butene conversion levels due to its lower acidity while the remaining zeolites, due to their similar acidities, had similar conversion levels.

Table 4-8: Effect of La$^{3+}$ loading on the overall product distribution of zeolite Beta (12.5) after 10 hours on stream

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Beta (12.5)</th>
<th>1La-B</th>
<th>5La-B</th>
<th>10La-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Converted (%)</td>
<td>91.14</td>
<td>89.20</td>
<td>88.83</td>
<td>80.34</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_5$-C$_7$</td>
<td>1.72</td>
<td>1.47</td>
<td>1.16</td>
<td>0.34</td>
</tr>
<tr>
<td>C$_8$</td>
<td>32.86</td>
<td>30.64</td>
<td>26.4</td>
<td>14.62</td>
</tr>
<tr>
<td>C$<em>7$-C$</em>{12}$</td>
<td>46.33</td>
<td>45.27</td>
<td>47.13</td>
<td>31.84</td>
</tr>
<tr>
<td>C$_{12+}$</td>
<td>19.09</td>
<td>22.62</td>
<td>25.31</td>
<td>53.2</td>
</tr>
<tr>
<td>Composition of C$_8$ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>59.71</td>
<td>55.45</td>
<td>46.03</td>
<td>17.58</td>
</tr>
<tr>
<td>DMHs</td>
<td>23.16</td>
<td>24.03</td>
<td>28.82</td>
<td>30.31</td>
</tr>
<tr>
<td>MHs</td>
<td>9.55</td>
<td>11.72</td>
<td>15.59</td>
<td>26.1</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>42.97</td>
<td>43.13</td>
<td>42.06</td>
<td>32.66</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.59</td>
<td>12.10</td>
<td>11.11</td>
<td>9.20</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>30.21</td>
<td>29.15</td>
<td>29.81</td>
<td>38.63</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>14.23</td>
<td>15.62</td>
<td>17.02</td>
<td>19.51</td>
</tr>
</tbody>
</table>

To examine the nature of the acidic sites on the alkylation activity the 10La-B catalyst was excluded from the comparison because of its significantly lower acidity (Figure 4-8). The variation of the Brønsted and Lewis acidity affected conversion levels. Beta (12.5) had the highest number of Brønsted acid sites (Figure 4-8) and therefore had the highest stability while 1La-B and 5La-B deactivated more (Figure 4-25 A). Also, the Lewis acidity influenced the conversion as shown in Figure 4-25 B. The increase in the Lewis acidity increased the oligomerisation and reduced the activity of the catalyst.

The decrease in the Bronsted acidity as a result of the lanthanum loading decreased the C$_8$ selectivity indicating that in zeolite Beta, the alkylation reaction was promoted by high Bronsted acidity (Figure 4-23 A). The Lewis acid site increased with increasing lanthanum content leading to an increase in the oligomerisation activity and a reduction in the alkylation
activity indicating that the oligomerisation was promoted by the Lewis acid sites as shown in Figure 4-23 B.

Figure 4- 23: Effect of the Brønsted acidity (A) and Lewis acidity (B) on the overall conversion levels

Owing to its higher Brønsted acidity, Zeolite Beta (12.5) produced the most C₈s amongst the tested catalysts indicating that the alkylation reaction occurred predominantly on the Brønsted acid sites (Figure 4-24). Conversely, the increased Lewis acidity in the lanthanum Beta zeolites promoted higher C₁₂⁺ formation s shown in Figure 4-24 B.

Figure 4- 24: Effect of Brønsted acidity on C₈ selectivity (A) and Lewis acidity on C₁₂⁺ selectivity (B)

Moreover, the reduction in the number of Brønsted acid sites can also increase the distance between such sites. It was proposed that the hydride transfer step may require the presence of two adjacent Brønsted acid sites [14]. Lanthanum replaced up to three Brønsted acid sites from the bridging-OH groups with La-OH groups which could have reduced the number of adjacent sites and increased the distance between the available Brønsted acid sites. The
decrease in the Brønsted acid sites reduced the TMP selectivity since the number of adjacent Brønsted sites was reduced.

The deactivation of the zeolite can be directly attributed to the C_{12}^+ fraction. The most active catalyst produced the least C_{12}^+ while as the catalyst deactivated further; the C_{12}^+ selectivity was increased (Figure 4-25).

![Figure 4-25: Effect of the overall conversion on the C_{12}^+ selectivity during the alkylation reaction over zeolite Beta with varying lanthanum content](image)

4.4 Conclusions

The effect of Si/Al and La^{3+} loading on the alkylation performance of zeolite Beta was studied in a well-mixed reactor. The highest aluminium content catalyst had a significantly improved performance in terms of catalytic activity, stability and C_8 selectivity. Zeolite Beta with a Si/Al ratio of 12.5 was shown to be the most active catalyst for the alkylation of 2-butene with isobutane. Increasing the Si/Al ratio significantly decreased the catalyst lifetime and C_8 selectivity. The reduction in the catalyst conversion was attributed to the lack of acid sites which led to the formation of oligomerisation products. The turnover behaviour indicated that the conversion of butenes improved with increasing Si/Al ratio due to the reduction of the Lewis acid sites. The TMP selectivity however was reduced due to the decrease in adjacent acidic sites.

Lanthanum loading did not improve the alkylation performance of zeolite Beta. The lanthanum species reduced the Brønsted acid sites while the preparation procedure promoted the formation of Lewis acid sites during the impregnation and subsequent calcination. The reduction of the Brønsted acidity and the increase in the Lewis acidity led to a decrease in the butene conversion and alkylate selectivity. Increasing the lanthanum
content to 10% significantly altered the porosity of the catalyst and reduced its acidity. The low number of external silanols in the 10La-B catalyst indicated that the lanthanum species were deposited on the surface of the zeolite due to the lanthanum content increasing beyond the ion-exchange capacity.

4.5 References


5. The Effect of Si/Al and Lanthanum Exchange on the Alkylation Activity of Zeolite Y
5.1 Introduction

Three dimensional large-pore zeolites have been shown to be active for the alkylation reaction with a product distribution similar to a typical alkylate. The Faujasite family of zeolites, which includes zeolites Y, X and EMT amongst other types, have gathered significant interest due to the availability of large pores and high acidity which can be manipulated and tailored to improve the acidity profile. Figure 5-1 shows the structure of zeolite Y.

![Figure 5-1: The framework of zeolite Y and the supercages formed in the framework, taken from [1]](image)

Faujasites were first explored as alkylation catalysts by Kirsch et al. in 1972. The authors utilised a rare-earth exchanged zeolite Y (REY) as a catalyst however the catalyst rapidly deactivated [2]. The acidity of the zeolite seems to have the highest impact on its catalytic performance. Mostad et al. compared iso-structural H-Y and SAPO-37; H-Y, despite being severely dealuminated, produced more C₈s while SAPO-37 mainly produced olefins. The vast acidity difference between the highly acidic H-Y zeolite and the SAPO-37 was proposed as the main factor affecting the alkylation performance of the catalysts at hand. Hence, high acidity is required for the alkylation reaction [3]. Diaz-Mendoza et al. compared REY and USY with a Si/Al ratio of 2.7. The authors concluded that despite the higher acidity of USY, the high number of strong Lewis acid sites led to a faster deactivation and lower C₈ selectivity which highlighted the important role played by the acidity type during the alkylation reaction [4].

The Si/Al ratio of the zeolite plays a major role in its alkylation activity. Generally, lowering the Si/Al improves the alkylation performance. Yoo et al. compared USY zeolites using a Si/Al ratio of 2.5, 6, 30 and 40. The Low Si/Al zeolites (2.5 and 6) had higher stability while the high silica zeolites deactivated rapidly. Furthermore, the slightly dealuminated USY with a Si/Al of 6 was shown to have a higher TMP selectivity than the 2.5 zeolite. The authors claimed that the slight dealumination, despite decreasing the acidity, led to a reduction in the cracking reaction and thus improved the C₈ selectivity [5]. Corma et al. examined a set of
USY zeolites with varying Si/Al ratios, between 2.6 and 60 and demonstrated that the zeolite with the lowest Si/Al ratio had the highest TMP selectivity [6]. Another study by the same cited group compared USY zeolites with a variety of Si/Al ratios achieved by steaming and acid-leaching with ammonium hexafluorosilicate (AHF) to manipulate the Si/Al ratio. At low Si/Al ratios, slight dealumination via AHF treatment removed extraframework aluminium and improved the stability of the zeolite compared to the untreated samples. Interestingly, the catalysts with higher Si/Al, despite having almost no extraframework aluminium, had lower lifetime and TMP selectivity. The loss of activity was attributed to the decrease in the total acidity of the catalyst and the lack of polarisation of the Brønsted sites by extraframework aluminium which enhanced the strength of the Brønsted sites in the slightly dealuminated samples [7]. Figure 5-2 shows the synergistic polarisation between the Brønsted and Lewis acid sites.

![Figure 5-2: Polariisation of the Brønsted acid site by EFAL, adopted from [8]](image)

Stabilisation of the zeolite’s lattice by ion exchange with rare-earth metals is a common procedure in catalysis. In Faujasites, the effect of rare-earth ion exchange is comparable to mild steaming which improves the thermal stability of the zeolite. Dealumination by steaming however generates extraframework aluminium species which exhibit Lewis acidity.

![Figure 5-3: Migration of the lanthanum ions into the sodalite cages during calcination, adopted from [9]](image)
The lanthanum cations start to migrate into the sodalite cages at temperatures above 100 °C. Once the lanthanum cations enter the sodalite cages, their preferred location will be at the centre of the six-membered ring next to the hexagonal prism and the supercages (SI’ and SII’) as shown in Figure 5-3. The hydrolysis of the hydrated La\(^{3+}\) cations via calcination releases the hydration shells and thereby the La\(^{3+}\) migrate irreversibly to the sodalite cages [10]. However, not all the lanthanum cations migrate to the sodalite cages. Lee and Rees found that about 17% of the lanthanum species remained in the zeolite Y’s supercages even after calcination [11].

Lanthanum-exchanged Faujasites were extensively explored in the literature as alkylation catalysts [12-16]. Feller et al. compared LaX zeolite with varying degrees of ion-exchange with zeolite Beta. All the LaX zeolites had higher catalyst lifetimes due to the higher B/L ratio of the LaX samples [17]. Sievers et al. compared LaX and LaY zeolites. The fully exchanged LaX zeolite had improved catalytic stability and TMP selectivity due to the higher ratio of strong-Brønsted/strong-Lewis acid sites. Furthermore, the high residual sodium in LaY contributed toward the reduction in the Brønsted acid sites of the zeolite as it was not possible to fully exchange the sodium with lanthanum [18].

It is well known that sodium ions are difficult to remove in zeolite Y [19]. Moreover, the acidity of zeolite Y was significantly reduced by the sodium content as shown by Sandoval-Díaz et al. by back-exchanging zeolite USY with sodium [20]. Therefore, a set of Ultrastable Y zeolites with negligible sodium content (<0.1 wt. %) was selected to examine the effect of Si/Al ratio on the alkylation activity of zeolite Y under ideal reaction conditions. Furthermore, lanthanum ion-exchange on post-stabilised zeolite Y was not studied in literature and can provide a thermally stable catalyst due to the high thermal stability of the USY zeolite.

5.2 Experimental

5.2.1 Materials

Zeolite Y with varying Si/Al ratios, between 2.6 and 30, was supplied by Zeolyst as shown in Table 5-1. Lanthanum was supplied by Sigma Aldrich as Lanthanum (III) nitrate hexahydrate.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product Number</th>
<th>Reported Si/Al</th>
<th>Form</th>
<th>Preparation Procedure(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>CBV 500</td>
<td>2.6</td>
<td>NH(_4^+)</td>
<td>Steaming</td>
</tr>
<tr>
<td>Y(6)</td>
<td>CBV 712</td>
<td>6</td>
<td>NH(_4^+)</td>
<td>Steaming + Acid Leaching</td>
</tr>
<tr>
<td>Y(15)</td>
<td>CBV 720</td>
<td>15</td>
<td>H(^+)</td>
<td>Steaming + Acid Leaching</td>
</tr>
<tr>
<td>Y(30)</td>
<td>CBV 760</td>
<td>30</td>
<td>H(^+)</td>
<td>Steaming + Acid Leaching</td>
</tr>
</tbody>
</table>
5.2.2 Catalyst Preparation and Testing

Ammonium zeolites were calcined in a muffle furnace at ramp rate of 0.5 °C/min to 450 °C and kept there for 6 hours to transform the zeolite into its protonic form. Lanthanum was introduced onto the zeolite by ion-exchange with 0.20 M La(NO$_3$)$_3$ solution at a ratio of 10 mL solution / g-catalyst. The ion exchange was conducted in a 800 mL glass beaker at 80 °C for 3 hours under intense stirring followed by filtration, washing with ample amounts of deionised water and drying at 100 °C for 16 hours. The preparation procedure for each catalyst is summarised in Table 5-2. The zeolites were then calcined at 450 °C in a muffle furnace at a ramp rate of 0.5 °C/min for 6 hours. A similar set of catalysts was prepared using wet impregnation with lanthanum contents of 1, 5, 10 and 15 wt.% and the catalytic results are available in appendix (D).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>2.6</td>
<td>Calc.</td>
</tr>
<tr>
<td>Y(6)</td>
<td>6</td>
<td>Calc.</td>
</tr>
<tr>
<td>Y(15)</td>
<td>15</td>
<td>None</td>
</tr>
<tr>
<td>Y(30)</td>
<td>30</td>
<td>None</td>
</tr>
<tr>
<td>1 LaE</td>
<td>2.6</td>
<td>1 x La EX, Calc.</td>
</tr>
<tr>
<td>3 LaE</td>
<td>2.6</td>
<td>3 x La EX, Calc.</td>
</tr>
<tr>
<td>6 LaE</td>
<td>2.6</td>
<td>3 x La EX, Calc. additional 3 x La EX, Calc.</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

5.3.1 Catalyst Characterisation

5.3.1.1 Effect of Si/Al

5.3.1.1.1 Physical Properties

The BET surface area and pore volume values are reported in Table 5-3. A slight variation between the reported bulk-Si/Al and the elemental results was noted. The acidity results used further in this work were based on the elemental analysis of the zeolites results and not the reported Si/Al. Moreover, the sodium content in all the catalysts was less than 0.1 wt. %.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Reported Si/Al</th>
<th>ICP-OES Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>591</td>
<td>0.24</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Y(6)</td>
<td>571</td>
<td>0.25</td>
<td>6</td>
<td>6.7</td>
</tr>
<tr>
<td>Y(15)</td>
<td>660</td>
<td>0.26</td>
<td>15</td>
<td>16.8</td>
</tr>
<tr>
<td>Y(30)</td>
<td>721</td>
<td>0.27</td>
<td>30</td>
<td>28.7</td>
</tr>
</tbody>
</table>
5.3.1.1.2 Acidity Measurements

The acidity of the zeolite decreased with increasing the Si/Al ratio. For a similar zeolite structure, high silica zeolites typically exhibit lower acidity than their high aluminium counterparts [22]. Zeolite Y(2.6) exhibited higher acidity than the remaining zeolites. Figure 5-4 shows the pyridine FTIR spectra of the zeolites in the region of 1400 – 1600 cm\(^{-1}\).

![FTIR spectra of the varying Si/Al zeolites](image)

Figure 5-4: FTIR spectra of the varying Si/Al zeolites in the region of 1400-1600 cm\(^{-1}\) after pyridine desorption at 150 °C.

The acidity measurement results are displayed in Table 5-4 and as expected, the acidity decreased significantly with increasing the Si/Al ratio of the zeolite.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Py-B (mmol/g)</th>
<th>Py-L (mmol/g)</th>
<th>B+L (mmol/g)</th>
<th>B/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>0.84</td>
<td>0.82</td>
<td>1.66</td>
<td>1.02</td>
</tr>
<tr>
<td>Y(6)</td>
<td>0.37</td>
<td>0.56</td>
<td>0.93</td>
<td>0.66</td>
</tr>
<tr>
<td>Y(15)</td>
<td>0.33</td>
<td>0.20</td>
<td>0.53</td>
<td>1.65</td>
</tr>
<tr>
<td>Y(30)</td>
<td>0.24</td>
<td>0.13</td>
<td>0.37</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Zeolite Y(2.6) had the highest Brønsted and Lewis acidity among the zeolites. Figure 5-5 describes the effect of dealumination on the Brønsted and Lewis acidity. The nature the acidic sites are discussed in the next section.
5.3.1.1.3 Nature of the Acidic Sites in Zeolite Y

Stabilisation of the zeolite's structure through dealumination is a well-known procedure that is usually applied to enhance the thermal stability of the zeolite. The removal of the aluminium from the zeolite's framework through steaming generates extraframework aluminium species (EFAL) which exhibit Lewis acidity and enhance the thermal stability of the zeolite during regeneration. Acid leaching meanwhile removes the aluminium from the zeolite entirely which decreases its bulk Si/Al [23]. Figure 5-6 shows the IR spectra of the various Y zeolites in the OH-stretching region. Calculating the area under each band could provide insights into the effect of the dealumination on the chemical properties of the zeolite. Gaussian deconvolution was used to calculate the area of some bands. An example of the deconvolution is presented in appendix (D).

Figure 5-6: IR Spectra of the zeolites in the OH-stretching region (3800-3400 cm$^{-1}$)
The preparation of all the zeolites used in this work included dealumination (Table 5-1). The dealumination procedures significantly altered the OH stretching region (3800-3400 cm\(^{-1}\)) as shown in Figure 5-6. The terminal Si-OH band intensity located at ca. 3742 cm\(^{-1}\) increased with increasing the zeolite’s bulk Si/Al ratio. This was in agreement the elemental analysis results (Figure 5-7). The Si-OH band is non-acidic and is associated with terminal silanols located on the surface of the crystal or the remaining amorphous silica from the silica gel used in the preparation of the zeolite [24].

![Graph showing the relationship between Si/Al ratio and Si-OH intensity.](image)

Figure 5- 7: Effect of Si/Al ratio on the Si-OH band intensity

5.3.1.1.3.1 Location of the Brønsted Acid Sites
The bridging-OH groups were significantly altered by the dealumination. The area of the band associated with the acidic-OH groups inside the supercages centred at ca. 3624 cm\(^{-1}\) [25, 26] decreased as a result of the dealumination procedure albeit at a lower rate than the area of the band associated with the bridging-OH groups inside the sodalite cages (located at ca. 3564 cm\(^{-1}\) [27]). The 3527 cm\(^{-1}\) band which is attributed to OH-groups inside the sodalite cages polarised by Lewis acid sites, was also reduced [28]. This seems to indicate that the acid used to dealuminate the samples was more selective to the aluminium species inside the sodalite cages rather than the supercages. Figure 5-8 summarises the location of the bridging-OH groups.
5.3.1.1.3.2 Accessibility of the Acid Sites to Pyridine

Accurate quantification of the acidic sites is necessary to understand the effect of such sites on the catalytic performance during the alkylation reaction. Pyridine is usually used as a probe base to determine the Brønsted and Lewis acidity of zeolites [33]. However, pyridine might be too bulky to interact with some acid sites. Acidic sites located in small and in distorted channels, channel distortion usually arises from dealumination, might not be accessible to pyridine. The accessibility of pyridine to the acidic sites can be determined from the FTIR spectra of the zeolites. The OH stretching bands of acidic sites accessible to pyridine should be neutralised upon the adsorption of pyridine and thus its band should disappear from the spectra.

5.3.1.1.3.2.1 Brønsted Acid Sites

Brønsted acidity in zeolites arises from bridging-OH groups [27]. Figure 5-9 shows the relation between the area of the bands associated with bridging-OH groups, located at 3624, 3564 and 3527 cm\(^{-1}\) and Brønsted acidity.

The linear relation indicated that most of the bridging-OH groups were accessible to pyridine. This result was anticipated since the kinetic diameter of pyridine, 5.85 Å [29] is lower than the pore size of zeolite Y, 7.40 Å [30].

Figure 5-8: Variation of the location of the bridging-OH groups with the Si/Al ratio of zeolite Y
Lewis Acid Sites

The dealumination procedure used to dealuminated zeolite Y(2.6) led to the formation of extra-framework aluminium species (EFAL). The location of the OH-stretching bands associated with EFAL species is around 3666 cm\(^{-1}\) and 3598 cm\(^{-1}\) [26, 31].

Zeolite Y(2.6) had the highest Lewis acidity amongst the zeolites listed above (Table 5-4). However not all Lewis acid sites were accessible to pyridine. Figure 5-10 shows the spectra collected before and after the introduction of pyridine to zeolite Y(2.6).

The band located at 3666 cm\(^{-1}\) was shifted after the introduction of pyridine and displayed high intensity which signified that not all the pyridine was accessible to the acidic sites located at 3666 cm\(^{-1}\). The shift in the band could be explained by the interaction between the electrostatic fields associated with EFAL species and adsorbed bases [31], a similar shift was also observed by Corma [25]. The band at 3598 cm\(^{-1}\) also displayed high intensity after
the pyridine adsorption which indicated lower accessibility to the acidic sites located in the EFAL. The acidic OH-stretching regions in the remaining zeolites, Y(6), Y(15) and Y(30) disappeared upon the addition of pyridine indicating better accessibility to the Lewis acid sites (Figure 5-11).

This result could indicate that in zeolite Y(2.6), the Lewis acid sites not accessible to pyridine were located in distorted channels. The kinetic diameter of pyridine can be assumed to be the same as benzene which has a kinetic diameter of 5.85 Å [29]. The butene used in the catalytic experiment, cis-2-butene, had a kinetic diameter of 5.00 Å [32] which indicated that a portion of Lewis acid sites located in the distorted channels were certainly accessible to the feed butenes.

5.3.1.2 Influence of La³⁺ Exchange

5.3.1.2.1 Elemental Analysis

The elemental analysis for the ion exchanged zeolites is provided in Table 5-5. An increase in the Si/Al ratio was observed due to the acidity of the lanthanum salt solution during the ion exchange process. The pH of the solution was ~ 5.0. It should be noted that the sodium content in the catalysts was below 0.1 wt. %. An example of the degree of ion exchange (La-EX) calculations is provided in appendix (C).
Table 5-5: Elemental analysis of the lanthanum exchanged samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>No. of ion-exchanges</th>
<th>Si/Al (EDX)</th>
<th>La wt.% (EDX)</th>
<th>% La-EX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>0</td>
<td>2.60</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>1 LaE</td>
<td>1</td>
<td>2.66</td>
<td>3.88</td>
<td>24.56</td>
</tr>
<tr>
<td>3 LaE</td>
<td>3</td>
<td>2.74</td>
<td>4.85</td>
<td>30.70</td>
</tr>
<tr>
<td>6 LaE</td>
<td>6</td>
<td>3.34</td>
<td>10.62</td>
<td>67.20</td>
</tr>
</tbody>
</table>

The effect of the number of ion exchanges on the dealumination and the degree of ion-exchange is summarised in Figure 5-12. It is important to note that an intermediate calcination step was conducted for the 6LaE catalyst to increase the degree of ion-exchange.

5.3.1.2.2 BET Surface Area and Pore Volume

The BET surface area and pore volume are reported in Table 5-6. A decrease in the surface area and pore volume was observed after the initial ion-exchange. This decrease can be attributed to higher degrees of ion-exchange which were shown to decrease both the surface area and pore volume in zeolite Y [10].

Table 5-6: Effect of La$^{3+}$ exchange on the surface area and pore volume of zeolite Y(2.6)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>591</td>
<td>0.24</td>
</tr>
<tr>
<td>1 LaE</td>
<td>603</td>
<td>0.24</td>
</tr>
<tr>
<td>3 LaE</td>
<td>541</td>
<td>0.22</td>
</tr>
<tr>
<td>6 LaE</td>
<td>472</td>
<td>0.18</td>
</tr>
</tbody>
</table>
5.3.1.2.3 Crystallinity
X-ray diffraction was used to examine the effect of the lanthanum ion-exchange on the zeolite’s crystallinity. The reference material used to calculate the crystallinity was the ammonium form of the zeolite. Figure 5-13 shows the XRD patterns of the lanthanum exchanged samples along with the ammonium and protonic form of the zeolite.

A decrease in the crystallinity of the zeolites was observed upon the lanthanum exchange. Furthermore, as the number of lanthanum exchange increased, the crystallinity decreased. This can be attributed to the removal of aluminium during the ion-exchange process. Figure 5-14 shows the relation between the relative crystallinity and the degree of ion-exchange.
5.3.1.2.4 Acidic Properties of the Lanthanum-Exchanged Zeolites

The acidic properties of the zeolites were significantly altered upon the lanthanum exchange. A combination of dealumination and replacement of the bridging-OH groups by La-OH species altered the acidic properties of the zeolite. Infrared spectroscopy in association with pyridine desorption experiments was used to investigate the changes in the acidic properties of the zeolites.

5.3.1.2.4.1 OH-Stretching Region

The infrared spectra of the ion exchanged samples are presented in Figure 5-15. The terminal silanol Si-OH band located at $3743 \text{ cm}^{-1}$ showed a decrease upon lanthanum exchange. The decrease in the band intensity implies that lanthanum species interacted with the Si-OH groups. Although the Si-OH groups are non-acidic, the polarisation of the Si-OH bond due to the presence of extraframework aluminium species, especially in high aluminium zeolites, can increase the polarity of the bond [33]. The increased polarisation of the Si-OH bond can induce an interaction with the lanthanum species thus reducing the intensity of the band. This might also indicate the presence of lanthanum on the surface of the zeolite.

Furthermore, the bands associated with EFAL species were also decreased. The band at $3666 \text{ cm}^{-1}$ showed a slight decrease while the band at $3598 \text{ cm}^{-1}$ was significantly decreased. The decrease in the EFAL bands can be attributed to the dealumination of the zeolite during the ion exchange.
The bridging hydroxyl groups were also altered upon the lanthanum exchange. A significant and progressive reduction in the bridging-OH groups inside the zeolite’s supercages, located at 3624 cm\(^{-1}\), was observed upon the ion-exchange. The decrease in the bridging-OH groups inside the supercages can be attributed to the interaction of the lanthanum with such groups. Lee and Rees found that \(\sim 17\%\) of the lanthanum remained in the supercages of zeolite Na-La-Y rather than fully migrating to the sodalite cages [11]. In this work, the bridging-OH groups in the sodalite cages, located at 3564 cm\(^{-1}\) and 3527 cm\(^{-1}\) also showed a decrease in the intensity from the original Y(2.6). The decrease can be explained by lanthanum-OH replacing up to 3 bridging-OH groups in the sodalite cages [10]. Moreover, a slight shoulder located at 3532 cm\(^{-1}\) was also observed in the 6LaE sample which can indicate the presence of lanthanum species inside the sodalite cages in larger quantities due to a higher degree of ion exchange [26].

### 5.3.1.2.4.2 Pyridine Desorption Results

Pyridine desorption experiments were conducted to identify the nature and the strength of the acid sites. Figure 5-16 shows the FTIR spectra after pyridine desorption at different temperatures (150, 300, 450 °C).

![FTIR spectra after pyridine desorption](image)

Figure 5-16: FTIR spectra after pyridine desorption at different temperatures for A: Y(2.6), B: 1LaE, C: 3LaE and D: 6LaE

The acidity of the zeolites was significantly altered after the ion-exchange. Table 5-7 describes the acidity changes with the lanthanum exchange. After the ion-exchange, all the
tested catalysts displayed a reduction in both the Brønsted and Lewis acid sites. The 3LaE zeolite displayed the highest ratio of strong Brønsted/Lewis acid sites. The additional calcination step in the 6LaE catalyst seemed to reduce the B/L ratio at 450 °C despite the higher degree of ion-exchange.

Table 5-7: Pyridine-FTIR desorption results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Y(2.6)</th>
<th>1La E</th>
<th>3La E</th>
<th>6La E</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T_{des}(°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-B (mmol/g)</td>
<td>0.84</td>
<td>0.47</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>Py-L (mmol/g)</td>
<td>0.82</td>
<td>0.47</td>
<td>0.47</td>
<td>0.32</td>
</tr>
<tr>
<td>B/L</td>
<td>1.02</td>
<td>1.01</td>
<td>0.94</td>
<td>1.18</td>
</tr>
<tr>
<td>B+L (mmol/g)</td>
<td>1.66</td>
<td>0.94</td>
<td>0.91</td>
<td>0.70</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-B (mmol/g)</td>
<td>0.74</td>
<td>0.39</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Py-L (mmol/g)</td>
<td>0.46</td>
<td>0.26</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td>B/L</td>
<td>1.61</td>
<td>1.49</td>
<td>1.30</td>
<td>1.81</td>
</tr>
<tr>
<td>B+L (mmol/g)</td>
<td>1.20</td>
<td>0.65</td>
<td>0.62</td>
<td>0.54</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-B (mmol/g)</td>
<td>0.30</td>
<td>0.10</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Py-L (mmol/g)</td>
<td>0.34</td>
<td>0.16</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>B/L</td>
<td>0.88</td>
<td>0.62</td>
<td>0.75</td>
<td>0.74</td>
</tr>
<tr>
<td>B+L (mmol/g)</td>
<td>0.64</td>
<td>0.26</td>
<td>0.28</td>
<td>0.21</td>
</tr>
<tr>
<td>Py-B_{150}/Py-B_{150}</td>
<td>0.35</td>
<td>0.21</td>
<td>0.27</td>
<td>0.23</td>
</tr>
<tr>
<td>Py-L_{150}/Py-L_{150}</td>
<td>0.41</td>
<td>0.34</td>
<td>0.34</td>
<td>0.38</td>
</tr>
</tbody>
</table>

5.3.2 Catalytic Results

5.3.2.1 Effect of Si/Al Ratio

5.3.2.1.1 Initial Catalytic Behaviour

The initial 2-butene conversion and product distribution are compared in Table 5-8. The C8 selectivity was clearly dependent on the Si/Al ratio even at high conversions (X > 90%). The low Si/Al zeolites Y(2.6) and Y(6) exhibited higher initial C8 selectivity with zeolite Y(2.6) reaching a C8 selectivity of 89 wt. %. The C8 selectivity decreased with increasing the Si/Al ratio reaching a value of 11.94 wt. % in Y(30). In similar fashion to zeolite Beta, a high aluminium content and thus high acidity was required for alkylation while the oligomerisation of butenes can occur even on a weekly acidic catalyst. Moreover, the C9-C12 fraction was
also directly tied to the zeolite’s acidity with zeolite Y(2.6) producing the least amount of the C₉-C₁₂ fraction while the content of the fraction increased with increasing the Si/Al ratio. The high number of acidic sites available for the reaction in zeolite Y(2.6) maintained high butene conversion and thus suppressed the oligomerisation reaction. The low number of acid sites available for the reaction in the more siliceous zeolites led to a drop in the conversion levels which promoted oligomerisation.

Table 5-8: Effect of Si/Al ratio on the initial alkylation activity of zeolite Y

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Butene Conversion (%)</th>
<th>C₁₆-C₁₈ Fraction Selectivity (wt. %)</th>
<th>Composition of C₈ Fraction (%)</th>
<th>TMP Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₅-C₇</td>
<td>C₈</td>
<td>C₉-C₁₂</td>
</tr>
<tr>
<td>Y(2.6)</td>
<td>100</td>
<td>2.54</td>
<td>89.03</td>
<td>8.24</td>
</tr>
<tr>
<td>Y(6)</td>
<td>95.64</td>
<td>3.79</td>
<td>53.64</td>
<td>32.96</td>
</tr>
<tr>
<td>Y(15)</td>
<td>93.33</td>
<td>0.73</td>
<td>17.97</td>
<td>53.27</td>
</tr>
<tr>
<td>Y(30)</td>
<td>92.01</td>
<td>0.63</td>
<td>11.94</td>
<td>50.57</td>
</tr>
</tbody>
</table>

Within the C₈ fraction, the high aluminium Y zeolites, Y(2.6) and Y(6), exhibited the highest selectivity towards trimethylpentanes (TMPs), around 80%, while the TMP content significantly dropped with increasing Si/Al ratios due to the lack of acid sites available for the alkylation reaction. The TMP distribution varied significantly between the zeolites. The high aluminium Y zeolite Y(2.6), due to high acidity, showed the highest content of the primary product of the alkylation reaction (2,2,3 TMP) indicating faster hydride transfer rates [34]. The content of the 2,2,3 TMP decreased with increasing Si/Al ratios which indicated that the hydride transfer rate was significantly tied to the zeolite’s acidity. The low hydride transfer
rates in the high Si/Al zeolites forced the 2,2,3 alky-cation to isomerise to mostly to the 2,3,4 and 2,3,3 TMPs indicating the steric constraints inside the zeolite pores. Furthermore, the content of the smallest TMP, the 2,3,4 TMP increased with increasing Si/Al ratio which indicates the steric limitations in the more siliceous Y zeolites.

5.3.2.1.2 Catalytic Stability
The catalytic stability of the Y zeolites with varying Si/Al ratio is presented in Figure 5-17. The high aluminium zeolite Y(2.6) showed the highest catalytic stability while increasing the Si/Al of the zeolites led to lower activity and faster deactivation. Zeolite Y(2.6) maintained high conversions and started to deactivate after 4 hours while the deactivation occurred immediately in all the other investigated zeolites.

![Figure 5-17: Effect of Si/Al on the butene conversion of zeolite Y](image)

The lack of acid sites available for the hydride transfer in the siliceous zeolites caused the conversion level to drop. Once the conversion dropped, the increase in the olefin concentration inside the zeolite’s pores and around the remaining acidic sites promoted oligomerisation that produced bulky molecules which blocked the channels and caused further deactivation. Therefore, high acidity was essential to maintain the catalyst stability.

The C₈ selectivity was also significantly affected by the zeolite’s acidity. Figure 5-18 showed how the C₈ selectivity varied with time. The low Si/Al zeolite Y(2.6) exhibited the highest C₈ selectivity with the C₈ selectivity decreasing from 89 wt. % to 36 wt. %. Zeolite Y(6) also produced higher C₈s than Y(15) and Y(30) albeit being much lower than Y(2.6). The
siliceous zeolites $Y(15)$ and $Y(30)$ showed a low $C_8$ selectivity due to the reduction in the acidic sites available for alkylation.

Figure 5-18: Effect Si/Al on the time-on-stream $C_8$ selectivity zeolite $Y$

The $C_{12}^+$ fraction also increased with time (Figure 5-19). The build-up of bulky molecules in the zeolite’s pores might have led to the oligomerisation and dimerisation of butenes since coke was proposed as a hydride transfer medium for dimerisation and oligomerisation [35].

Figure 5-19: Effect of the Si/Al ratio on the $C_{12}^+$ selectivity of zeolite $Y$
5.3.2.1.3 Effect of the Turnover

The varying acidity of the tested zeolites meant that the butene turnover of the zeolite’s acidic sites was not even. At lower acidity, the turnover of butenes over the acidic sites of the zeolite was much higher than at a high acidity. Comparing the effect of the turnover on the conversion and TMP selectivity can provide insight on the effect of the dealumination on the zeolite activity. Assuming that only acidic sites accessible to pyridine contributed in the reaction, the butene turnover can be calculated from equation 4-1 and the results are presented in Figure 5-20.

![Figure 5-20: Effect of the turnover on the butene conversion behaviour during the alkylation reaction over zeolite Y](image)

The turnover behaviour indicated that the catalytic stability of the zeolites was slightly improved with the dealumination. The improvement in the turnover seems to have an optimum at Y(15). This can be attributed to the significant decrease in the Lewis acid sites (Table 5-4).

![Figure 5-21: Effect of the turnover on the TMP selectivity during the alkylation reaction over zeolite Y](image)
The TMP selectivity however did not follow the same trend. Increasing the Si/Al ratio of the zeolites led to a significant decrease in the TMP selectivity (Figure 5-21). This indicated that, in similar fashion to zeolite Beta (section 4.3.2.1.3), the TMP production seemed to require the presence of two adjacent acidic sites which was proposed to stabilise the alkyl-cation prior to the hydride transfer step [35]. The decrease in the aluminium content of the zeolite increased the distance between the acidic sites leading to decreasing the TMP production due to the lack of acid sites adjacency.

5.3.2.1.4 Overall Product Distribution

The overall product distribution is presented in Table 5-9. The butene conversion levels were clearly dependent on the zeolite’s acidity. Zeolite Y(2.6) exhibited the highest conversion level due to its high acidity. The conversion levels dropped with increasing the Si/Al ratio due to the lack of acid sites required for the reaction.

Table 5-9: Effect of Si/Al on the overall product distribution after 7 hours on stream

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y(2.6)</td>
</tr>
<tr>
<td>Butene Conversion (%)</td>
<td>89.04</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
</tr>
<tr>
<td>C5-C7</td>
<td>4.15</td>
</tr>
<tr>
<td>C8</td>
<td>67.45</td>
</tr>
<tr>
<td>C9-C12</td>
<td>23.47</td>
</tr>
<tr>
<td>C12+</td>
<td>4.93</td>
</tr>
<tr>
<td>Composition of C8 Fraction (%)</td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>80.22</td>
</tr>
<tr>
<td>DMHs</td>
<td>10.45</td>
</tr>
<tr>
<td>MHs</td>
<td>7.52</td>
</tr>
<tr>
<td>Other C8</td>
<td>1.81</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>25.91</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>13.54</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>27.04</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>33.51</td>
</tr>
</tbody>
</table>

The acidity of the zeolite seemed to have had the highest impact on the butene conversion. Figure 5-22 correlates the overall butene conversion with the zeolite’s acidity. The high
number of acidic sites available for the reaction in zeolite Y(2.6) maintained the olefin conversion levels high thus reducing the oligomerisation, which was the main cause of the catalytic deactivation. The butene conversion levels were progressively lowered with the decreasing acidity. Thus high acidity seems essential to maintain the stability of the zeolite.

The acidity of the zeolite also contributed towards the formation of C₈s (Figure 5-23). Zeolite Y(2.6) showed the highest C₈ content due to its high acidity while the C₈ content decreased rapidly with decreasing acidity. The high C₈ selectivity in zeolite Y(2.6), coupled with the low C₁₂⁺ selectivity indicated that the acidity required for the alkylation reaction was higher than the acidity required for both the oligomerisation and cracking. The C₁₂⁺ fraction was significantly decreased with the increase in the zeolite’s acidity. The high number of acidic sites available for the reaction maintained the olefin concentration low and limited the formation of the large C₁₂⁺ molecules while the lack of acid sites available for the alkylation reaction enhanced the oligomerisation and dimerisation of the butene to produce heavier molecules.

![Figure 5-22: Effect of the zeolite’s acidity on the butene conversion](image)

![Figure 5-23: Effect of acidity on the C₈ selectivity (A) and C₁₂⁺ selectivity (B) over zeolite Y](image)
Zeolites Y(6) and Y(15) had similar Brønsted concentration, 0.37 mmol/g and 0.33 mmol/g respectively (Table 5-4). Furthermore, zeolite Y(15) had significantly lower Lewis acidity, 0.20 mmol/g, compared to 0.56 mmol/g in Y(6). It can be fairly speculated that Y(15) should be more active to the reaction since it has a higher B/L ratio and similar Brønsted acidity. The results however indicated that Y(6) produced less oligomerisation products and more alkylates. This can be attributed to the inductive effect of the EFAL species which increased the polarisation of bridging-OH bonds thus increasing its strength [33].

The composition of the C₈s was also significantly affected by the acidity of the zeolite. High acidity contributed to the formation of the high-octane value TMPs while the decreasing acidity increased the formation of the thermodynamically-favoured and less octane-value DMHs.

The TMP distribution was also affected by the acidity of the catalyst. The primary product of the alkylation reaction, the 2,2,3 TMP is highest in Y(2.6) indicating faster hydride transfer while it decreased with decreasing acidity which indicated that the hydride transfer was much slower in the remaining zeolites. Moreover, the production of the smallest TMP, the 2,3,4 TMP increased with decreasing acidity due to the steric hindrance facing the TMP alkyl-cation as a result from the formation of the C₁₂⁺ molecules around the acidic site of the zeolite.

5.3.2.2 Effect of La³⁺ Exchange

5.3.2.2.1 Initial Catalytic Behaviour

The initial catalytic results, presented in Table 5-10, showed that all the catalysts had complete initial butene conversion. The differences in the acidity profiles of the catalysts did not reduce the initial catalytic activity of the zeolites as opposed to zeolites with varying Si/Al ratios where the variation in the Si/Al ratio resulted in differing initial catalytic activity and selectivity (Table 5-7).

The fraction selectivity showed similar distribution as well. Minor differences were observed in the C₈ selectivity while the heavy fractions (C₉-C₁₂ and C₁₂⁺) were slightly reduced upon the introduction of lanthanum. The C₈ fraction showed higher TMP selectivity in the lanthanum-exchanged samples. Furthermore, the lanthanum exchanged samples produced less DMHs and MHs. This indicated that the introduction of lanthanum improved the hydride transfer rates thus reducing the steric restrictions inside the pores of the zeolite. Another indication of the improved hydride transfer rates was the increase in the 2,2,3 TMP
selectivity which increased upon the ion exchange with lanthanum. Furthermore, the ion-exchanged samples produced less 2,3,4 TMP indicating improved steric conditions.

Table 5-10: Effect of La exchange on the initial catalytic results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Y(2.6)</th>
<th>1 LaE</th>
<th>3 LaE</th>
<th>6 LaE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Butene Conversion (%)</strong></td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td><strong>Time-on-stream (h)</strong></td>
<td>1.00</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td><strong>Fraction Selectivity (wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>2.54</td>
<td>3.27</td>
<td>3.38</td>
<td>2.45</td>
</tr>
<tr>
<td>C₈</td>
<td>89.03</td>
<td>89.85</td>
<td>90.01</td>
<td>89.97</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>8.24</td>
<td>6.76</td>
<td>6.61</td>
<td>6.90</td>
</tr>
<tr>
<td>C₁₂⁺</td>
<td>0.19</td>
<td>0.12</td>
<td>0.00</td>
<td>0.68</td>
</tr>
<tr>
<td><strong>Composition of C₈ Fraction (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>80.13</td>
<td>88.20</td>
<td>91.11</td>
<td>90.73</td>
</tr>
<tr>
<td>DMHs</td>
<td>12.62</td>
<td>9.29</td>
<td>5.91</td>
<td>5.87</td>
</tr>
<tr>
<td>MHs</td>
<td>6.88</td>
<td>2.51</td>
<td>2.98</td>
<td>3.40</td>
</tr>
<tr>
<td><strong>TMP Distribution (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>26.88</td>
<td>37.62</td>
<td>37.88</td>
<td>34.83</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.48</td>
<td>14.19</td>
<td>18.60</td>
<td>14.68</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.51</td>
<td>19.00</td>
<td>8.00</td>
<td>20.53</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>32.13</td>
<td>29.19</td>
<td>35.52</td>
<td>29.96</td>
</tr>
</tbody>
</table>

5.3.2.2.2 Catalytic Stability

The catalytic stability, presented in Figure 5-24, indicated that the ion-exchanged samples exhibited higher stability than the original zeolite Y(2.6). The reduction in the strong Lewis acid sites led to improved catalytic stability despite the reduction in the Brønsted acidity. Zeolite 3LaE, which had the highest concentration of strong Brønsted/Lewis (Py-B/Py-L) ratio (Table 5-7) had the highest catalytic stability amongst the ion-exchanged samples.
Furthermore, the C₈ selectivity also can highlight the role of Lewis acidity. In the alkylation reaction, the hydride transfer step was proposed to occur only on Brønsted acid sites while Lewis acid sites enhance the oligomerisation [36]. The reduction in the Brønsted acidity of the lanthanum exchanged samples did not reduce the C₈ selectivity significantly indicating that the reduction in the Lewis acidity was the main cause of the improved selectivity (Figure 5-25). Furthermore, lanthanum can also generate Brønsted acidity which could compensate for the loss of Brønsted acidity during the dealumination and the ion-exchange [12].
Comparing the TMP selectivity as a function of conversion indicated that at similar conversions, zeolite Y(2.6) produced the most TMPs (Figure 5-26). This can be attributed to the higher number of Brønsted acid sites in Y(2.6) which continued to produce TMPs while the deactivation was ensuing.

Figure 5-26: TMP selectivity as function of the butene conversion for the La$^{3+}$ exchanged catalysts

The C$_{12}^{+}$ fraction originated from the oligomerisation of the C$_8$ alkyl-cation with butenes to produce larger molecules. The reduction in the Lewis acidity in the lanthanum exchanged samples reduced the oligomerisation reaction thus reducing the C$_{12}^{+}$ fraction as shown in Figure 5-27.

Figure 5-27: The effect of La$^{3+}$ ion-exchange on the C$_{12}^{+}$ selectivity
5.3.2.2.3 Overall Product Distribution

The overall product distribution is presented in Table 5-11. After 10 hours on stream, all the catalysts maintained high butene conversion levels, above 80%. However, all the ion-exchanged samples had higher overall butene conversion levels ~90%.

Table 5-11: Effect of lanthanum exchange on the overall product distribution

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>Y(2.6)</td>
</tr>
<tr>
<td></td>
<td>80.14</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>3.16</td>
</tr>
<tr>
<td>C₈</td>
<td>54.38</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>32.08</td>
</tr>
<tr>
<td>C₁₂+</td>
<td>10.38</td>
</tr>
<tr>
<td>Composition of C₈ Fraction (%)</td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>66.07</td>
</tr>
<tr>
<td>DMHs</td>
<td>22.67</td>
</tr>
<tr>
<td>MHS</td>
<td>6.44</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>24.33</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.91</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.12</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>34.64</td>
</tr>
</tbody>
</table>

The reduction in Lewis acidity reduced the oligomerisation of butenes thus helped maintain high conversion levels. Lanthanum exchange seemed to reduce the oligomerisation activity as lanthanum-OH groups compensated the loss of Brønsted acidity. Interestingly, the catalyst with the highest ratio of strong Brønsted/strong Lewis (Py-B/Py-L)₄₅₀ had the highest stability. The reduction in the strong Lewis sites, Py-L₄₅₀, seemed to have the highest impact on the overall butene conversion. Strong Lewis acidity was also proposed to be the main cause of the catalyst deactivation [4]. The strength of the electrostatic fields in such sites caused the olefins to be preferentially adsorbed and oligomerise due to the polarity of the olefins, hence the improvement from the parent Y(2.6) zeolite [34]. Similar trends were also observed by Guzman and Sievers [12, 15] who attributed the zeolite deactivation to the strong Lewis acidity.
The C₈ fraction was also improved due mainly to the improved conversion levels as shown in Figure 5-28.

![Diagram](image1)

**Figure 5- 28: Effect of the butene conversion on the C₈ selectivity**

Within the C₈ fraction, the TMP content significantly improved upon the lanthanum exchange. The 3LaE catalyst had the highest overall TMP content due to its low number of strong Lewis acid sites. The improved TMP production seemed to be a function of the improved C₈ production as shown in Figure 5-29.

Moreover, the lanthanum exchanged catalysts produced significantly less MHs and DMHs indicating better hydride-transfer rates and less steric limitations. Another indication of the improved hydride transfer was the increase in the 2,2,3 TMP content. Additionally, the lower content of the 2,3,4 TMP in the lanthanum exchanged zeolites indicated lesser steric restrictions.

![Diagram](image2)

**Figure 5- 29: TMP selectivity as a function of the C₈ fraction**
5.4 Conclusions

The effect of Si/Al and lanthanum ion exchange on the alkylation performance of zeolite Y was studied in a well-mixed reactor. The highest aluminium content zeolite had significantly improved performance. Increasing the Si/Al ratio significantly decreased the catalyst lifetime and alkylate selectivity. The reduction in the catalyst conversion was attributed to low acidity and the decrease. The turnover behaviour indicated that the conversion was slightly improved in the lower Si/Al zeolites. The TMP selectivity however was reduced by increasing the Si/Al which could indicate that the TMP production requires the presence of adjacent acidic sites.

Lanthanum exchange significantly improved the alkylation performance of zeolite Y mainly due to the reduction in strong Lewis acidity. The accompanied reduction in the Bronsted acidity upon the introduction of lanthanum was attributed to the lanthanum species replacing up to 3 bridging hydroxyl groups in the zeolite’s framework. Lewis acidity was reduced due to the acid-leaching of aluminium during the ion exchange procedure. The optimum number of lanthanum exchanges was three exchanges followed by calcination. This procedure created the highest ratio of strong-Bronsted/strong-Lewis ratio ($\text{Py-B/Py-L}_{450}$) and enhanced the catalytic stability. Increasing the exchange levels beyond three exchanges seem to decrease the ratio of strong-Bronsted/strong-Lewis ($\text{Py-B/Py-L}_{450}$).

5.5 References


6. The Effect of Catalyst Dilution by Inert Additives on the Alkylation Activity of Zeolite Y
6.1 Introduction

The alkylation reaction produces a wide mixture of products. During high activity, the catalyst produces mainly C₈s while at low activity the oligomerisation/cracking reactions prevail. The catalytic deactivation is due to the formation of large molecules which causes pore blockage [1]. The blockage of the zeolite’s pores leads to an increases in the olefin concentration around the acidic sites thus promoting further oligomerisation. In addition, the heavy molecules, once formed, can be adsorbed on an adjacent zeolite clusters thus promoting further deactivation [2]. Furthermore, olefins are preferentially adsorbed inside the zeolite’s pores due to their polarisable nature which will increase their concentration around the acidic sites, especially in high alumina zeolites [3]. It was reported by Simpson et al. that the alkylation reaction is severely diffusion limited [4] while another study by the same group identified the intra-particle diffusion limitations as the major cause of deactivation in zeolite Y [5]. The majority of the reported literature work focused on increasing the Brønsted acidity while maintaining very low Lewis acidity that is known to promote oligomerisation [6-8]. It is therefore ostensibly that the separation of the zeolite clusters can enhance the removal of the large molecules from the catalyst’s pellet without causing further deactivation, thus alleviating the intra-particle diffusion limitations. Moreover, the use of inert materials can reduce the preferential olefin adsorption associated with Lewis acidity thus reducing the oligomerisation.

The use of zeolite without a binder in industrial applications is very rare [9, 10]. The low self-binding property of the zeolites necessitates the use of binders for zeolite-based catalysts [11]. Silica, alumina and clay binders are typically used to control the catalyst shape and hence they provide the catalyst with mechanical and thermal stability. Furthermore, the binders also provide additional physical and chemical properties based on the type of the binder used. Hargreaves and Munnoch summarised the binder effects on the catalyst as follows [12]:

1. Modification of the coking properties.
2. Poison entrapment.
3. Transfer of reactants/products to or from the catalytically-active phase.
4. Improved heat transfer properties.
5. Alteration of the catalyst porosity.
6. Improved mechanical strength.

The alkylation reaction has been extensively researched yet surprisingly, there is only little published work involving catalyst dilution. The alkylation reaction is extremely diffusion limited due to the plugging of the catalyst pores by oligomerised products [5]. Moreover, the heavy hydrocarbons can be transferred and adsorbed on adjacent catalytic layers promoting
further deactivation [2, 13]. The only reported alkylation work involving catalytic dilution was conducted by Taylor and Sherwood. The catalyst used by the authors was an H-USY based catalyst composed of 80% USY (Si/Al ~ 3) and 20% alumina binder. The type of the alumina was not disclosed. However, the authors did not vary the type or the content of the binder [14]. In one of the AlkyClean process patents, the authors claimed that using an alumina binder with a Faujasite-based catalyst improved the product's octane values; the optimum alumina content was reported to be 20% [15].

Alumina binders alter both the physical and chemical properties of the catalysts. Choudhary et al. introduced alumina and kaolin binders at 10 and 50 wt. % to H-Ga-MFI used for propane aromatisation. The authors concluded that the external acidity increased by the addition of the alumina while the internal acidity remained constant while the kaolin binder decreased both. Moreover, the shape selectivity of the catalyst increased with the use of binders due to increased coking [16]. Wu et al. introduced both alumina and silica binders to ZSM-5 and Y zeolites. The acidity of the catalysts increased with the addition of alumina while it decreased after the addition of silica. Furthermore, the porosity of the catalyst was reduced in both cases. The cited authors suggested that alumina was inserted into the zeolite as extraframework aluminium species hence the increase in acidity. However no further analysis was conducted to confirm the transfer of aluminium into the zeolite [11] although other studies have confirmed the transfer of aluminium to the zeolite [17, 18]. Lee et al. examined the effect of silica, alumina and aluminium phosphate (APS) on the performance of ZSM-5 during the methanol to propylene process. The authors found that the acidity increased upon the addition of the alumina and decreased with the addition of silica. The mechanical strength of the catalyst was considerably improved upon the addition of the APS followed by the alumina while the silica binder had the lowest crush strength. Furthermore, the addition of the APS significantly reduced the strong acid sites, most probably due to the dilution of the catalyst, which enhanced propylene selectivity [19].

Michels et al. studied the effect of silica, alumina and clay binders on the catalytic conversion of pyrolysis oil over ZSM-5. The increased acidity of the catalysts containing the alumina led to increased coke formation and furan production whereas the catalysts containing silica and clay produced aromatics exclusively [20].

The interaction of ions from the binder with the zeolite can greatly affect the catalytic properties of the zeolite. de Lucas et al. used bentonite as a binder for Pd-MOR, Pd-ZSM-5 and Pd-Beta whilst studying the skeletal hydroisomerisation of n-octane. The solid-state ion-exchange with sodium ions from the bentonite reduced the acidity of the zeolite. Furthermore, the meso- and macro-porosity provided by the binder significantly improved the selectivity of the catalysts especially zeolite Beta [9]. Dorado et al. compared bentonite and montmorillonite as binders for Pd-ZSM-5 during the hydroisomerisation of n-butane. The
cited authors confirmed the transfer of sodium ions from the clay binders into the zeolite thus reducing the acidity. The reduction in the acidity reduced the n-butane conversion however this was compensated by an increase in the isobutane selectivity due to a combination of improved porosity and reduced disproportionation [10].

It is therefore apparent that the catalyst dilution by inerts/binders can significantly alter the chemical and physical properties of the catalyst and alleviate the diffusional limitations in the alkylation reaction. Also, the separation of the zeolite clusters by inert materials could perhaps reduce the preferential olefin adsorption around the clusters. Therefore, the selection of an appropriate additive type and content can significantly improve the catalytic performance.

6.2 Experimental

6.2.1 Materials
Zeolite USY, (Si/Al = 2.6, CBV 500) was provided by Zeolyst international while the MCM-41 was provided by ACS Materials, the γ-Al₂O₃, was provided by Alfa Aesar and the fumed silica was provided by Sigma-Aldrich (S5130). SBA-15 was synthesised using the procedure provided by Zholobenko et al. [21]. The SBA-15 was extracted with ethanol 5 times prior to calcination to remove the template.

6.2.2 Catalyst Preparation and Testing
The Y zeolite was calcined in a muffle furnace at a ramp rate of 0.5 °C/min to 450 °C and held for 6 hours to transform the zeolite into its protonic form. For mixtures, the ammonium zeolite was mixed with the additive in deionised water using a magnetic stirrer for 3 hours at room temperature to ensure appropriate mixing. The catalyst was then filtered and dried for 16 hours at 110 °C. After drying, the catalyst was rehydrated in open air for 3 hours. The catalyst was then calcined in the same furnace using the same temperature and ramping rate.

6.3 Results and Discussion

6.3.1 Catalyst Characterisation

6.3.1.1 X-ray Diffraction
The x-ray diffraction patterns of some the materials used in this work are provided in Figure 6-1. Moreover, an example of the variations in the XRD patterns upon the addition of the Al₂O₃ to zeolite Y is shown in Figure 6-2.
Figure 6- 1: Low-angle XRD patterns for MCM-41 (A) and SBA-15 (B)

Figure 6- 2: XRD pattern of the catalysts containing Al₂O₃

6.3.1.2 SEM

The SEM images of a group of materials used in this work are presented in Figure 6-2. An example of the SEM images of some mixed catalysts is provided in Figure 6-3.

Figure 6- 3: SEM images of A: Zeolite Y, B: MCM-41 and C: Al₂O₃
6.3.1.3 BET Measurements

The BET surface area and pore volume of the materials used in this work are provided in Table 6-1. The materials selected to conduct this experiment had different surface areas. It should be noted that the fumed silica was non-porous and hence had no pore volume.

Table 6-1: BET measurement results

<table>
<thead>
<tr>
<th>Catalyst/Additive</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y</td>
<td>591</td>
<td>0.24</td>
</tr>
<tr>
<td>MCM-41</td>
<td>1087</td>
<td>0.88</td>
</tr>
<tr>
<td>SBA-15</td>
<td>882</td>
<td>0.58</td>
</tr>
<tr>
<td>Fumed Silica (F.S.)</td>
<td>388</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>101</td>
<td>0.01</td>
</tr>
</tbody>
</table>

6.3.1.4 Acidity Measurements

The pyridine desorption results at 150 °C of the parent materials are provided in Table 6-2. The MCM-41 exhibited low acidity which indicated the presence of aluminium in small quantities. The SBA-15 and fumed silica showed no acidity due to the absence of aluminium in their structures. The alumina meanwhile showed higher acidity, specifically Lewis acidity, typically observed in alumina.

Table 6-2: Acidity measurements for the materials used in this work

<table>
<thead>
<tr>
<th>Catalyst/Additive</th>
<th>Py-B (mmol/g)</th>
<th>Py-L (mmol/g)</th>
<th>B/L</th>
<th>B+L (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y</td>
<td>0.84</td>
<td>0.82</td>
<td>1.02</td>
<td>1.66</td>
</tr>
<tr>
<td>MCM-41</td>
<td>0.01</td>
<td>0.05</td>
<td>0.20</td>
<td>0.06</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>F.S.</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.00</td>
<td>0.18</td>
<td>0.00</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Figure 6-4: SEM images of the 20% F.S. and the 20% Al₂O₃ catalysts
The acidity measurements for the mixtures containing MCM-41 and Al₂O₃ at 20 wt. % are provided in Table 6-3. For the MCM-41, the Brønsted acidity exhibited close values to the theoretical values while the Lewis acidity varied more while in the case of the alumina, the opposite was observed.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Py-B (mmol/g)</th>
<th>Py-L (mmol/g)</th>
<th>B/L</th>
<th>B+L (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Y</td>
<td>0.84</td>
<td>0.82</td>
<td>1.02</td>
<td>1.66</td>
</tr>
<tr>
<td>20% MCM-41</td>
<td>0.69</td>
<td>0.40</td>
<td>1.73</td>
<td>1.09</td>
</tr>
<tr>
<td>20% Al₂O₃</td>
<td>0.51</td>
<td>0.60</td>
<td>0.84</td>
<td>1.11</td>
</tr>
</tbody>
</table>

This could be attributed to the variation during the calcination process which could reduce the Lewis acidity since MCM-41 is much less hydrophilic than both alumina and zeolite Y and thus could reduce the auto-steaming during the calcination leading to a reduction in the Lewis acidity. Variation in the mixing and sampling could also affect the acidity measurements.

The alumina meanwhile could block the pyridine from accessing some of the Brønsted acid sites due to its low porosity thus affecting the quantification of such sites since not all pyridine was accessible to the acidic sites of alumina as shown in Figure 6-5.

![Figure 6-5: FTIR spectra of the alumina before and after pyridine adsorption in the OH-stretching region](image)

Varying the MCM-41 content indicated a similar trend as the Brønsted acidity values were close to their theoretical values, calculated from the acidity measurements in Table 6-2, while the Lewis acidity varied more as presented in Figure 6-6.
In the case of alumina, both Brønsted and Lewis acidities were below the theoretical values as shown in Figure 6-7. This could be attributed to the reduced accessibility of pyridine to the acidic sites due to its low porosity (Figure 6-5).

It is interesting to note that at the highest alumina dilution level, the acidity measurements were closest to their theoretical calculated values. This could be explained by the improved mixing of the zeolite in the additive which ensured that the sample taken from the mixture for the acidity measurements was a representative one.

6.3.2 Catalytic Results

6.3.2.1 Effect of the Additive Type

6.3.2.1.1 Initial Catalytic Behaviour

The initial conversion and product distribution results are provided in Table 6-4. All the tested catalysts showed complete initial 2-butene conversions suggesting that the reduction
of the active-sites in the reactor did not affect the initial activity. Additionally, the product distribution was also remarkably similar with the $C_8$ selectivity values around 90%. The catalysts containing the meso-porous silica (MCM-41 and SBA-15) had the highest $C_8$ selectivity and the lowest $C_{12+}$ content. The improved product selectivity can be attributed to the separation of the zeolite clusters by the addition of inerts (dilution effect). The catalyst dilution reduced the preferential olefin adsorption in and around the zeolite clusters and that reduced the oligomerisation. The TMP content of the $C_8$ fraction also improved as a result of the reduced oligomerisation. All the catalysts had improved TMP content in comparison to the original H-Y catalyst. The catalysts containing the meso-porous silica (MCM-41 and SBA-15) had the highest TMP content but the TMP content decreased in the remaining catalysts. The improvement in the TMP content can also be attributed to the reduced oligomerisation and enhanced hydride transfer. The TMP distribution also showed that the primary reaction product, 2,2,3 TMP, increased from its initial value of 12.48% in the original H-Y. This finding is usually observed when operating at higher OSV because the alkyl-cation has less time to isomerise to the other TMPs [22].

Table 6-4: Effect of the additive type on the initial alkylation activity

<table>
<thead>
<tr>
<th>Initial Catalytic Results</th>
<th>H-Y</th>
<th>20% MCM-41</th>
<th>20% SBA-15</th>
<th>20% F.S.</th>
<th>20% γ-Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Product Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_5$-$C_7$</td>
<td>2.54</td>
<td>4.21</td>
<td>4.36</td>
<td>3.87</td>
<td>3.09</td>
</tr>
<tr>
<td>$C_8$</td>
<td>89.03</td>
<td>93.15</td>
<td>91.15</td>
<td>89.02</td>
<td>89.81</td>
</tr>
<tr>
<td>$C_9$-$C_{12}$</td>
<td>8.24</td>
<td>2.55</td>
<td>4.38</td>
<td>6.91</td>
<td>6.98</td>
</tr>
<tr>
<td>$C_{12+}$</td>
<td>0.19</td>
<td>0.09</td>
<td>0.11</td>
<td>0.20</td>
<td>0.12</td>
</tr>
<tr>
<td>Composition of $C_8$ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>80.13</td>
<td>89.01</td>
<td>87.80</td>
<td>86.66</td>
<td>84.10</td>
</tr>
<tr>
<td>DMHs</td>
<td>12.62</td>
<td>7.64</td>
<td>8.28</td>
<td>8.98</td>
<td>8.05</td>
</tr>
<tr>
<td>MHS</td>
<td>6.88</td>
<td>3.35</td>
<td>3.92</td>
<td>4.36</td>
<td>7.85</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>26.88</td>
<td>32.43</td>
<td>34.06</td>
<td>32.46</td>
<td>32.59</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.48</td>
<td>16.38</td>
<td>15.39</td>
<td>14.47</td>
<td>12.54</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.51</td>
<td>20.50</td>
<td>20.08</td>
<td>21.96</td>
<td>17.02</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>32.13</td>
<td>30.69</td>
<td>30.47</td>
<td>31.11</td>
<td>37.85</td>
</tr>
</tbody>
</table>

6.3.2.1.2 Catalytic Stability

The effect of the additive type on the catalytic stability of the zeolite is shown in Figure 6-8. Remarkably, all the additive-containing catalysts showed an improved catalytic stability in comparison to the original H-Y regardless of the reduction in the acidic sites. The parent H-Y
zeolite started to deactivate after 4 hours on stream reaching a final conversion value of 57% while the remaining catalysts showed improved stability. The catalysts containing both MCM-41 and SBA-15 had the best catalytic stability reaching a final butene conversion value of 88% and 85% respectively followed by the fumed silica catalyst which had a final conversion value of 76%; whereas the catalyst containing the alumina had the lowest final conversion of 63%.

The improvement in the catalyst stability from the parent H-Y zeolite can be explained by the dilution of the zeolite. Increasing the distance between the zeolite clusters reduced the preferential olefin adsorption in and around the zeolite clusters leading to a reduction in the olefin concentration around the acidic sites. This allowed the major products (C₈ alkyl-cation) to undergo hydride transfer with the isobutane to concomitantly desorb from the catalyst without oligomerising with the 2-butene.

Moreover, the C₈ selectivity differed here from the original H-Y catalyst as shown in Figure 6-9. When the silica inerts were added, the C₈ selectivity of the catalysts significantly improved while the catalyst containing the alumina produced similar C₈s to the Y zeolite. The original H-Y zeolite showed the lowest initial and final selectivity whereas the catalysts containing the additives had improved alkylates production with the C₈ selectivity mimicking the conversion trends albeit being at lower values.

Figure 6-8: Effect of the additive type on the catalytic stability of zeolite Y during the alkylation reaction

The improvement in the catalyst stability from the parent H-Y zeolite can be explained by the dilution of the zeolite. Increasing the distance between the zeolite clusters reduced the preferential olefin adsorption in and around the zeolite clusters leading to a reduction in the olefin concentration around the acidic sites. This allowed the major products (C₈ alkyl-cation) to undergo hydride transfer with the isobutane to concomitantly desorb from the catalyst without oligomerising with the 2-butene.

Moreover, the C₈ selectivity differed here from the original H-Y catalyst as shown in Figure 6-9. When the silica inerts were added, the C₈ selectivity of the catalysts significantly improved while the catalyst containing the alumina produced similar C₈s to the Y zeolite. The original H-Y zeolite showed the lowest initial and final selectivity whereas the catalysts containing the additives had improved alkylates production with the C₈ selectivity mimicking the conversion trends albeit being at lower values.
Given the acidic properties of the active sites in the catalyst, the zeolite, was not significantly altered; the TMP content of the C₈ fraction seemed to be unaffected by the introduction of the additives (Figure 6-10).

Catalytic deactivation during the alkylation reaction is a result of the formation of large molecules from the oligomerisation reaction. The C₁₂+ fraction was specifically tied to the deactivation since it caused pore blockages. The effect of the additive type on the C₁₂+ selectivity is presented in Figure 6-11.
The C_{12}^+ compounds were significantly limited by the dilution of catalyst. Silica compound in particular significantly reduced the C_{12}^+ fraction. The improvement in the hydride transfer as a result of the dilution suppressed the oligomerisation of the C_8 alkyl-cation and promoted alkylation instead.

Comparing the C_{12}^+ selectivity as a function of conversion (Figure 6-12) showed that at similar conversion levels, the catalysts containing the porous silica additives had the highest selectivity to C_{12}^+. Increasing the porosity of the additive allowed the C_{12}^+ molecule to desorb from the catalyst without it being adsorbed on an adjacent zeolite cluster, which in turn reduced pore blockage and deactivation in that cluster.
6.3.2.1.3 Overall Product Distribution

The overall product distribution after 10 hours on stream is presented in Table 6-5 and all the catalysts maintained high butene conversion levels >80%. All the modified catalysts had higher overall conversion than the parent H-Y zeolite. A significant improvement in the butene conversion was noticed in the catalysts containing the meso-porous silica additives (MCM-41 and SBA-15). The improvement in the conversion results were attributed to the dilution of the zeolite clusters which reduced the preferential olefin adsorption in and around the zeolite clusters thus limiting the oligomerisation reaction.

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-Y</td>
</tr>
<tr>
<td>Total Butene Converted (%)</td>
<td>80.14</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>3.16</td>
</tr>
<tr>
<td>C₈</td>
<td>54.38</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>32.08</td>
</tr>
<tr>
<td>C₁₂⁺</td>
<td>10.38</td>
</tr>
<tr>
<td>Composition of C₈ Fraction (%)</td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>66.07</td>
</tr>
<tr>
<td>DMHs</td>
<td>22.67</td>
</tr>
<tr>
<td>MHS</td>
<td>6.44</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>24.33</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.91</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.12</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>34.64</td>
</tr>
</tbody>
</table>

The conversion results seem to be correlated with the additive’s surface area as shown in Figure 6-13. Increasing the porosity of the additive allowed the bulky molecules to desorb from the catalyst pores without being adsorbed on an adjacent zeolite cluster thus limiting the deactivation.
Moreover, the Lewis acidity provided by the alumina also contributed to the lower conversion levels. The silica additives exhibited non/insignificant Lewis acidity and thus did not enhance the olefin adsorption. Comparing the silica additives only showed that the there was a near-linear correlation between the additive’s surface area and the overall butene conversion as presented in Figure 6-14. This indicated that although the alumina helped in diluting the zeolite clusters, it also enhanced the olefin adsorption due to its higher Lewis acidity.

The fraction selectivity also showed that the separation of the zeolite clusters improved the C₈ selectivity. The dilution of the zeolite clusters helped to maintain high butene conversion which inhibited the oligomerisation. The C₈ selectivity exhibited a significant resemblance to
the conversion behaviour with the meso-porous silica producing the highest C₈s and the least C₁₂⁺ (Figure 6-15).

High conversion resulted in high C₈ selectivity due to the reduced olefin concentration around the acidic site of the catalyst and that limited the formation of the C₁₂⁺ fraction; a well-known characteristic of the alkylation reaction (Figure 6-16).

Within the C₈ fraction, the overall TMP content also improved from the H-Y catalyst. Moreover, the TMP content also varied amongst the different additives and seems to correlate with the additive’s surface area (Figure 6-17 A). Moreover, the TMP/DMH ratio also mimicked the TMP content of the C₈ fraction with the meso-porous silica additives exhibiting higher TMP/DMH ratios indicating better hydride transfer rates (Figure 6-17 B).
The catalysts containing the inert additives showed different TMP distribution from the H-Y zeolite. The thermodynamically favoured 2,2,4 TMP, which has the largest kinetic diameter and transition-state intermediate amongst the TMPs [24], was higher in all modified catalysts indicating less steric hindrance inside the pores.

### 6.3.2.2 Effect of MCM-41 Addition at Different Levels

#### 6.3.2.2.1 Initial Catalytic Results

To further understand the effect of the additives, the percentage of MCM-41 was increased to 40 wt. % and 60 wt. %. The initial catalytic results are shown in Table 6-6. Despite the catalysts having significantly less active sites, complete initial conversion levels were observed. It should be noted that the olefin space velocity was based on the weight of the entire catalyst and not the H-Y zeolite content.

The C₈ selectivity was also improved upon the addition in larger amounts of MCM-41. Although the active sites available for alkylation were reduced, the performance of such sites improved due to the dilution effect. The dilution of the zeolites reduced the olefin concentration which helped to promote alkylation instead of oligomerisation and therefore the heavy fractions, C₉-C₁₂ and C₁₂+ were also reduced.
Table 6-6: Effect of the MCM-41 levels on the initial alkylation activity

<table>
<thead>
<tr>
<th>Initial Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-Y</td>
</tr>
<tr>
<td>Butene Conversion (%)</td>
<td>100.00</td>
</tr>
<tr>
<td><strong>Fraction Selectivity (wt. %)</strong></td>
<td></td>
</tr>
<tr>
<td>C5-C7</td>
<td>2.54</td>
</tr>
<tr>
<td>C8</td>
<td>89.03</td>
</tr>
<tr>
<td>C9-C12</td>
<td>8.24</td>
</tr>
<tr>
<td>C12+</td>
<td>0.19</td>
</tr>
<tr>
<td><strong>Composition of C8 Fraction (%)</strong></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>80.13</td>
</tr>
<tr>
<td>DMHs</td>
<td>12.62</td>
</tr>
<tr>
<td>MHS</td>
<td>6.88</td>
</tr>
<tr>
<td><strong>TMP Distribution (%)</strong></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>26.88</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.48</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.51</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>32.13</td>
</tr>
</tbody>
</table>

The TMP content also increased and the TMP distribution changed upon the addition of the MCM-41. The content of the 2,2,3 TMP, the primary product from the reaction of 2-butene with isobutane, increased due to an increase in the effective flow rate over the active sites which reduced the time available for the 2,2,3 TMP alkyl-cation to isomerise. Also, the production of the thermodynamically favoured 2,2,4 TMP was higher than the H-Y catalyst indicating less steric limitations inside the zeolite’s pores.

6.3.2.2.2 Catalytic Stability

The catalytic stability of the catalysts containing the MCM-41 is presented in Figure 6-18. A high catalytic stability was observed upon the addition of the MCM-41 despite the reduction in the catalytic sites available for the reaction. Even the 60% MCM-41 catalysts which had less than 40% of the acidity of the H-Y zeolite exhibited more stability and less deactivation than the unmodified zeolite. The improvement in the catalytic stability was the result of the dilution of the zeolite clusters with the non-reactive meso-porous MCM-41.
Moreover, the C₈ selectivity improved from the original H-Y catalyst as shown in Figure 6-19. When the MCM-41 levels were varied, the C₈ selectivity of the catalysts significantly improved from the H-Y catalyst. However the selectivity decreased with the progressive addition of the MCM-41. This indicated that although a significant improvement in the conversion and selectivity was achieved due to the enhanced separation and dilution of the zeolite clusters, the deactivation seemed inevitable due to the high Lewis acidity of the zeolite.
The C_{12}^+ selectivity also decreased as a result of the dilution of the zeolite clusters which reduced the preferential olefin adsorption and led to a decrease in the oligomerisation. Successive addition of the MCM-41 content led to an increase in the C_{12}^+ selectivity albeit being at lower values than the parent H-Y catalyst as shown in Figure 6-20.

![Figure 6-20: Effect of MCM-41 levels on the C_{12}^+ selectivity](image)

Furthermore, the enhanced porosity of the catalysts as a result of the MCM-41 addition allowed the bulky hydrocarbons to desorb from the catalyst pellet without becoming adsorbed on adjacent zeolite clusters. At similar conversion levels, the catalysts containing the MCM-41 produced more C_{12}^+ molecules which indicated that the enhanced porosity of the catalyst assisted in the desorption of the bulky hydrocarbons (Figure 6-21).

![Figure 6-21: Effect of conversion on the C_{12}^+ selectivity](image)
6.3.2.2.3 Effect of the Turnover

In the previous experiments, the olefin space velocity was calculated based on the weight of the entire catalyst and not the weight of the active part, i.e. the zeolite. Therefore, the olefin flow over the acidic sites was not equal. In order to study the performance of the acidic sites, the turnover behaviour should be considered. Assuming that only acid sites accessible to pyridine contributed to the reaction, the turnover can be calculated from eq 4-1.

The conversion of the catalysts containing the MCM-41 as a function of the turnover is presented in Figure 6-22 and the catalysts containing MCM-41 had evidently higher conversion at higher turnovers than the parent H-Y. However, increasing the MCM-41 content to 60% slightly improved the turnover. The variation of the conversion results with respective turnover between the catalysts containing MCM-41 is in contrast to what have been proposed by Nirvathy [25] and Taylor and Sherwood [14].

![Figure 6-22: Effect of the turnover on the conversion](image)

In the cited work above, the olefin space velocity was varied by changing the catalyst weight while maintaining a constant olefin flow rate. The authors agreed on the conclusion that the amount of butene turnover was only a function of the number of active sites of the catalyst. However, the physical properties of the catalysts presented in the current work were significantly altered by the introduction of the MCM-41. While the active sites (zeolite) remain relatively unchanged, the porosity of the catalyst was significantly improved. Moreover, increasing the amount of MCM-41 in the catalyst evidently led to higher zeolite dilution that could decrease the olefin concentration in and around the zeolite clusters leading to a significant reduction in the oligomerisation and enhanced C₈ selectivity (Figure 6-23).
Figure 6-23: Effect of the turnover on the C8 selectivity

The improvement in the conversion clearly improved the C8 selectivity as shown in Figure 6-23. Although the 20% MCM-41 and the 40% MCM-41 catalysts were similar, the 60% MCM-41 catalyst had improved C8 selectivity due to the reduction in the olefin concertation around the acidic sites. This promoted hydride transfer and limited oligomerisation.

Figure 6-24: Effect of the butene turnover on the C12+ selectivity

As the MCM-41 content increased, the preferential olefin adsorption was decreased which improved the catalyst lifetime by limiting the oligomerisation reaction. The turnover behaviour indicated that increasing the MCM-41 content from 40 wt. % to 60 wt. % slightly lowered the production of the C12+ molecules as shown in Figure 6-24. No significant
changes were observed between 20% and 40% MCM-41 catalysts. Once the deactivation occurred, the higher porosity of the 60% MCM-41 catalyst allowed the C_{12}^+ molecules to desorb without being adsorbed on adjacent zeolite clusters which in turn contributed to the increase in the catalyst turnover.

6.3.2.2.4 Overall Product Distribution
The overall product distribution is provided in Table 6-7. Evidently all the modified catalysts had significantly higher conversion levels. Despite the progressive reduction of the number of active sites, the performance of such sites was significantly improved due to a combination of catalyst dilution and enhanced porosity.

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-Y</td>
</tr>
<tr>
<td>Total Butene Converted (%)</td>
<td>80.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction Selectivity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_5-C_7</td>
</tr>
<tr>
<td>C_8</td>
</tr>
<tr>
<td>C_9-C_{12}</td>
</tr>
<tr>
<td>C_{12}^+</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition of C_8 Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPs</td>
</tr>
<tr>
<td>DMHs</td>
</tr>
<tr>
<td>MHs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TMP Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4 TMP</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
</tr>
</tbody>
</table>

The improvement in the conversion behaviour also led to a significant increase in the C_8 selectivity and a reduction in the C_{12}^+ formation as shown in Figure 6-25. Although successive additions of the MCM-41 slightly improved the turnover, the initial addition of the MCM-41 seems to have had the most significant on the catalyst stability and alkylate selectivity.
The improved conversion levels upon the addition of the MCM-41 also improved the C_8 selectivity and suppressed the C_{12+} production due to the dilution of the zeolite clusters (Figure 6-26). The 60% MCM-41 catalyst produced higher C_8s at lower conversion levels due to its higher turnover (Figure 6-26 A).

Figure 6- 25: Effect of the MCM-41 content on the butene conversion (A) and the C_{12+} selectivity (B)

6.3.2.3 Effect of γ-Alumina Addition at Different Levels

6.3.2.3.1 Initial Catalytic Results
The effects of the acidity and reduced porosity provided by the alumina were examined by increasing the γ-alumina to 40 wt. % and 60 wt. %. The initial catalytic results are provided in Table 6-8. Despite the significant reduction of the zeolite content in the catalyst, the initial conversion levels were almost complete (x > 99 %) and the fraction selectivity resembled the parent H-Y catalyst. The C_8 selectivity of the catalysts containing the Al_2O_3 was also very close to the parent H-Y whilst the C_{12+} fraction was also similar despite the significant
difference in the zeolite content. The similarity of the conversion and product distribution indicates that initially, the dilution of the zeolite clusters counteracted the reduction of the active sites and the increase in the Lewis acidity.

Table 6-8: Effect of Al₂O₃ addition at different levels on the initial catalytic results at t = 1 h

<table>
<thead>
<tr>
<th>Initial Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-Y</td>
</tr>
<tr>
<td>Butene Conversion (%)</td>
<td></td>
</tr>
<tr>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>2.54</td>
</tr>
<tr>
<td>C₈</td>
<td>89.03</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>8.24</td>
</tr>
<tr>
<td>C₁₂⁺</td>
<td>0.19</td>
</tr>
<tr>
<td>Composition of C₅ Fraction (%)</td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>80.13</td>
</tr>
<tr>
<td>DMHs</td>
<td>12.62</td>
</tr>
<tr>
<td>MHs</td>
<td>6.88</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>26.88</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.48</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.51</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>32.13</td>
</tr>
</tbody>
</table>

Additionally, the TMP content of the modified catalysts slightly improved from the parent H-Y whilst the production of DMHs was inhibited due to the catalyst dilution. The reduction of the DMHs indicated that the TMP alkyl-cation faced less steric hindrance in the modified catalysts due to the catalyst dilution. Moreover, the TMP distribution also confirms that the modified catalysts faced less steric limitations since all the modified catalysts had a lower ratio of the 2,3,4 TMP that has the lowest kinetic diameter amongst the TMPs [24].

6.3.2.3.2 Catalytic Stability

The catalytic stability after the Al₂O₃ addition is presented in Figure 6-27. The catalytic stability was improved upon the initial addition of the alumina yet further increments decreased the conversion levels due to the lack of acid sites available for the reaction.
The C₈ selectivity also benefited from the improved conversion of the 20% Al₂O₃ catalyst which produced slightly more C₈s. Increasing the Al₂O₃ content beyond 20% did not improve the C₈ selectivity as the 40% Al₂O₃ and 60% Al₂O₃ catalysts produced less C₈s as shown in Figure 6-28. This further suggests that despite the improved zeolite dispersion, the diffusional constraints and the increased Lewis acid sites might counteract the dilution.

The initial Al₂O₃ addition slightly lowered the C₁₂+ selectivity (Figure 6-29). Further increments led to an increase in the C₁₂+ selectivity albeit being at lower levels than the differences found in the zeolite content. This indicated that the turnover behaviour might improve upon the addition of the alumina due to the dilution of the zeolite. For the time-on-stream:

![Figure 6-27: Effect of Al₂O₃ addition on the catalytic stability of zeolite Y(2.6) during the alkylation reaction](image1)

![Figure 6-28: Effect of Al₂O₃ addition on the time-on-stream C₈ selectivity during the alkylation reaction over zeolite Y (2.6)](image2)
stream behaviour, the alumina seemed to counteract the catalyst dilution due to a combination of decreased porosity and enhanced Lewis acidity.

![Figure 6-29: Effect of Al2O3 levels on the time-on-stream C12+ selectivity during the alkylation reaction over zeolite Y(2.6)](image)

6.3.2.3.3 Effect of Butene Turnover
The addition of alumina reduced the active sites available for alkylation due to the reduction in the zeolite content. Therefore, the turnover might provide better insight on the catalytic performance than the time-on-stream. The butene turnover can be calculated from eq 4-1. The conversion results as a function of the turnover as shown in Figure 6-30.

![Figure 6-30: Effect of the turnover on the conversion of the catalyst containing the alumina during the alkylation reaction over zeolite Y(2.6)](image)

The initial addition of the alumina improved the turnover behaviour while, in contrast to the MCM-41 results, further additions of alumina did not improve the conversion suggesting that the Lewis acidity and the decreased porosity of the alumina seemed to counteract the
dilution. Moreover, the C₈ selectivity also mirrored the conversion results with the initial dilution only providing improved C₈s as shown in Figure 6-31.

Figure 6-31: Effect of the turnover on the C₈ selectivity of the catalysts containing alumina and zeolite Y(2.6)

In similar fashion to the conversion, increasing the alumina content did not improve the C₈ selectivity. Furthermore, the reduction in the C₁₂⁺ selectivity was dependant on the initial addition of alumina whilst increasing the alumina content marginally reduced the C₁₂⁺ fraction (Figure 6-32).

Figure 6-32: Effect of turnover on the C₁₂⁺ selectivity of the catalysts containing alumina and zeolite Y(2.6)
6.3.2.3.4 Overall Product Distribution

The overall product distribution after 10 hours on-stream is provided in Table 6-9. Despite the significant reduction of the active-site density, the 20% Al₂O₃ catalyst had higher overall conversion than the parent H-Y. Also, the C₈ selectivity slightly improved upon the initial addition of the alumina while it decreased below the parent's in the 40 wt. % Al₂O₃ and 60% wt. % Al₂O₃ catalysts.

Table 6-9: Effect of Al₂O₃ addition on the overall catalytic results of zeolite Y(2.6) during the alkylation reaction

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-Y</td>
</tr>
<tr>
<td>Total Butene Converted (%)</td>
<td>80.14</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td>3.16</td>
</tr>
<tr>
<td>C₈</td>
<td>54.38</td>
</tr>
<tr>
<td>C₇-C₁₂</td>
<td>32.08</td>
</tr>
<tr>
<td>C₁₂⁺</td>
<td>10.38</td>
</tr>
<tr>
<td>Composition of C₈ Fraction (%)</td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>66.07</td>
</tr>
<tr>
<td>DMHs</td>
<td>22.67</td>
</tr>
<tr>
<td>MHS</td>
<td>6.44</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>24.33</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.91</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.12</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>34.64</td>
</tr>
</tbody>
</table>

Furthermore, the C₁₂⁺ selectivity was decreased as a result of the initial addition of the alumina due to the zeolite dilution. Increasing the alumina content did not reduce the C₁₂⁺ selectivity and that was due to a combination of reduced porosity and increased Lewis acidity.
The improvement in the conversion levels upon the addition of alumina enhanced the $C_8$ selectivity and reduced the $C_{12+}$ selectivity as shown in Figure 6-34.

Enhancing the catalytic activity and stability seemed to have the most considerable impact on the product distribution. The increased alumina content did not improve the butene conversion after the initial step due to the combination of reduced porosity and enhanced Lewis acidity which counteracted the dilution by increasing the preferential olefin adsorption around the catalyst. This led to increased oligomerisation activity and reduced alkylation.

### 6.3.2.4 Measurement of the Deactivation Kinetics

The time-on-stream behaviour of the catalysts studied previously indicates that the catalytic deactivation seemed inevitable. The high Lewis acidity of the zeolite will eventually enhance the olefin adsorption around it leading to oligomerisation and deactivation. Upon the onset of the deactivation, the rate of the deactivation seems to differ between the catalysts tested.
above. Measurement of the deactivation rate constant can provide insights to accurately determine the effect of the additive type on the deactivation. Taylor and Sherwood proposed that the deactivation can be approximated by first order kinetics [14]. Although the reaction network is complex and involves many reaction pathways, the major reaction may be represented as:

\[ i - C_4 + C_4^+ \rightarrow \text{Products} \]  \hspace{1cm} (6-2)

Due to the high \( i\text{-C}_4/C_4^+ \) ratio used in the current work, \( i\text{-C}_4/C_4^+ = 15 \), the butene was considered as the limiting reactant and thus the disappearance of the butene can be used to determine the deactivation rate constant more accurately. The first-order disappearance of butene can be expressed as:

\[ -r_{2B} = k_r C_p \]  \hspace{1cm} (6-3)

where \( k_r \) is the reaction rate constant and \( C_p \) is the concentration of the butene in the reactor.

To measure the deactivation over time, a deactivation function \( d(t) \) must be introduced. Assuming first order deactivation, the deactivation function can be expressed as:

\[ d(t) = \exp(-k_d t) \]  \hspace{1cm} (6-4)

where \( k_d \) is the deactivation rate constant and \( t \) is the time-on-stream.

For a well-mixed heterogeneous CSTR, the reaction rate \( (r_{2B}) \) can be expressed as:

\[ -r_{2B} = F_{2B} X_{2B} / W_{\text{cat}} \]  \hspace{1cm} (6-5)

where \( F_{2B} \) is the flow rate of butene, \( X_{2B} \) is the butene conversion and \( W_{\text{cat}} \) is the weight of the catalyst.

However, since the active part of the catalyst is the zeolite, the concentration of the acidic sites inside the reactor ought to replace the catalyst weight. Hence \( W_{\text{cat}} \) was be replaced by the summation of the Brønsted and Lewis acidity for each catalyst factored by the weight of the catalyst inside the reactor in a similar fashion to the turnover calculations. Moreover, the weight-time factor \( \tau \) can be expressed by:

\[ \tau = C_f W_{\text{cat}} / F_{2B} \]  \hspace{1cm} (6-6)

where \( C_f \) is the butene concentration in the feed = 6.25% hence \( \tau \) can be calculated for each catalyst as:
\[ \tau = C_f (P_{Y_B} + P_{Y_l}) W_{cat}/F_{2B} \]  \hfill (6-7)

While \( C_p \) can be calculated from:

\[ C_p = C_f (1 - X_{2B}) = 6.25 (1 - X_{2B}) \]  \hfill (6-8)

Rearranging the equations above, equation 6-9 can be developed:

\[ \frac{X_{2B}}{1-X_{2B}} = k_r \tau \exp(-k_d t) \]  \hfill (6-9)

And hence,

\[ \ln \left[ \frac{X_{2B}}{1-X_{2B}} \right] = \ln[k_r \tau] - k_d t \]  \hfill (6-10)

Equation 6-10 is a straight line equation where the slope is the deactivation rate constant and the first order reaction rate constant is calculated from the intercept. Therefore, the model conversion can be calculated from

\[ X_{2B} = \frac{\exp(-k_d t) k_r \tau}{1+\exp(-k_d t) k_r \tau} \]  \hfill (6-11)

Figure 6-35 shows the model fit for the 20% MCM-41 and the 20% SBA-15 catalysts. The deactivation model seems to provide an accurate fit for the experimental data in the case of the 20% MCM-41 and 20% SBA-15 catalysts. However, the model fails to accurately estimate the deactivation behaviour in the remaining catalysts as shown in Figure 6-36.
To correct for the model deviation, additional consideration must be applied to incorporate the effect of pore blockages from the oligomerisation reaction. The catalytic activity in the alkylation reaction is characterised by three stages (Figure 6-37). Initially, the catalyst exhibits high activity and low deactivation followed by a stage where the build-up of large molecules inside the catalyst pores causes rapid deactivation. The third stage is the oligomerisation stage where the catalyst produces mostly oligomerised products yet the deactivation rate remains relatively constant due to the reactivity of the butene [1]. Figure 6-35 above shows that the model used can accurately estimate the conversion behaviour at the initial stage where the conversion levels are above ~ 85%. The high conversion levels observed in the 20% MCM-41 and 20% SBA-15 catalysts allowed for an accurate fit while the rapid loss of activity in the remaining catalysts necessitates incorporating a more intrinsic model which takes into account the accelerated deactivation from the formation of the oligomerised products and the adsorption of such products on the zeolite clusters.
Figure 6-37: The three stages of catalytic activity in the alkylation cycle

6.4 Conclusions

The use of inert additives to dilute and physically separate the zeolite clusters was shown to have a significant improvement on the alkylation activity of zeolite Y. The additives improved the catalyst lifetime by reducing the preferential olefin adsorption around the zeolite clusters and hence reducing the oligomerisation and promoting hydride transfer. Meso-porous silica compounds were shown to be the best additives due to their high porosity that allowed the C_{12} molecules, once formed, to desorb from the catalyst without being adsorbed on an adjacent active site. Increasing the surface area of the additive had a significant impact on the catalyst lifetime and alkylates selectivity with MCM-41 providing the best diluent due to its high surface area. Increasing the MCM-41 content had a minor improvement on the turnover behaviour of the catalyst due to the increased dilution of the zeolite clusters. The initial separation however seems to have had the highest impact while further additions suffered from diminishing returns. The initial addition of alumina was shown to improve the catalytic stability and alkylate selectivity of zeolite Y. Increasing the alumina content did not improve the catalyst turnover due to the Lewis acidity and reduced porosity of the alumina which counteracted the catalyst dilution.

Applying a first-order deactivation model to the conversion results indicated that such model accurately represents the reaction only under high activity. Once the reaction enters the rapid deactivation stage, the build-up of large molecules accelerates the deactivation and hence the first-order deactivation model will over-estimate the conversion. Incorporating a more fundamental model which takes into account the
interaction of the bulkier molecules with the additives and the effect of the porosity and acidity of the additive could assist in designing an improved alkylation catalyst.

6.5 References


7. *Comparison of Selected Catalysts for the Alkylation Reaction*
7.1 Introduction

Three dimensional large-pore zeolites were shown to be active for the alkylation reaction [1]. Zeolite Y in particular had the best overall selectivity and stability. The lowest Si/Al zeolite Y(2.6) had the highest catalytic stability and alkylate selectivity. Lanthanum exchange was also shown to significantly improve the stability of Y(2.6) Three ion-exchanges were shown to the optimum level due to the reduction in the strong Lewis acidity, which was shown to promote deactivation [2, 3]. Furthermore, the addition of inert mesoporous silica materials was shown to considerably improve the catalytic stability of the Y(2.6) zeolite. The dilution delayed the onset of oligomerisation while the enhanced porosity allowed heavy molecules to desorb from the catalyst without causing further blockages. The surface area of the inert had the highest impact on catalytic stability with the MCM-41 material providing the best diluent. The initial dilution level of 20 wt. % seems to have had the most significant improvement while further additions only improve the turnover slightly. Zeolite Beta (12.5) also exhibited the highest activity towards the alkylation reaction amongst the Beta zeolites. Comparing the optimum catalyst from each section of this work could provide better insight towards designing an improved alkylation catalyst.

7.2 Experimental

7.2.1 Catalyst Preparation

The preparation procedure for zeolite Beta (12.5) is available in section 4.2.2 while the preparation procedure for zeolites Y(2.6) and 3LaE are available in section 5.2.2. The 20% MCM-41: 80% Y(2.6) catalyst was prepared using the procedure in 6.2.2.

7.3 Results and Discussion

7.3.1 Catalyst Characterisation

7.3.1.1 BET Surface Area and Pore Volume

The BET surface area and pore volume values are reported in Table 7-1. A variation in the surface area and pore volume between the Y zeolite before and after the lanthanum exchange was observed due to the higher degree of ion-exchange.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(2.6)</td>
<td>591</td>
<td>0.24</td>
</tr>
<tr>
<td>3LaE</td>
<td>541</td>
<td>0.22</td>
</tr>
<tr>
<td>MCM-41</td>
<td>1087</td>
<td>0.88</td>
</tr>
<tr>
<td>Beta (12.5)</td>
<td>534</td>
<td>0.18</td>
</tr>
</tbody>
</table>
7.3.1.2 **Acidity Measurements**

The FTIR spectra of the materials used in this section is provided in Figure 7-1 while the acidity measurements are provided in Table 7-2.

![FTIR Spectra](image)

Figure 7-1: FTIR Spectra recorded before and after Pyridine desorption at 150 °C for A: Y(2.6), B: 3La E, C: MCM-41, D: 20% MCM-41 and E: Beta (12.5)

The acidity of the MCM-41 was negligible in comparison to the zeolites and hence it showed no activity under the reaction conditions.
Table 7-2: Acidity measurements for the materials used in this work

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Y(2.6)</th>
<th>3La E</th>
<th>20% MCM-41</th>
<th>MCM-41</th>
<th>Beta (12.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-B (mmol/g)</td>
<td>0.84</td>
<td>0.44</td>
<td>0.69</td>
<td>0.01</td>
<td>0.43</td>
</tr>
<tr>
<td>Py-L (mmol/g)</td>
<td>0.82</td>
<td>0.47</td>
<td>0.40</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>B/L</td>
<td>1.02</td>
<td>0.94</td>
<td>1.73</td>
<td>0.20</td>
<td>1.02</td>
</tr>
<tr>
<td>B+L (mmol/g)</td>
<td>1.66</td>
<td>0.91</td>
<td>1.09</td>
<td>0.06</td>
<td>0.85</td>
</tr>
</tbody>
</table>

7.3.2 Catalytic Results

7.3.2.1 Initial Catalytic Behaviour

The initial catalytic activity behaviour showed complete initial butene conversion levels (Table 7-3). The C₈ selectivity was relatively close between the Y-zeolites with the 20% MCM-41 producing the highest content of C₈s. Furthermore, the heavy fractions (C₉-C₁₂ and C₁₂+) were significantly reduced in all the modified catalysts. Within the C₈ fraction, the 3LaE produced the most TMPs and the least amount of DMHs and MHs. The increased TMP production indicated the improved hydride transfer rates due to the lanthanum exchange which enhanced its hydride transfer rates. Furthermore, the TMP distribution indicated that the lanthanum exchanged sample had higher transfer rates as evident by the increase in the 2,2,3 TMP.

Table 7-3: Initial catalytic results of Y(2.6), 20% MCM-41, 3LaE and Beta (12.5) catalysts

<table>
<thead>
<tr>
<th>Initial Product Distribution</th>
<th>Y(2.6)</th>
<th>20% MCM-41</th>
<th>3 LaE</th>
<th>Beta (12.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Time-on-stream (h)</td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction Selectivity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₇</td>
</tr>
<tr>
<td>C₈</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
</tr>
<tr>
<td>C₁₂+</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition of C₈ Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPs</td>
</tr>
<tr>
<td>DMHs</td>
</tr>
<tr>
<td>MHs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TMP Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4 TMP</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
</tr>
</tbody>
</table>
7.3.2.2 Catalytic Stability

The catalytic stability results of the parent zeolites Y(2.6), Beta (12.5) and the modified catalysts are shown in Figure 7-2. The catalytic stability for all the modified catalysts showed significant improvement over the parent Y zeolite. The 20% MCM-41 catalyst had the highest catalytic stability reaching a final conversion level of 88% after 10 hours on stream.

The separation of the zeolite clusters and the enhanced porosity of the catalyst delayed the onset of the oligomerisation and aided in the removal of the bulky hydrocarbons which improved its lifetime. The significant decrease in the strong Lewis acidity after the lanthanum exchange of the 3LaE catalyst reduced the deactivation. Comparing the catalytic stability of 20% MCM-41 and the 3LaE catalysts indicated that the improved porosity of the catalyst outweighed the reduction in the strong Lewis acidity resulting from the lanthanum exchange. This might indicate that in zeolite Y(2.6), the adsorption of the heavy molecules on the surface of the zeolite crystals may cause faster deactivation than the formation of such molecules inside the pores of the zeolite. Zeolite Beta meanwhile exhibited high stability compared to Y(2.6), however the C₈ selectivity of zeolite Beta was much lower.

The improved catalytic stability of the modified catalysts enhanced the C₈ selectivity at longer times-on-stream as shown in Figure 7-3. After 10 hours, the 20% MCM-41 had a final C₈ selectivity of 51 wt. %. In similar fashion to the conversion behaviour, the separation of the zeolite Y clusters by the meso-porous MCM-41 seemed to prevail over the lanthanum exchange. Zeolite Beta meanwhile produced the least amount of C₈s.
Furthermore, the oligomerisation activity was significantly reduced in the modified catalysts. The decrease in the strong Lewis acid sites in 3LaE reduced the preferential olefin adsorption leading to a reduction in the oligomerisation. The porosity of the 20% MCM-41, despite having a similar acidic nature to the Y(2.6) catalyst, allowed the oligomerised products to desorb from the catalyst pellet without interacting on adjacent zeolite clusters (Figure 7-4).

Figure 7- 3: Selectivity to C₈s as a function of time-on-stream

Figure 7- 4: Selectivity to C₁₂+ as a function of time-on-stream
Comparing the C\textsubscript{12}+ selectivity as a function of conversion indicated that at similar conversion levels, the most stable catalyst produced higher C\textsubscript{12}+ compounds (Figure 7-5). The addition of the inert meso-porous MCM-41 potentially allowed the removal of the heavy molecules from the catalyst without causing further deactivation. For the zeolites, it must be noted that the formation of the heavy hydrocarbons inside the pores seemed inescapable due to the Lewis acidity of the zeolite. The formation of the heavy molecules would eventually lead to pore blockages, which in turn, contributes to the loss of catalytic activity.

![Graph](image)

**Figure 7-5**: Effect of the butene conversion on the C\textsubscript{12}+ selectivity for the Y-based catalysts

### 7.3.2.3 Overall Product Distribution

The catalytic performance after 10 hours on stream is summarised in Table 7-4. The modified catalysts had higher conversion levels. In similar fashion to the time-on-stream behaviour, Figure 7-2, the dilution by the MCM-41 seemed to outperform the lanthanum exchange.

A significant increase in the C\textsubscript{8} selectivity in all the modified catalysts was observed as a result from the improved conversion levels. Furthermore, the heavy fraction production was significantly limited through a combination of reduced Lewis acidity and improved catalyst porosity. Within the C\textsubscript{8} fraction, the 20% MCM-41 had the highest TMP content due the dilution of the catalyst which enhanced alkylation selectivity. The 3LaE also had improved TMP production from the reduction in the strong Lewis acidity. The catalyst dilution seemed to have a larger influence on the overall TMP selectivity although as evident by the improved TMP content of the 20% MCM-41 in comparison to the 3LaE catalyst.
Table 7-4: Overall product distribution after 10 hours on stream

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>Y(2.6)</td>
</tr>
<tr>
<td></td>
<td>80.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction Selectivity (wt. %)</th>
<th>Y(2.6)</th>
<th>20% MCM-41</th>
<th>3La E</th>
<th>Beta (12.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₇</td>
<td>3.16</td>
<td>4.99</td>
<td>4.44</td>
<td>1.72</td>
</tr>
<tr>
<td>C₈</td>
<td>54.38</td>
<td>76.52</td>
<td>68.44</td>
<td>32.86</td>
</tr>
<tr>
<td>C₄-C₁₂</td>
<td>32.08</td>
<td>16.20</td>
<td>23.40</td>
<td>46.33</td>
</tr>
<tr>
<td>C₁₂⁺</td>
<td>10.38</td>
<td>2.29</td>
<td>3.72</td>
<td>19.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition of C₈ Fraction (%)</th>
<th>Y(2.6)</th>
<th>20% MCM-41</th>
<th>3La E</th>
<th>Beta (12.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPs</td>
<td>66.07</td>
<td>88.54</td>
<td>81.36</td>
<td>59.71</td>
</tr>
<tr>
<td>DMHs</td>
<td>22.67</td>
<td>10.01</td>
<td>15.07</td>
<td>23.16</td>
</tr>
<tr>
<td>MHs</td>
<td>6.44</td>
<td>1.44</td>
<td>1.80</td>
<td>9.55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TMP Distribution (%)</th>
<th>Y(2.6)</th>
<th>20% MCM-41</th>
<th>3La E</th>
<th>Beta (12.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4 TMP</td>
<td>24.33</td>
<td>31.07</td>
<td>32.12</td>
<td>42.97</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.91</td>
<td>13.12</td>
<td>15.33</td>
<td>12.59</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.12</td>
<td>23.80</td>
<td>18.77</td>
<td>30.21</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>34.64</td>
<td>32.01</td>
<td>33.78</td>
<td>14.23</td>
</tr>
</tbody>
</table>

The TMP distribution indicated that the 3LaE had the highest hydride transfer rates as evident by the high 2,2,3 selectivity. Furthermore, the 3LaE catalyst had the lowest content of 2,3,4 TMP which also indicated better steric conditions. This result could indicate that the deactivation in the 3LaE catalyst might be from the adsorption of heavy molecules on the zeolite’s surface rather than the build-up of such molecules inside the pores. Furthermore, all the modified catalysts had lower content of the 2,3,4 TMP, which has the lowest kinetic diameter, indicating less steric hindrance around the acidic sites. Figure 7-6 describes the relation between the overall conversion and the cumulative C₈ and C₁₂⁺ selectivity (zeolite Beta was excluded from the comparison due to its lower C₈ selectivity).

![Figure 7-6: Effect of the overall butene conversion on the cumulative selectivity of C₅⁺ (A) and C₁₂⁺ (B)](image)
7.4 Conclusions

Partial lanthanum-ion exchange and the addition of the inert meso-porous MCM-41 contributed to the enhanced catalyst lifetime of zeolite Y(2.6). Comparing both effects indicated that the addition of the MCM-41 outweighed the lanthanum exchange. This implies that the catalyst dilution, using a meso-porous non-acidic inert, reduced the preferential olefin adsorption more efficiently than the reduction of the strong Lewis acidity by the lanthanum exchange. Furthermore, the meso-porosity provided by the MCM-41 allowed the bulky C_{12}^{+} molecules to desorb from the catalyst without causing further deactivation. The TMP distribution indicated that the 3LaE catalyst had the highest hydride transfer rates and the lowest selectivity toward the smaller 2,3,4 TMP. This result could indicate that the deactivation of the 3LaE catalyst was mainly due to the adsorption of heavier molecules onto the zeolite rather than internal pore blockages. However, the formation of the C_{12}^{+} molecules would eventually lead to the deactivation of the catalyst. This work suggested that a combination of both partial lanthanum-ion exchange and the addition of the inert meso-porous MCM-41 could yield a further improved catalyst. Initial work has been carried out and encouraging results indicate improved performance. The preliminary results are discussed in Appendix F.

7.5 References

8. Conclusions and Recommendations
8.1 Conclusions

The production of high-quality, environmentally friendly gasoline remains a major challenge. Current and future global specifications necessitate the reduction of aromatics, sulfur and oxygenates in the gasoline pool thus reducing the content of reformulated and cracked gasoline \([1]\). The only other major refining processes capable of replacing the gasoline gap are the isomerisation and alkylation processes. Isomerisation requires C\(_5\)-C\(_9\) hydrocarbons which are liquids at ambient conditions while alkylation converts low value gases to higher value liquids that are free of aromatics, sulfur and nitrogen compounds \([2]\). Therefore both processes could work synergistically to reduce the gasoline gap.

Currently, alkylation processes employ highly corrosive acids that presents health and safety concerns along with the high mitigation costs associated with the use of such acids \([3-5]\). Solid and liquid acids have been and still are extensively researched to produce an alternative catalyst. Zeolites could present an ideal, cost-effective alternative to the current technologies due to their relatively benign nature.

Large-pore zeolites were shown to be active for the alkylation reaction with a product distribution high in TMPs \([6]\). The low lifetime typically observed in the alkylation over zeolite catalysts is attributed to the oligomerisation of butenes. The oligomerisation can be reduced by improving the mixing patterns inside the reactor. Increasing the agitation significantly improved the stability while other factors such as the catalyst loading and the feed entry location also improved the stability. Furthermore, three-dimensional large-pore zeolites Beta and Y were shown to favour the alkylation reaction while the single-channel system in MOR caused rapid deactivation and prevented the formation of alkylates. This was attributed to the lack of intersecting channels in MOR which could help to enhance the desorption of the bulky molecules.

Owing to its high stability during the alkylation reaction, zeolite Beta was further examined by varying the Si/Al ratio and incorporating lanthanum on to the zeolite to manipulate the B/L ratio. Reducing the aluminium content of the zeolite significantly reduced its alkylation capacity and enhanced the oligomerisation of butenes due to reduction in the acidic sites available for alkylation. The optimum Si/Al ratio was the lowest, 12.5. The turnover behaviour indicated that the conversion behaviour was improved while the TMP selectivity was reduced. The improvement in the conversion was attributed to the reduction in Lewis acidity while the deterioration in the TMP selectivity was attributed the reduction of adjacent acidic sites required to produce the TMPs. Incorporating lanthanum by impregnation reduced the Brønsted acidity and generated Lewis acidity, both were shown to be detrimental to the activity of the zeolite. The reduction in the Brønsted acidity was attributed to the interaction of lanthanum with the bridging-OH groups in the zeolite’s framework while
the increased Lewis acidity was attributed to the preparation procedure which generated EFAL species due to the acidity of the solution and the remaining nitrates from the lanthanum salt.

Zeolite Y due to its high acidity and large-pore structure was also examined. The Si/Al ratio of zeolite Y was shown to have a significant effect on its alkylation activity. The lowest Si/Al zeolite exhibited the highest stability and selectivity while increasing the Si/Al ratio decreased both. The dealumination reduced the acidity of the catalyst which reduced the number of acidic sites available for alkylation thus causing faster deactivation. The lower value of Lewis acidity in Y(15) was shown to reduce its performance when compared to Y(6) although both catalysts had close Brønsted acidity due to the loss of the inductive effect of EFAL in Y(15). Furthermore, the dealumination procedure seemed to selectively remove acidic sites located in the sodalite cages which could have increased the ratio of acidic sites in the supercages. The increased ratio of the acidic groups in the super cages could have influenced the formation of the bulky molecules. Metal-ion exchange with lanthanum provided significant catalytic stability even though the ion-exchange reduced both the Brønsted and Lewis acidity. The dealumination of the zeolite during the ion exchange removed EFAL hence reducing the Lewis acidity. The lanthanum species meanwhile provided Brønsted acidity to compensate for the sites lost during the dealumination, even though the total Brønsted acidity decreased. The optimum number of lanthanum exchanges was three exchanges since it produced the highest ratio of strong-Brønsted/strong-Lewis ratio $(\text{Py-B/Py-L})_{450}$. Increasing the number of exchanges decreased the ratio of $(\text{Py-B/Py-L})_{450}$ even though the degree of ion-exchange was increased.

The dilution of zeolite Y with inerts had the most significant impact on the stability and alkylation activity of the catalyst. The separation of the zeolite clusters reduced the preferential olefin adsorption which decreased the oligomerisation and promoted hydride transfer. All the materials used to dilute the zeolite produced a more active and stable catalysts than the parent Y zeolite even though the active sites in the catalysts were reduced. Silica materials in particular were shown improve the alkylation behaviour while alumina created additional Lewis acidity which increased the olefin concentration near the zeolite clusters. A correlation was observed between the surface area of the silica material and the overall butene conversion. MCM-41, which had the highest surface area, was shown to provide the best diluent for zeolite Y. Varying the MCM-41 content marginally improved the turnover indicating that the initial dilution seemed to be the most important step. Increasing the alumina content indicated that the turnover behaviour was independent from the alumina content due to the Lewis acidity and reduced porosity from the alumina which counteracted the catalyst dilution.
Overall, the combination of both the partial lanthanum-ion exchange and the addition of the inert meso-porous MCM-41 suggested a further improved catalyst with initial work showing encouraging improved performance (Appendix F).

8.2 Recommendations and Research Advancement

8.2.1 Reactor Type and Reactor Design

Industrial alkylation processes typically employ intricate reactor designs to ensure high levels of mixing to reduce the oligomerisation [7]. Although not economically favoured, the tendency of butenes to oligomerise to produce higher molecular weight compounds necessitates the use of unconventional reactors. High levels of butene dispersion become even more important for zeolites due to the propensity of zeolites to preferentially adsorb polarisable molecules [8]. Thus a CSTR-like reactor would be the most feasible for a zeolite-based technology. Another alternative could be the use of a fluidised bed reactor in similar fashion to the FCC process to enable continuous catalyst regeneration. Figure 8-1 shows a concept reactor for the alkylation process.

Figure 8-1: Concept stirred reactor for the alkylation of isobutane with butene showing a proposed way for ensuring high internal recycles, adopted from [9].

8.2.2 Zeolite Structures

Large-pore three-dimensional zeolites were shown to be active for the alkylation reaction. Zeolites Beta and in particular zeolite Y are the most promising candidates for the alkylation reaction due to their high acidity and three-dimensional nature. The availability of side channels in the three dimensional zeolites makes it easier for the bulky hydrocarbons to escape the zeolite’s framework. Extra-large pore zeolites, consisting of 14 or more MRs [10], such as ITQ-33 and ITQ-37, could provide better catalysts for the alkylation reaction due to their large pore size which can alleviate the steric hindrance facing the bulky hydrocarbons.
Synthesising highly acidic extra-large pore zeolites could lead to a better alkylation catalyst. Figure 8-1 shows the proposed structures of ITQ-33 and ITQ-37.

![Proposed structures of ITQ-33 and ITQ-37](image)

**Figure 8-1:** The proposed structures of the extra-large pore zeolites ITQ-33 (a) and ITQ-37 (b), adopted from [11]

### 8.2.3 Zeolite Beta

Zeolite Beta is still an attractive catalyst for the alkylation reaction. The three-dimensional structure of the zeolite coupled with its large pore dimension allows the formation of the alkylation products. Furthermore, the high acidity of the zeolite enhances its potential as an alkylation catalyst. The zeolite’s aluminium content seems to have the most important effect on its alkylation activity. Increasing the aluminium content of the zeolite increases its acidity, therefore synthesising a highly crystalline zeolite Beta with a low Si/Al content (ideally 3-6) could provide a highly selective and stable catalyst. More recently, desilication of zeolite Beta was proven to be an excellent additive for the FCC catalyst [12]. The hierarchical zeolite exhibited higher propylene and diesel yields. The removal of silicon created meso-porosity and increased the zeolite’s acidity, both of which could contribute to a better catalyst for the alkylation reaction. Metal incorporation with rare-earth elements via impregnation was shown to be an ineffective method to improve the zeolite’s stability. The lanthanum ions reduced the Brønsted acidity thus reducing the catalyst's selectivity and the preparation procedure created additional Lewis acidity. Incorporating lanthanum via ion-exchange should be explored albeit at low concentrations of the lanthanum salt, ideally 0.05-0.10 M, to reduce dealumination. Furthermore, synthesising a low Si/Al Beta zeolite might require the ion-exchange with rare-earth metals to provide thermal stability during the calcination and reduce the structural damage observed by Yoo and Smirniotis while synthesising a low Si/Al Beta zeolite [13].

### 8.2.4 Zeolite Y

Faujasites seem to be the most promising catalyst for the alkylation reaction. The large-pore structure of the faujasites combined with its high acidity which can be further manipulated and tailored makes it the most attractive candidate for commercialisation. Indeed, the only solid-acid alkylation process under commercialisation is based on zeolite Y.
The hexagonal faujasite EMT was shown to be more active for the alkylation reaction both in its protonic and rare-earth exchanged forms than zeolite Y due to its higher Brønsted acidity [15, 16]. Synthesising low silica hexagonal EMT (Si/Al ~ 1.5) and exchanging it with rare-earth metals could provide an improved alkylation catalysts than the fully exchanged zeolite X, which exhibited very high stability [17].

Hierarchical Y zeolites are also very attractive catalysts for the alkylation reaction and should be investigated. Various studies examined hierarchical Y zeolites and the improved physical properties of the zeolite had significant advantages [18]. Liu et al. compared regular and hierarchical zeolite Y achieved by the addition of an organosilane surfactant during the synthesis. The meso-porosity created by the surfactant enhanced the stability of the zeolite during the aldol condensation of benzaldehyde with n-butyl alcohol. This reaction is typically utilised to study the diffusional effects in large-pore zeolites and is also promoted by Brønsted acidity [19]. The similarities between the reaction studied by the authors and the alkylation reaction are apparent as both are severely diffusion limited and promoted by Brønsted acidity. Moreover, it was shown recently by Li et al. that hierarchical Y zeolites can be synthesised without a loss in crystallinity [20]. Therefore hierarchical Y zeolites should also be thoroughly investigated both in protonic and rare-earth exchanged forms.

Additionally, growing the zeolite crystals onto meso-porous silica materials such as MCM-41 or SBA-15 could also reduce the olefin adsorption and provide the meso-porosity required to alleviate the diffusional limitations typically observed during the alkylation reaction over zeolites. This has been shown elsewhere to be feasible [21, 22]. Preferably, growing zeolite X crystals onto MCM-41 or SBA-15 and fully exchanging the zeolite with lanthanum could provide an ideal catalyst for the reaction.

8.2.5 Inerts and Additives

The catalyst dispersion had the highest impact zeolite Y’s alkylation behaviour. Dispersing the zeolite with silica compounds significantly improved its lifetime and enhanced the alkylate selectivity. Meso-porous silica compounds and MCM-41 in particular, were shown to be the best dispersing agents. While the initial dilution/dispersion seems to be the most important step, attention must be taken to ensure thorough mixing of the materials. Ideally, the zeolite and the diluent should have the same particle size to reduce the pockets of highly concentrated zeolite clusters. Moreover, the content of the diluent could be reduced further if the dilution procedure is improved. Also, the thermal stability of the diluent must be ensured to enable catalyst regeneration since it was shown that MCM-41 was not stable under elevated temperatures [23]. Binders or additives containing alkali metals or alkaline earth metals should be avoided since it was shown that such elements are transferred into the zeolite and reduced its acidity [24, 25].
8.3 References


[16] T. Rørvik, H.B. Mostad, A. Karlsson, O.H. Ellestad, Isobutane/2-butene alkylation on fresh and regenerated La-EMT-51 compared with H-EMT. The catalysts selectivity...
changes at high butene conversion in a slurry reactor, Applied Catalysis A: General, 156 (1997) 267-283.


Appendix A: Mass balance, Conversion and Selectivity Calculations

1. **Mass Balance:**

   T = 75 °C, P = 1.7 MPa, OSV = 0.30 h⁻¹, Zeolite Beta (12.5).

   \[ T_{ambient} = 288.15K \]

   \[ P_{ambient} = 1.00 \text{ atm.} \]

   R = 0.08205 (L.atm)/(mol.K)

   **Input:** MFC set point = 80 gh⁻¹

   **Output:**

   **Gas Output:**

   \[ V_1 = 31.26 \text{ L/h} \]

   \[ V_2 = 31.11 \text{ L/h} \]

   \[ V_3 = 33.07 \text{ L/h} \]

   Average \[ V = 31.81 \text{ L h}^{-1} \]

   Total Molar Flow (n) = PV/RT = 1.35 mol h⁻¹

   Gas Composition (GC-FID) Results:

<table>
<thead>
<tr>
<th>Component</th>
<th>Area</th>
<th>Rf</th>
<th>Concentration (mol %)</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>Total Molar Flow (mol)</th>
<th>Molar Flow (mol)</th>
<th>Mass Flow (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-C₄</td>
<td>332526.32</td>
<td>2.77E-04</td>
<td>92.11</td>
<td>58.12</td>
<td>1.35</td>
<td>1.24</td>
<td>72.06</td>
</tr>
<tr>
<td>2-butene</td>
<td>250.64</td>
<td>2.77E-04</td>
<td>0.07</td>
<td>56.12</td>
<td>1.35</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>C₅</td>
<td>101.22</td>
<td>2.26E-04</td>
<td>0.02</td>
<td>72.15</td>
<td>1.35</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>C₆</td>
<td>92.20</td>
<td>1.91E-04</td>
<td>0.02</td>
<td>86.18</td>
<td>1.35</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>C₇</td>
<td>106.50</td>
<td>1.66E-04</td>
<td>0.02</td>
<td>100.21</td>
<td>1.35</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>C₈</td>
<td>272.50</td>
<td>1.47E-04</td>
<td>0.04</td>
<td>114.23</td>
<td>1.35</td>
<td>0.00</td>
<td>0.06</td>
</tr>
</tbody>
</table>

   Total gas collected = 72.25 g

   Liquid products = 6.61 g
Total Products = 78.86 g

Mass balance closure = 78.86/80.00 x 100 % = 98.57 %

2. **Conversion:**

The conversion was calculated using equation (2-1):

\[
\text{Butene Conversion (X)} = \frac{C_F - C_P}{C_F} \times 100 \%
\]

\(C_F\) = Area of 2-butene in the feed x \(R_F\) = 22543.26 x 2.77E-04 = 6.24 mol%

\(C_P\) = 0.07 mol%, (Table A-1)

\(X\) (%) = (6.24-0.07)/(6.24) = 98.87 %

3. **C₈ Selectivity:**

The \(C₈\) selectivity was calculated using equation (2-2):

\[
\text{Fraction Selectivity (S)} = \frac{m_{\text{Fraction}}}{m_{\text{Products}}} \times 100 \%
\]

\(m_{\text{Fraction}}\) = \(m_{\text{Products}}\)

Total \(C₈\) = \(C₈\)-gas + \(C₈\)-liquid

\(C₈\)-gas = 0.06 g (Table A-1)

\(C₈\)-liquid = Liquid products x Area of % \(C₈\)'s in liquids = 6.61 x 45.98 % = 3.04 g

Total \(C₈\)= 3.04 + 0.06 = 3.10 g

\(S_{C₈}\) = 3.10 / (6.61+0.12) x 100% = 46.05 %

Since the products were mostly in the liquids collected, the selectivity was based on the liquid analysis.
Appendix B: Product Identification

1. Identification of the major components in the C₈ fraction:

A SUPELCO ASTM D5134 was used to identify the major compounds in the C₈ fraction. Figure B-1 shows a GC trace of the standard.

![GC trace of the SUPELCO ASTM D5134 standard](image)

The elution times of some of the major compounds in the standard are shown in Table B-1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elution Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2,4-TMP</td>
<td>38.42</td>
</tr>
<tr>
<td>2,2,3-TMP</td>
<td>52.23</td>
</tr>
<tr>
<td>2,3,4-TMP</td>
<td>59.73</td>
</tr>
<tr>
<td>2,3,3-TMP</td>
<td>61.41</td>
</tr>
<tr>
<td>DMHs</td>
<td>52.99, 65.05, 67.82</td>
</tr>
<tr>
<td>MHs</td>
<td>68.21, 68.51, 70.65</td>
</tr>
</tbody>
</table>

2. Identification of the fractions:

The products from the alkylation reaction were split into 4 distinct fractions, namely: C₅-C₇, C₈, C₉-C₁₂ and C₁₂+. For the products ranging from C₈ and lighter, the standard used in section B.1 allows the identification of each fraction. For the heavy fraction (C₉+), the elution time for the normal paraffin was used to estimate the fraction. The range of elution times for each fraction is shown in Table B-2.
Table B- 2: Fraction’s elution time

<table>
<thead>
<tr>
<th>Range</th>
<th>Elution Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₇</td>
<td>17.85 - 34.27</td>
</tr>
<tr>
<td>C₈S</td>
<td>38.42 - 74.46</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td>74.46 - 124.22</td>
</tr>
<tr>
<td>C₁₂+</td>
<td>124.22 - 180</td>
</tr>
</tbody>
</table>

Figure B-2 shows a liquid product’s GC-trace taken during the alkylation reaction over zeolite Beta with an overlay of a GC-trace of normal paraffins. The fractions are highlighted at the bottom of the figure and unidentified C₈S were assumed as olefins.

![Figure B-2: GC trace taken during the alkylation reaction over zeolite Beta](image)

3. **Repeatability of the liquid analysis**

Table B-3 shows an example of the GC results from a repeated sample containing C₆ and C₉ hydrocarbons.

Table B- 3: Repeated GC analysis of liquids

<table>
<thead>
<tr>
<th>Run</th>
<th>Area of C₆</th>
<th>Area of C₉</th>
<th>% Error in C₆</th>
<th>% Error in C₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43505.4</td>
<td>39254.9</td>
<td>1.84</td>
<td>0.51</td>
</tr>
<tr>
<td>2</td>
<td>44369.7</td>
<td>39531.3</td>
<td>0.11</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>43505.4</td>
<td>39254.9</td>
<td>1.84</td>
<td>0.51</td>
</tr>
<tr>
<td>4</td>
<td>45109.4</td>
<td>39623.8</td>
<td>1.78</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>45109.4</td>
<td>39623.8</td>
<td>1.78</td>
<td>0.42</td>
</tr>
<tr>
<td>Average</td>
<td>44319.9</td>
<td>39457.7</td>
<td>1.47</td>
<td>0.41</td>
</tr>
</tbody>
</table>
4. **Response factor calculations for the liquid GC:**

Six standards containing $C_6$, $C_7$, $C_8$ and $C_9$ hydrocarbons were prepared with varying percentages based on weight. The response factor was nearly identical for all the components and hence the area percentages were considered as weight percentages.

<table>
<thead>
<tr>
<th>Standard 1</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>0</td>
<td>0</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>60</td>
<td>43453.6</td>
<td>0.00138</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>30</td>
<td>20924</td>
<td>0.00143</td>
<td></td>
</tr>
<tr>
<td>$C_9$</td>
<td>10</td>
<td>7982</td>
<td>0.00125</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 2</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>25</td>
<td>16822</td>
<td>0.00149</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>50</td>
<td>33481</td>
<td>0.00149</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>25</td>
<td>20666</td>
<td>0.00121</td>
<td></td>
</tr>
<tr>
<td>$C_9$</td>
<td>0</td>
<td>0</td>
<td>na</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 3</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>0</td>
<td>0</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>90</td>
<td>64029.6</td>
<td>0.00141</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>5</td>
<td>4114.8</td>
<td>0.00122</td>
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<tr>
<td>$C_9$</td>
<td>5</td>
<td>3645.9</td>
<td>0.00137</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 4</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>0</td>
<td>0</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>80</td>
<td>57440.7</td>
<td>0.00139</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>10</td>
<td>7493.8</td>
<td>0.00133</td>
<td></td>
</tr>
<tr>
<td>$C_9$</td>
<td>10</td>
<td>7715</td>
<td>0.00130</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 5</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>15</td>
<td>10794.5</td>
<td>0.00139</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>50</td>
<td>36182.7</td>
<td>0.00138</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>25</td>
<td>17989.2</td>
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<td></td>
</tr>
<tr>
<td>$C_9$</td>
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<td>8024</td>
<td>0.00125</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 6</th>
<th>Component</th>
<th>wt. %</th>
<th>Area count</th>
<th>$R_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6$</td>
<td>5</td>
<td>3620</td>
<td>0.00138</td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>70</td>
<td>50769.8</td>
<td>0.00138</td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>3</td>
<td>1988.8</td>
<td>0.00151</td>
<td></td>
</tr>
<tr>
<td>$C_9$</td>
<td>25</td>
<td>16371</td>
<td>0.00153</td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>Average $R_f$</td>
<td>$\log R_f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6$</td>
<td>0.00142</td>
<td>-2.848</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>0.00141</td>
<td>-2.852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_8$</td>
<td>0.00135</td>
<td>-2.870</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_9$</td>
<td>0.00134</td>
<td>-2.873</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix C: Degree of Ion-Exchange Calculations

For zeolites, the maximum theoretical number of lanthanum species for ion exchange is $n_{\text{La}}/n_{\text{Al}} = 0.33 \text{ mol-La/mol-Al}$ [1].

**Example, 3LaE:**

Elemental analysis results:

Al: 9.29 wt. % = $9.29 \frac{\text{g-Al}}{\text{g-cat}}/(27 \text{ g-Al/mol-Al}) = 0.344 \text{ mol-Al/g-cat}$

La: 4.85 wt. % = $4.85 \frac{\text{g-La}}{\text{g-cat}}/(139 \text{ g-La/mol-La}) = 0.0349 \text{ mol-La/g-cat}$

$\Rightarrow n_{\text{La}}/n_{\text{Al}} = 0.0349/0.3874 = 0.1014 \text{ mol-La/mol-Al}$

$\Rightarrow \text{IEX} = 0.1013/0.33 = 30.7 \%$

---

Appendix D: Lanthanum Impregnation Results on Zeolite Y(2.6)

Figure D-1: Effect of lanthanum impregnation on the catalytic stability of zeolite Y(2.6)

Figure D-2: Effect of lanthanum impregnation on the C₈ selectivity of zeolite Y(2.6)
Figure D-3: Effect of lanthanum impregnation on the $C_{12}^+$ selectivity of zeolite $Y(2.6)$
Appendix E: Deconvolution of Zeolite Y(6)’s OH-Stretching Region

Figure E-1 shows the steps required to deconvolute the OH-stretching region.

- **Step 1: The experiment**
  - Measure and record the weight of the sample disk
  - Conduct the FTIR experiment

- **Step 2: OMNIC**
  - Normalize the weight of the sample
  - In OMNIC, perform baseline correction
  - Save the data as CSV

- **Step 3: Origin**
  - Export the data to ORIGIN
  - Use Gaussian deconvolution to fit the data
  - Ensure that the deconvolute peak centre locations are at the reported peak locations in literature

**Raw data:**

Figure E-2: IR spectra of the Y(6) zeolite in the OH-stretching region
Figure E-3: IR spectra of the Y(6) zeolite in the OH-stretching region after baseline correction in OMNIC

Figure E-4: Deconvoluted peaks from Origin
Appendix F: Performance of Cat 8

F.1 Catalytic Results

F.1.1 Initial Catalytic Behaviour
The initial catalytic activity behaviour showed complete initial butene conversion levels (Table F-1). The C₈ selectivity was relatively close with the 20% MCM-41 producing the highest content of C₈s. Furthermore, the heavy fractions (C₉-C₁₂ and C₁₂+) were significantly reduced in all the modified catalysts. Within the C₈ fraction, Cat 8 produced the most TMPs and the least amount of DMHs and MHs. The increased TMP production indicated the improved hydride transfer rates due to a combination of the lanthanum exchange and improved porosity from the MCM-41 addition. Furthermore, the TMP distribution indicated that the lanthanum exchanged samples had higher transfer rates as evident by the increase in the 2,2,3 TMP.

Table F-1: Initial catalytic results of Cat 8 compared to Y(2.6), 20% MCM-41 and 3LaE catalysts

<table>
<thead>
<tr>
<th>Initial Product Distribution</th>
<th>Catalyst</th>
<th>Y(2.6)</th>
<th>20% MCM-41</th>
<th>3 LaE</th>
<th>Cat 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Time-on-stream (h)</td>
<td></td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅-C₇</td>
<td></td>
<td>2.54</td>
<td>4.21</td>
<td>3.38</td>
<td>4.51</td>
</tr>
<tr>
<td>C₈</td>
<td></td>
<td>89.03</td>
<td>93.15</td>
<td>90.01</td>
<td>92.45</td>
</tr>
<tr>
<td>C₉-C₁₂</td>
<td></td>
<td>8.24</td>
<td>2.55</td>
<td>6.61</td>
<td>3.01</td>
</tr>
<tr>
<td>C₁₂+</td>
<td></td>
<td>0.19</td>
<td>0.09</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Composition of C₈ Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td></td>
<td>80.13</td>
<td>89.01</td>
<td>91.11</td>
<td>93.34</td>
</tr>
<tr>
<td>DMHs</td>
<td></td>
<td>12.62</td>
<td>7.64</td>
<td>5.91</td>
<td>5.64</td>
</tr>
<tr>
<td>MHs</td>
<td></td>
<td>6.88</td>
<td>3.35</td>
<td>2.98</td>
<td>1.02</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td></td>
<td>26.88</td>
<td>32.43</td>
<td>37.88</td>
<td>34.83</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td></td>
<td>12.48</td>
<td>16.38</td>
<td>18.60</td>
<td>18.32</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td></td>
<td>28.51</td>
<td>20.50</td>
<td>8.00</td>
<td>16.89</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td></td>
<td>32.13</td>
<td>30.69</td>
<td>35.52</td>
<td>29.96</td>
</tr>
</tbody>
</table>

F.1.2 Catalytic Stability
The catalytic stability results of the parent Y zeolite and the modified catalysts are provided in Figure F-1. The catalytic stability for all the modified catalysts showed significant
improvement from the parent Y zeolite. Cat 8 had the highest catalytic stability reaching a final conversion level of 98.7% after 10 hours on stream.

The significant decrease in the strong Lewis acidity after the lanthanum exchange reduced the deactivation of the catalyst. Furthermore, the improved porosity of the catalyst allowed the heavy molecules to desorb from the catalyst without adsorbing on adjacent zeolite clusters. Comparing the catalytic stability of 20% MCM-41 and the 3La E catalysts indicated that the improved porosity of the catalyst outweighed the reduction in the strong Lewis acidity resulting from the lanthanum exchange. This might indicate that in zeolite Y(2.6), the adsorption of the heavy molecules on the surface of the zeolite crystals may cause higher pore blockages than the formation of such molecules inside the pores of the zeolite.

Figure F-1: Catalytic stability of Cat 8 during the alkylation reaction
Figure F-2: Selectivity to C₈ as a function of time-on-stream of Cat 8

The improved catalytic stability of the modified catalysts enhanced the C₈ selectivity at longer times-on-stream as shown in Figure F-2. After 10 hours, Cat 8 had a final C₈ selectivity of 85 wt. %. Furthermore, the oligomerisation activity was significantly reduced in the modified catalysts. The decrease in the strong Lewis acid sites in 3LaE reduced the preferential olefin adsorption leading to a reduction in the oligomerisation. The porosity of the MCM-41, despite having similar acidic nature to the Y(2.6) catalyst, allowed the oligomerised products to desorb from the catalyst pellet without interacting on adjacent zeolite clusters. Cat 8, due to a combination of enhanced porosity and a reduction in the strong Lewis acidity, produced the least C₁₂⁺ (Figure F-3).
Comparing the C\textsubscript{12}+ selectivity as a function of conversion indicated that at similar conversion levels, the most stable catalyst produced higher C\textsubscript{12}+ compounds (Figure F-4). The addition of the inert meso-porous MCM-41 allowed the removal of the heavy molecules from the catalyst without causing further deactivation. It must be noted that the formation of the heavy hydrocarbons inside the zeolite’s pores seemed inescapable due to the Lewis acidity of the zeolite. The formation of the heavy molecules would eventually lead to pore blockages which in turn might contribute to the loss of the catalytic activity.
F.1.3 Overall Product Distribution

The catalytic performance after 10 hours on stream is summarised in Table F-2. The modified catalysts had higher conversion levels. Combining the reduced Lewis acidity from the lanthanum exchange and increasing the porosity of the catalyst resulted in almost complete butene conversion levels after 10 hours for Cat 8. In similar fashion to the time-on-stream behaviour, spotlighted in Figure F-1, the dilution by the MCM-41 seemed to outperform the lanthanum exchange.

Table F-2: Overall product distribution after 10 hours on stream

<table>
<thead>
<tr>
<th>Overall Product Distribution</th>
<th>Catalyst Y(2.6)</th>
<th>20% MCM-41</th>
<th>3La E</th>
<th>Cat 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Conversion (%)</td>
<td>80.14</td>
<td>97.46</td>
<td>93.88</td>
<td>99.80</td>
</tr>
<tr>
<td>Fraction Selectivity (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5-C7</td>
<td>3.16</td>
<td>4.99</td>
<td>4.44</td>
<td>4.33</td>
</tr>
<tr>
<td>C8</td>
<td>54.38</td>
<td>76.52</td>
<td>68.44</td>
<td>89.21</td>
</tr>
<tr>
<td>C9-C12</td>
<td>32.08</td>
<td>16.20</td>
<td>23.40</td>
<td>4.29</td>
</tr>
<tr>
<td>C12+</td>
<td>10.38</td>
<td>2.29</td>
<td>3.72</td>
<td>2.17</td>
</tr>
<tr>
<td>Composition of C8 Fraction (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
<td>66.07</td>
<td>88.54</td>
<td>81.36</td>
<td>90.49</td>
</tr>
<tr>
<td>DMHs</td>
<td>22.67</td>
<td>10.01</td>
<td>15.07</td>
<td>7.32</td>
</tr>
<tr>
<td>MHS</td>
<td>6.44</td>
<td>1.44</td>
<td>1.80</td>
<td>1.65</td>
</tr>
<tr>
<td>TMP Distribution (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4 TMP</td>
<td>24.33</td>
<td>31.07</td>
<td>32.12</td>
<td>35.36</td>
</tr>
<tr>
<td>2,2,3 TMP</td>
<td>12.91</td>
<td>13.12</td>
<td>15.33</td>
<td>16.42</td>
</tr>
<tr>
<td>2,3,4 TMP</td>
<td>28.12</td>
<td>23.80</td>
<td>18.77</td>
<td>19.82</td>
</tr>
<tr>
<td>2,3,3 TMP</td>
<td>34.64</td>
<td>32.01</td>
<td>33.78</td>
<td>28.40</td>
</tr>
</tbody>
</table>

A significant increase in the C8 selectivity in all the modified catalysts was observed as a result from the improved conversion levels. Furthermore, the heavy fraction production was significantly limited through a combination of reduced Lewis acidity and improved catalyst porosity in Cat 8. Within the C8 fraction, Cat 8 had the highest TMP content due to the reduction in Lewis acidity and the dilution of the catalyst. Both effects combined to reduce the preferential olefin adsorption around the active sites which promoted hydride transfer reactions instead of oligomerisation. The catalyst dilution seemed to have a larger influence on the overall TMP selectivity although as evident by the improved TMP content of the 20% MCM-41 in comparison the 3LaE catalyst.

The TMP distribution of Cat 8 resembled that of the 3LaE catalyst. This indicated that the TMP isomer selectivity was more influenced by the nature of the acidic sites. Furthermore, all the modified catalysts had lower content of the 2,3,4 TMP, which has the lowest kinetic
diameter, indicating lower steric conditions around the acidic sites. Figure F-5 describes the relation between the overall conversion and the cumulative C₈ and C₁₂+ selectivity.

Figure F-5: Effect of the overall butene conversion on the cumulative selectivity of C₈s (A) and C₁₂+ (B)

**F.2 Conclusions**

A novel catalyst for the alkylation of 2-butene with isobutane was developed. A combination of partial lanthanum-ion exchange and the addition of the inert meso-porous MCM-41 contributed to the enhanced catalyst lifetime. Comparing both effects indicated that the addition of the MCM-41 outweighed the lanthanum exchange. This implies that the catalyst dilution, using a meso-porous non-acidic inert, reduced the preferential olefin adsorption more efficiently than the reduction of the strong Lewis acidity by the lanthanum exchange. Furthermore, the meso-porosity provided by the MCM-41 allowed the bulky C₁₂+ molecules to desorb from the catalyst without causing further deactivation. Combining the catalyst dilution and enhanced porosity from the MCM-41 with the reduction of strong Lewis acidity from the lanthanum ion exchange produced a highly active and catalytically stable catalyst. However, the formation of the C₁₂+ molecules would eventually lead to the deactivation of the catalyst.