สำนักงานกองทุนสนับสนุนการวิจัย
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# รายงานการวิจัยฉบับสมบูรณ์

**โครงการ : อิทธิพลของโครงสร้างผลึกต่อความว่องไวในการทำปฏิกิริยาของตัวเร่งโครงสร้างนาโน**

**The Influence of Crystal Framework on the Reactivity of Nanostructured Catalysts.**

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**พฤษภาคม 2554**

สัญญาเลขที่ RMU5180032

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# บทคัดย่อ

**รหัสโครงการ: RMU5180032**

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งานวิจัยนี้ได้นำวิธีการคำนวณทางกลศาสตร์ควอนตัม มาใช้ในการวิเคราะห์กลไกปฏิกิริยาอย่างมีระบบในปฏิกิริยา skeletal isomerisation ของ cis-butene เป็น isobutene ในตัวเร่งซีโอไลต์ชนิด ferrierite โดยกลไกปฏิกิริยาที่ศึกษามีสองชนิดได้แก่ ชนิดแรกเรียกว่า conventional mechanism ซึ่งกลไกปฏิกิริยาจะเกิดผ่าน alkoxide intermediate ที่เป็นโครงสร้างที่เสถียร ส่วนชนิดที่สองกลไกจะเกิดผ่าน carbenium ions

แบบจำลองที่ใช้ในการศึกษากลไกปฏิกิริยาข้างต้น ใช้แบบจำลองขนาด 27T cluster เพื่อแทนซีโอไลต์ชนิด ferrierite ซึ่งใช้ระเบียบวิธีการคำนวณ density functional theory (M062X DFT functional)

ผลจากการคำนวณจาก พบว่าโครงสร้างที่เป็น carbenium ions จะมีความเสถียรน้อยกว่าโครงสร้างที่เป็น alkoxide intermediates ที่เกิดขึ้นในกลไกที่เป็นแบบ conventional mechanism โดยพิจารณาจากขั้นกำหนดอัตราที่มีพลังงานต่ำกว่าประมาณ 10 kcal/mol การที่พลังงานที่สูงกว่าอธิบายได้ว่ามีการเกิด intermediate ขึ้นภายในโพรงของซีโอไลต์ ซึ่งจากข้อมูลที่มีอยู่สามารถสรุปได้ว่า จะเกิด intermediate ขึ้นมาในระหว่างการเกิดปฏิกิริยา skeletal isomerisation ของ butene ใน ferrierite จะเกิดผ่านกลไกที่เกิด carbenium เท่านั้น ซึ่งผลการศึกษานี้สอดคล้องกับผลการทดลองที่ alkoxide intermediate จะเป็น species ที่พบในการทดลอง

**Keywords :** Zeolite catalysis, carbenium, alkoxide, skeletal isomerisation, QM, DFT, FER

## Abstract

**Project code: RMU5180032**

**Project title: The Influence of Crystal Framework on the Reactivity of Nanostructured Catalysts.**

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In this study, quantum mechanical calculations have been performed to systematically analyse two different reaction mechanisams for the skeletal isomerisation of cis-butene to isobutene in ferrierite zeolite. One involves a conventional mechanism that proceeds via stable alkoxide intermediates and the other one which proceeds via carbenium ions only.

The calculations were performed using 27T quantum mechanical cluster model representations of ferrierite, which is described using the M062X density functional.

Although the carbenium ion structures formed over the pathway are inherently less stable than the alkoxide intermediates formed in the conventional mechanism, the rate determining step is predicted to be almost 10 kcal/mol lower in energy. The higher barrier for the latter process is due to the inherent stability of the intermediates formed within the pore. This appears to suggest that while these intermediates are formed over the course of a reaction, the skeletal isomerisation of butenes in ferrierite only occurs via a carbenium based mechanism. This proposal is consistent with experimental results that alkoxide intermediates are experimentally observed species.

**Keywords —** Zeolite catalysis, carbenium, alkoxide, skeletal isomerisation, QM, DFT, FER

## EXECUTIVE SUMMARY

Quantum chemical calculations of model zeolites can be used to analyse the mechanisms of catalysis by the consideration of the relative energies, geometries, and interactions of the substrate, transition state, intermediate and product with the catalytic active site. A considerable amount of scientific resource has been devoted to the research of zeolites as replacements for traditional media that are employed as catalysts in the transformation of hydrocarbons. In particular, quantum mechanical (QM) simulations have been extensively employed to study concepts in zeolite catalysis since it is possible to study the energetics and structures of catalytic reactions, offering a unique way to rationalise experimental results.

Here we propose a study of a ferrierite (FER) zeolite, which is of considerable interest to industry at present for a number of potential applications. We focus on the skeletal isomerisation of n-butene to isobutene in FER which experimentally is found to be more selective in the formation of the desired end product, isobutene, because of its reduced acidity and smaller interconnecting channels.

We propose an investigation into the mechanism of skeletal isomerisation of n-butene within the FER pore via (a) a conventional monomolecular mechanism and (b) a dimerisation mechanism recently proposed, to see which is energetically more favourable. Importantly, we also explore the nature of the computational model by employing clusters of 27T model and simulate using DFT methods. Single point calculations of the full model are subsequently carried out at M062X functional with the 6-311+G(2df,dp) basis set used for the 6T region and 6-31G* for the remainder. Additionally, the key bond distances, angles, interaction distances and charges for the stationary points derived from each model are rigorously compared assess the differences that result from the different simulation conditions. This will provide useful insight into the strength and weakness of the different models.

# กิตติกรรมประกาศ

โครงการวิจัยนี้ได้รับทุนอุดหนุนจากสำนักงานคณะกรรมการการอุดมศึกษา และ สำนักงานกองทุนสนับสนุนการวิจัย คณะผู้วิจัยขอขอบคุณหน่วยงานดังกล่าวที่ให้การสนับสนุนทุนวิจัยตลอดโครงงานวิจัยนี้ จนได้จัดเป็นรูปเล่มรายงานฉบับสมบูรณ์ของงานวิจัยนี้

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# บทที่ 1
# บทนำ

## 1.1 ที่มาและความสำคัญของปัญหา

The potential of zeolites has been identified by the chemical and petrochemical industries as an affordable, efficient material to selectively crack, alkylate or oligomerise hydrocarbons - . Benefits are widespread, including the production of chemical precursors such as isobutene, key in the production of petrol additive MTBE and ETBE used to increase the octane rating of fuel, or ethyl-benzene, an intermediate used in the production of polystyrene .

A considerable amount of scientific resource has been devoted to the research of zeolites as replacements for traditional media employed as catalysts in the transformation hydrocarbons. In particular, quantum mechanical (QM) simulations have been extensively employed to study concepts in zeolite catalysis, since it is possible to study the energetics and structures of catalytic reactions, offering a unique way to rationalise experimental results.

Here we propose a study of a medium pore zeolite ZSM-5, which is of considerable interest to industry at present for a number of potential applications. We focus on the skeletal isomerisation of n-butene to isobutene in ZSM-5 which experimentally shows a greater conversion of n-butenes than another medium pore zeolite, ferrierite (FER). Interestingly, the latter is found to be more selective in the formation of the desired end product, iso-butene, because of its reduced acidity and smaller interconnecting channels10. ZSM-5's increased reactivity is believed to be a result of its greater acidity, larger pore size and less restricted diffusion characteristics, exacerbated with time on stream10. As this selectivity difference arises with time on stream, it is effectively beyond the limits of current simulations.

We propose an investigation into the mechanism of skeletal isomerisation of n-butene within the more reactive ZSM-5 pore via (a) a conventional monomolecular mechanism and (b) a dimerisation mechanism recently proposed , to see which is energetically more favourable. Importantly, we shall also explore the nature of the computational model by employing gas phase clusters of varying size tetrahedra (3T, 5T, 10T) and

simulate using DFT methods. More rigorous ONIOM 46T models will also be simulated with an inner core of varying size, (3T, 5T, 10T) treated using DFT, and the remaining 46T region treated via an MM potential. Single point calculations of the full 46T model will subsequently be carried out at DFT levels to obtain more reliable energetics. Additionally, the key bond distances, angles, interaction distances and charges for the stationary points derived from each model will be rigorously compared using principal components analysis (PCA) to quantitatively assess the differences that result from the different simulation conditions. This will provide useful insight into the strength and weakness of each of the different models.

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## 1.2 วัตถุประสงค์ของงานวิจัย

1. To model the catalytic reactivity of zeolite catalysts.
2. To elucidate experimental phenomena of zeolite catalysed reactions such as reaction mechanisms, and spectroscopic data.
3. To study the reaction mechanism of the catalytic conversion of butene to isobutene.
4. To analyse the structures and properties of zeolite active sites in an attempt to improve our understanding of the physical basis for the catalytic effect of zeolites.

## 1.3 ขอบเขตของงานวิจัย

This research project will involve the prediction of the stationary points and transition state structures of zeolite catalysts using state-of-the-art computational chemistry methods. The goal of this study is to elucidate the physical basis for experimental phenomenon in zeolite catalysts by probing their structure using quantum chemical calculations.

Of the variety of computational methods available, we choose to employ the ONIOM method which has been successful in reproducing experimental results. This method has also been applied to ZSM-5 on a number of pervious occasions making it an ideal method to apply here. The system to be studied is illustrated in Figure 1 with a bound isobutene molecule.

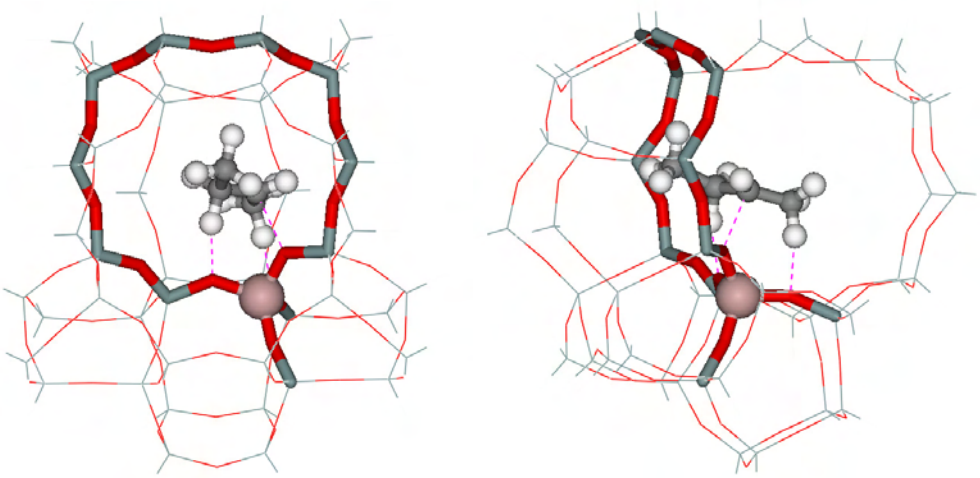

Figure 1. Illustration of the proposed 10T:46T ONIOM model with a physisorped n-butene molecule. Stick indicates the inner layer and line indicates outer layer. The aluminium atom is illustrated as CPK.

The reactions to be studied are (a) the cis-trans isomerisation of butene and the skeletal isomerisation of 1-butene to isobutene via (b) a conventional, monomolecular mechanism and (b) an autocatalytic “dimerisation” mechanism. Calculations will initially focus on the cis-trans isomerisation to allow the most reliable computational system to be defined for the complex skeletal isomerisation studies.

ZSM-5, one of the most frequently studied zeolites in the theoretical literature, is to be represented in two distinct ways; (a) using small nT clusters and (b) using ONIOM nT:46T models. In each case three different QM cluster sizes (3T, 5T and 10T) will be used. The latter cluster sizes will also be employed as the inner QM region in the 46T ONIOM simulations. The models will be cut from the cross section of the straight channel and zigzag channel as used by others. The dangling bonds will be saturated with hydrogen atoms and these will be kept fixed during geometry optimization. Additionally, the 3T heavy atoms (Si, Al and O) and the substrate molecule will be allowed to relax for all 3T cluster and 3T:46T ONIOM calculations, while the 5T region and substrate molecule will be allowed to relax in the 5T, 5T:46T, 10T and 10T:46T

simulations. Based on the reports by Namuangruk et al. for propene oxide isomerisation in ZSM-576, this system should be sufficiently accurate to model the skeletal isomerisation reactions of butene.

All the calculations will be performed using the Gaussian 03 program . The 3T, 5T and 10T QM clusters will be optimized at the B3LYP/6-31G(d,p) level of theory with single points obtained using the optimized coordinates at the MP2/6-311++g(d,p) level. ONIOM simulations will employ the B3LYP/6-31G(d,p) level of theory for the inner region and the universal force field (UFF) for the outer region. All stationary points will be confirmed as such using frequency calculations. Single point energies will be obtained in two distinct ways; (a) at the MP2/6-311++g(d,p):UFF level on the optimized nT:46T system and (b) at the B3LYP/6-31G(d,p) level for the full 46T optimized system.

To extract as much information as possible from our QM calculations on 6 different alkenes, we will employ Principle Components Analysis (PCA) - , a widely used statistical technique in both zeolite simulation and cheminformatics - . PCA is a method for reducing the amount of data to be analyzed by exploiting the correlated nature of the variables within a dataset. Linear combinations of the correlated variables are taken such that the majority of the variance of the original data can be described by a smaller number of orthogonal components. The components can then be used to assess the similarities in the reaction structures and the nature of the structural differences in a quantitative fashion. This method will allow us to systematically assess the difference between the different cluster model structures and those from the ONIOM models. Finally, linear regression will be used to assess the relationship between the energetics and structure, as represented by key distances, angles, dihedrals and atomic Mulliken charges.

A summary of the key features and expected finding of this study are given below.

A. Cis/Trans Isomerisation

- Inter comparison of cluster and ONIOM models
- Analysis of stationary point properties using PCA
- Identification of the key differences between clusters and ONIOM
- Identification of the key differences between different sized clusters
- Relationship between energetic differences and structure

B. Butene Skeletal Isomerisation

- Comparison of the conventional and autocatalytic mechanisms
- Key differences between ONIOM DFT:UFF and DFT single point.
- Assessment of the agreement of theory with experimental results of de Menorval
- Relationship between energetic differences and structure

## 1.4 ประโยชน์ที่คาดว่าจะได้รับ

1. Improve our understanding of the catalytic conversion reactions of zeolites.

2. To increase our general understanding of zeolite action such that the design of selective zeolites for specific purposes may be realised.

3. To determine how well the current simulation methods are by trying to differentiate between experimental results.

The combination of modern computational hardware and quantum mechanical software can provide an alternative to experiment while also providing an insight into molecular mechanisms impossible to observe experimentally. In relation to zeolite chemistry, this not only allows us to interpret experiment but also potentially assess reactions not yet considered. These efforts will help to improve the properties of inorganic catalysts through the proposal of plausible reaction mechanisms from an accurate description of active site interactions. Knowledge of the reactions should help in the realisation of new, improved catalysts.

# บทที่ 2
# การทบทวนเอกสารและงานวิจัยที่เกี่ยวข้อง

Zeolites are important silicon based catalysts employed in the petrochemical industry to transform crude materials into refined products[1,2]. The desirable catalytic activity of these materials mainly arises due to; (a) the replacement of individual silicon atoms in the 3D lattice structure with aluminum, giving rise to a strong acidic center and/or (b) the presence of additional heavy metals in the zeolite pores[3-5]. Combined with the diverse range of three dimensional pore structures that such materials exhibit[2,6-9], a range of useful chemical reactions can be catalyzed by these materials[10,11]. One application where such materials have proved particularly useful is in the catalytic cracking and skeletal isomerisation of hydrocarbons employed in the petrochemical industry[2,10,12-14]. The skeletal isomerisation of linear butenes to isobutene in FER has been extensively studied experimentally[15-18] given that the latter is an important chemical precursor[19].

In this study the related catalytic conversion of cis-butene to iso-butene in the zeolite ferrierite (FER) is investigated. This zeolite is of significant interest from the point of view of butene isomerisation due to the high selectivity it displays for iso-butene compared to larger pore zeolites such as ZSM-5[20,21]. These differences arise due to the so called confinement effect of the unique zeolite lattice and their differing acidities[6-8]. There are still a number of uncertainties regarding the origin of the catalytic effect of zeolite on this reaction, including whether it occurs via a mono-molecular or pseudo bi-molecular route[2].

Extensive experimentation has been undertaken on zeolites using techniques such as infra-red, UV, NMR and EPR spectroscopy[22-24]. In addition extensive use of theoretical methods have been reported in the literature. Quantum mechanical (QM) calculations of various types have been employed to elucidate aspects of zeolite catalysis including QM cluster calculations[5,13,25], hybrid quantum mechanical/molecular mechanical (QM/MM)[14,26] and ONIOM methods[27-29], as well as periodic DFT simulations[30,31]. In this study, a relatively large DFT cluster model of FER is employed to study the local effects of the pore structure on the skeletal isomerisation of cis-butene in the zeolite (Figure 2) since reports from Hansen et al suggest that such a sized cluster is needed to enable

the locations of high energy carbenium or carbonium ions[32] . The improved M062X DFT functional[33-35] is employed here as it has been used quite extensively to study aspects of zeolite catalysis recently[7,13,28,35].

The investigations of Boronat et al[36] in the medium pore zeolite Theta-1 showed that the skeletal isomerisation reaction of linear butenes proceeds via two alkoxide intermediates (secondary and tertiary butyl) to the iso-butene product. The rate determining barrier is 22 kcal/mol and involve methyl group migration. No carbenium ion stationary points were reported in Theta-1 or in a related study on ZSM-5[37] by this author. Demuth et al investigated the related skeletal isomerisation of 2-pentene and they proposed that the most likely pathway involved the formation of high energy, but stable secondary carbenium ions as transient intermediates[38]. This differing result may be due to differences in the zeolite pore structures under investigation in the different studies since these are known to have a dramatic effect on the stability of carbenium ions[39,40]. Niemenan et al[41] has also assessed aspects of alkoxide species stabilities in FER using alkenes between 3 to 5 carbons in length. They showed that the stability of the alkoxy formed was very sensitive to the steric bulk of the alkene in question. In addition, a number of studies have discussed the importance of carbenium ions and their relevance in skeletal isomerisation of alkenes[28,40,42-44]. Tuma et al[42,43], followed by Boronat et al[40], concluded that carbenium ions should exist as true, albeit short lived reaction intermediates.

This study considers the skeletal isomerisation of linear butenes to iso-butene in FER the light of the most recent publications in the area. Both a conventional mechanism akin to that proposed by Boronat et al[36,40] that proceeds via alkoxide intermediates, and one that proceeds via carbenium based intermediates[39] is investigated. The zeolite FER has been chosen for this study due to its widespread use in skeletal isomerisation reactions[15-18] and (b) due to its rather small pore cavity which presumably makes carbenium ion formation more likely when compared to larger pore zeolites such as ZSM-5. The results are then contrasted with related theoretical studies which have been performed in either other zeolites and/or using similar alkenes: Theta-1[40], ZSM-22[36,38], ZSM-5[37] and FER[28,41,42] or generic zeolite models[45].

# บทที่ 3

# วิธีการดำเนินงานวิจัย

## 3.1 ขั้นตอนการดำเนินงานวิจัย

1. Build a number of structural models, i.e., clusters and zeolite frameworks.
2. Study the conversion of trans-butene to cis-butene in the gas phase and compare with the results from framework (active site's surrounding environment) of the zeolite.
3. Interpret the effect of the different active sites on the reaction and determine whether we can differentiate between the known experimental results using the ONIOM models.
4. Propose the mechanism for the reaction and interpret the results. Build a number of structural models, i.e., clusters and embedded clusters.
5. Build a number of structural models, i.e., clusters and zeolite frameworks.
6. Study the conversion of n-butene to isobutene in the framework (active site's surrounding environment) of the zeolite.
7. Study the reaction profile for the catalytic conversion of n-butene to isobutene.
8. Propose the mechanism for the reaction and interpret the results.
9. Build a number of structural models.
10. Study the autocatalytic conversion of n-butene to isobutene in the framework (active site's surrounding environment) of the zeolite.
11. Study the reaction profile for the autocatalytic conversion of n-butene to isobutene.
12. Propose the mechanism for the reaction and interpret the results
13. Compare the results from autocatalytic conversion calculations to those calculated based on the proposed mechanism in the second year.

Recent calculations on FER have used the cluster approach[7], the ONIOM approach[28] and periodic methods[42,46] to good effect to elucidate aspects of its catalytic function. Due to the relative simplicity of the cluster approach, and the ability of relatively large clusters to describe high energy intermediates formed within zeolite systems[32], the cluster method was chosen for this study. The cluster model of FER was generated using the X-ray diffraction data in Material Studio[47]. FER has a 2 dimensional pore structure with a large main 10T channel bisected by smaller 8T channels. A 27T cluster

model was carved from the X-ray coordinates, encompassing 2 complete pores either side of the 10T central ring. The bronsted acid site was created by replacing a silicon atom located at the T2 position of the 10T ring with an aluminium atom[7,41]. The 6T region of the cluster model surrounding the T2 site and acidic oxygen using the 6-31G(d) basis set and more distant atoms using the 3-21G basis set (Figure 2). This approach has been used in the past to allow a large QM cluster of a zeolite to be simulated in a reasonable amount of time[48,49]. The 3-21G basis set does appear to be sufficient to describe longer range effects based on the reports of Yumura et al[49]. This resulted in a model system with a total of 1226 basis functions.

The 6T region surrounding the T2 site and acidic oxygen was excised from the original X-ray coordinates with bonds cut across the O-Si bond. To avoid issues due to overly strong polarization due to the presence of OH groups, bonds were cut across the Si-O bonds for the more remaining 21T atoms[46]. This type of approach is similar to that employed to Zhao et al in their validation of the M062X functional for zeolite based applications[35]. To maintain the overall shape of the zeolite all terminal hydrogen atoms in the 6T region were fixed while only silicon atoms beyond this region were fixed. This allowed the electronegative oxygen atoms, which are directed into the FER pore, to subtly alter their positions over the course of the simulated reaction, thereby allowing better stabilization of the reactive species formed. Boronat et al note that the lack of flexibility in the zeolite lattice is one of the key issues in estimating the energies of intermediates in QM models of zeolites[40].

All geometry optimizations were performed using M06-2X functional in Gaussian 03[50] modified to use the Minnesota Density Functionals Module 3.1 by Zhao and Truhlar[33]. Minima and transition states were fully characterized as stationary points in the complete 27T model, in all cases displaying zero and one single negative frequently, respectively. Zero point energy corrections to the energetic were therefore possible. Single point energies of optimized coordinates were subsequently obtained using the M062X functional with the 6-311+G(2df,dp) basis set used for the 6T region and 6-31G* for the remainder.

With regards to model validity, the skeletal isomerization of linear butenes to isobutene has previously been studied by Boronat et al in Theta-1 using a 20T model of that zeolite[36]. The authors reported that the results were in agreement with periodic models that include longer range effects of the zeolite lattice[36,40]. This finding should mean that the results obtained here from a larger 27T model of FER are likely to be of reasonably accuracy.

## 3.2 เครื่องมือและอุปกรณ์ที่ใช้

1. High Performance Computer
2. Gaussian 98 Software
3. Statistical Analysis Software

# บทที่ 4

## ผลการทดลองและอภิปราย

The energetic results obtained from the calculations are reported in Table 1 and Figure 2. The structural parameters of the optimized geometries are displayed in Figure 3 for minima and Figure 4 for transition states. The energies of the optimized complexes are given in Table 1 along with their corresponding zero point correction and the single point energies. The single point and ZPE corrected energies are found to be in good agreement with the energies obtained at the original level or theory. All energies discussed henceforth correspond to the single point energies (M062X with 6-311+G(2df,dp) for cis-butene, and the 6T region and 6-31G(d) for 21T region) including zero point energy corrections, and  are expressed relative to the isolated reagents unless otherwise stated.

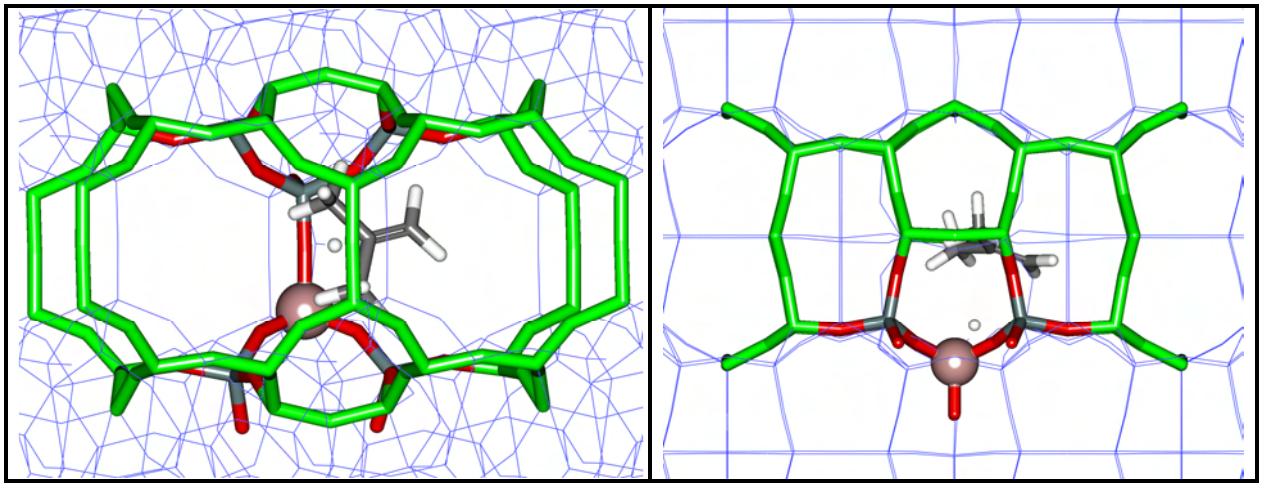

Figure 2 An illustration of the 27T model used in this study (illustrated using a stick representation). The 6T region surrounding the the T2 Al atom and acidic center are described using the 6-31G(d) basis set (O atoms coloured red and Si grey). To include the confinement effect of the zeolite, the two pores that bisect the main 10T ring are also included in the calculation at using the 3-21G basis set (stick representation with all atoms coloured green).

The skeletal isomerisation of cis-butene is first discussed in the context of the more conventional alkoxide based mechanism followed by a discussion on the relative likelihood of a carbenium based mechanism existing in this zeolite.

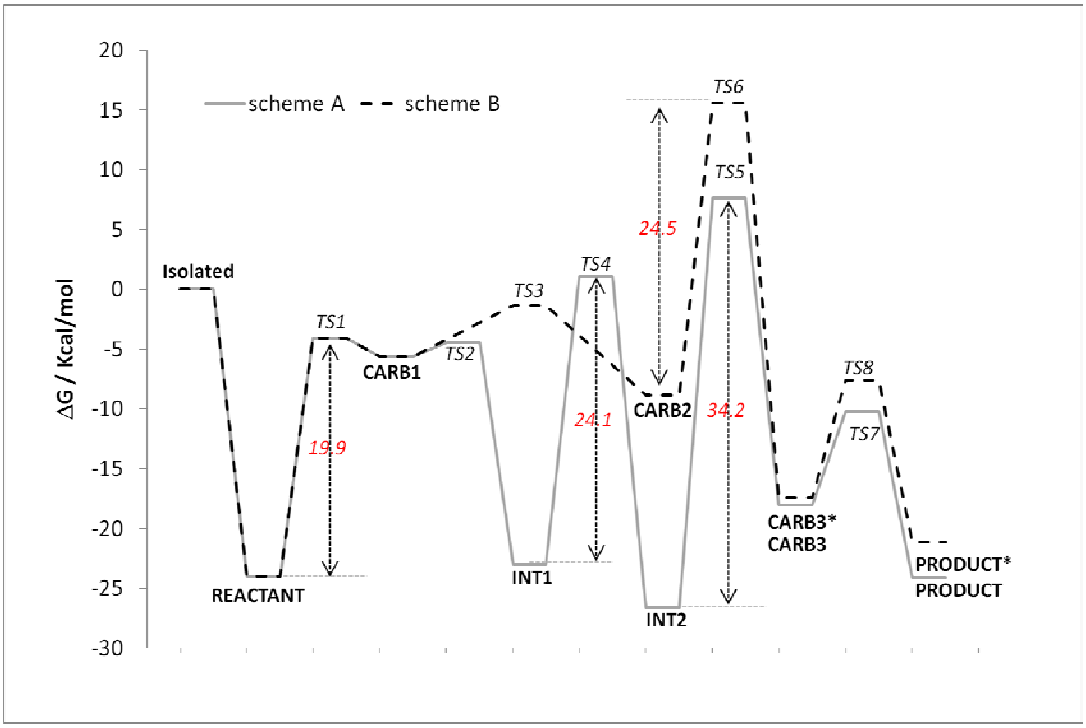


Figure 3 A graphical illustration of the energetic associated with the alkoxide (Scheme A, grey solid line) and carbenium (Scheme B, dashed black line) based mechanisms. The stationary points found on the two pathways are illustrated in Figure 4, Figure 5.

### 4.1 Alkoxide based mechanism

The traditional uni-molecular mechanism of butene isomerisation begins with the formation of the adsorbed alkene-FER complex. The estimated adsorption energy of 1-butene is -18.9 kcal/mol in Theta-1[51] and -18.4 kcal/mol for iso-butene in FER[42]. Thus, the value of -23.8 kcal/mol obtained here for cis-butene adsorbed to FER appears reasonable especially given that it is less sterically hindered than iso-butene. The π-complex displays short C---Hz interactions as expected (2.11 and 2.20 Å) while the C=C bond distance is only slightly elongated compared to the isolated gasphase value (1.34 vs 1.33 Å).

Table 1 The energies of the stationary points obtained in this study. All energies are relative to the isolated energies of the zeolite model and cis-butene in the gasphase. ΔH corresponds to the energy of optimized complexes using the default basis set (M062X with cis-butene and zeolite 6T described by 6-31G(d) and 21T atoms using 3-21G). ZPE corresponds to the zero point correction energy for the optimized stationary points at the default level of theory. ΔH SP corresponds to the single point energy of the optimized stationary point performed as follows: M062X with cis-butene and zeolite 6T described by 6-311+G(2df,dp) and 21T atoms using 6-31G(d). The ΔG (SP+ZPE) value corresponds to the ΔH SP plus the ZPE correction obtained using the default basis set calculation. All values are reported in Kcal/mol.

| **Scheme-A** | **ΔH** | **ZPE** | **ΔH SP** | **ΔG (SP+ZPE)** |
|---|---|---|---|---|
| REACTANT | -22.82 | -0.72 | -23.25 | -23.96 |
| TS1 | -4.51 | 0.44 | -4.50 | -4.06 |
| CARB1 | -6.91 | 0.42 | -6.05 | -5.63 |
| TS2 | -4.97 | 0.02 | -4.45 | -4.43 |
| INT1 | -21.65 | -3.98 | -19.03 | -23.01 |
| TS4 | -1.31 | -1.01 | 2.08 | 1.07 |
| INT2 | -29.80 | -3.18 | -23.41 | -26.60 |
| TS5 | 5.39 | 0.85 | 6.78 | 7.63 |
| CARB3 | -19.68 | 0.24 | -18.29 | -18.04 |
| TS7 | -11.38 | 1.42 | -11.62 | -10.21 |
| PRODUCT | -20.34 | -1.61 | -22.50 | -24.11 |
| **Scheme-B** | **ΔH** | **ZPE** | **ΔH SP** | **ΔG (SP+ZPE)** |
| REACT | -22.82 | -0.72 | -23.25 | -23.96 |
| TS1 | -4.51 | 0.44 | -4.50 | -4.06 |
| CARB1 | -6.91 | 0.42 | -6.05 | -5.63 |
| TS3 | -1.46 | -0.38 | -0.94 | -1.32 |
| CARB2 | -7.96 | -0.36 | -8.50 | -8.87 |
| TS6 | 13.36 | 2.11 | 13.48 | 15.59 |
| CARB3 (C) | -19.16 | 0.68 | -18.06 | -17.38 |
| TS8 | -9.72 | 1.76 | -9.38 | -7.62 |
| PRODUCT (C) | -18.62 | -2.21 | -18.94 | -21.15 |

The skeletal isomerisation in Theta-1 begins with the formation of a secondary alkoxy complex in a concerted mechanism with simultaneous transfer of a proton from the zeolite to butene and the formation of a C-O bond[36,40]. The next step requires a methyl group shift, leading to the formation of a primary alkoxide intermediate. The carbon atom from which the methyl group migrates forms a C-O bond with an adjacent nucleophilic oxygen, while the migrating methyl satisfies the valence of the carbon atom whose C-O bond must break. The secondary alkoxide is found to be 6.9 kcal/mol higher in energy than the adsorbed complex compared to the primary alkoxide which is -2.9 kcal/mol lower. The rate determining step in theta one is the decomposition of the primary alkoxide to give adsorbed iso-butene. This final step requires the C-O bond of the primary alkoxide to break and the transfer of a proton to the zeolite which has a rate determining barrier of 32.7 kcal/mol. Iso-butene is found to be adsorbed to theta-1 only 0.7 kcal/mol higher in energy than 1-butene. Boronat et al note that these energies are likely to be upper limits given the 20T ring was not optimized (a 5T optimized model was inserted into the larger model and a single point energy calculated performed) [36].

In FER, it is found that the formation of the initial alkoxide intermediate does not occur in a concerted manner, in contrast to than within theTheta-1 pore. Proton transfer from the O2 atom of the zeolite to the C2 of cis-butene via transition state one (TS1) leads to a stable carbenium ion 18.3 kcal/mol higher in energy than the adsorbed complex, with a barrier of 19.9 kcal/mol. The C2-C3 distance of the adsorbed cis-butene increases to 1.45 Å in carbenium ion 1 (CARB1), intermediate between the double and single bond values expected for cis-butene in the gasphase (1.33 vs 1.50 Å respectively). TS1 is considerably closer in structure to the corresponding carbenium ion than adsorbed cis-butene as might be expected given the energetic differences. TS1 has a C2-C3 distance that is very close to that of CARB1 (1.43 vs 1.45 Å), as well as the C2-Hz distance of (1.14 vs 1.13 Å). The principal difference being the two is the C1-C2-C3-C4 dihedral angle, which is $7^{o}$ in CARB1 but $46.6^{o}$ in TS1, facilitating the inductive stabilization of the positively charged carbon center in the former. CARB1 is stabilized by a single strong interaction formed between a C4 hydrogen atom and the O3 oxygen atom (1.98 Å), similar to those reported by Fang et al[28].

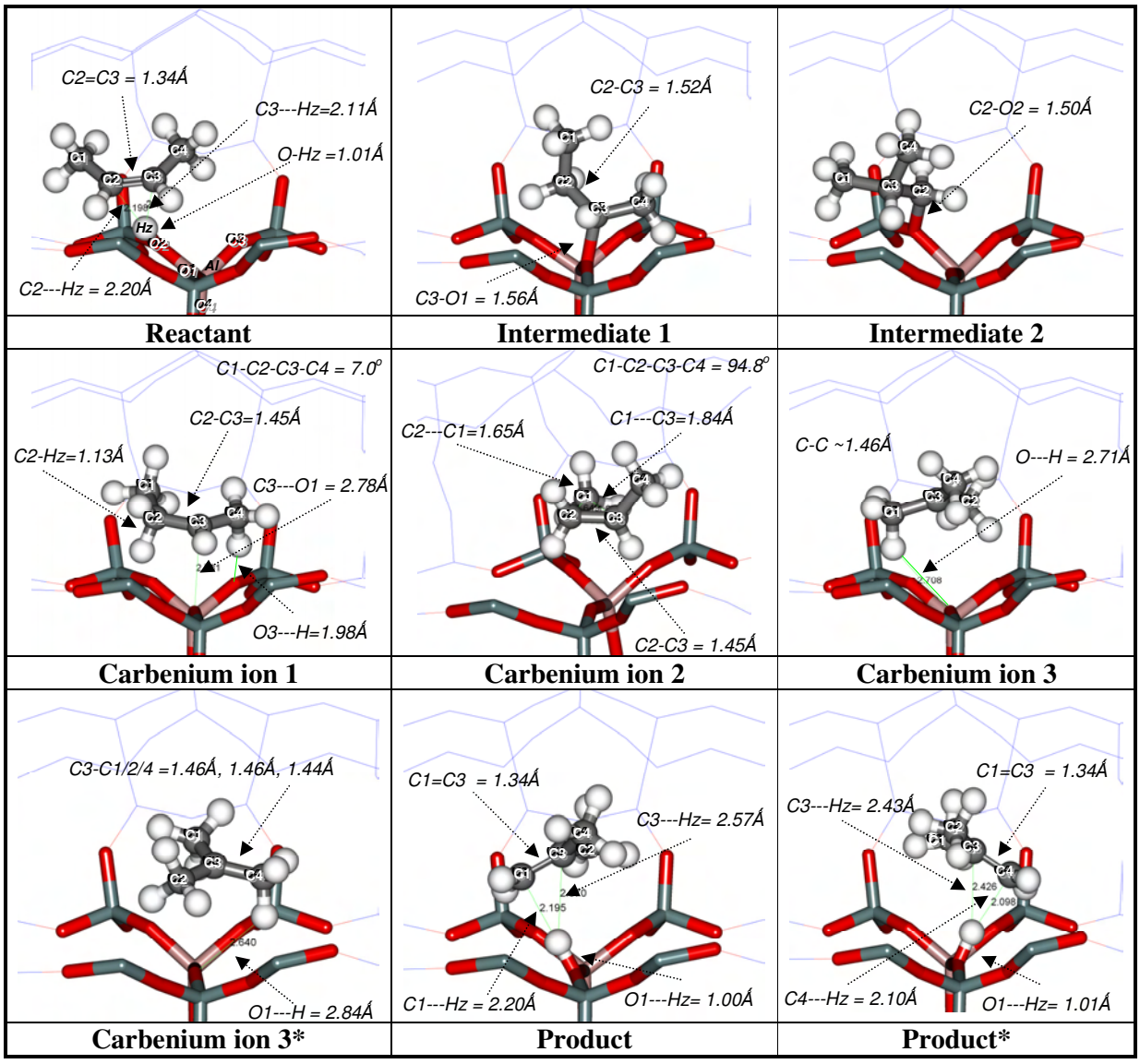


Figure 4 Minima obtained in this study. 6T region denoted using a stick representation and the 21T region using wireframe. Atoms in the foreground have been removed to aid visualisation. Carbon atoms are numbered 1 to 4 to facilitate interpretation. Only the key zeolite atoms are numbered in the top left panel. Key distances and angles are illustrated.

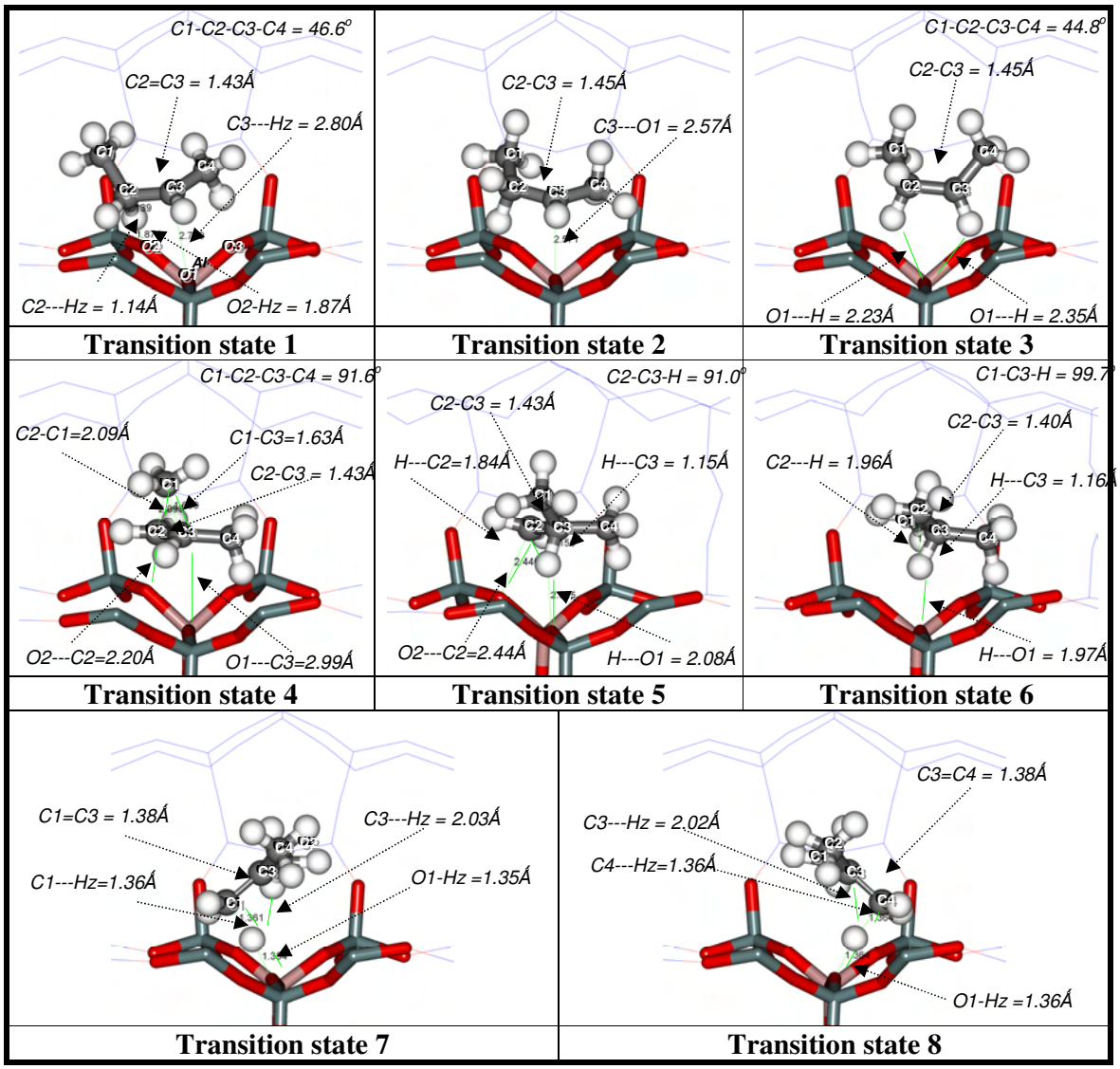


Figure 5 Transition states obtained in this study. See Figure 4 caption for additional details.

CARB1 can decompose in the forward direction to a secondary alkoxide intermediate by traversing a barrier of just 1.2 kcal/mol. The C3-O1 distance in TS2 is 2.57 Å, decreasing to 1.56 Å in the alkoxide intermediate (INT1). This structure is ~ 1kcal/mol lower in energy than the adsorbed cis-butene, lower than that reported by Boronat et al in Theta-1 (6.9 kcal/mol). This difference is not surprising given that the same authors show that alkoxides formed in Mordenite were shown to be heavily dependent on the T position[39], as do others[41].

Intermediate 2 (INT2) is formed when the methyl group (C1) migrates from C2 to to C3. This requires the O1-C3 bond to break and the O1-C3 bond to form in the process. The transition state (TS4) displays a partial C2=C3 double bond as observed by the 1.43 Å distance. This facilitates the migration of the methyl group between these two atoms. The C1-C2 distance is 2.09 Å and the C3-C1 distance is 1.63 Å while the C2-O2 and O1-C3 distances are 2.20 Å and 2.99 Å respectively. The barrier of 24 kcal/mol is consistent with that observed by Boronat et al in Theta-1 (25.8 kcal/mol). The secondary alkoxide is 2 kcal/mol higher in energy than the adsorbed isobutene in FER from the work of Tuma et al[42], which is consistent with what is found here (2.5 kcal/mol).

TS5 separates INT2 from carbenium ion 3, and not the product as is found in Theta-1. The breaking of the O2-C2 bond sees the migration of the hydrogen atom attached to C3 to C2 as the double bond begins to form. Proton transfer from this tertiary center to the zeolite was not observed due to the instability of the primary carbenium center that forms at C2. TS5 therefore displays a C2-O2 distance of 2.44 Å. The C3-H distance is 1.15 Å the C2-C3 distance is 1.42 Å. Crucially, the C2-C3-H angle is 91.0$^{o}$ indicating that the proton is in the process of migrating across the C2-C3 bond. This finding is consistent that the stability of carbenium ions are dependent on the accessibility of the acidic oxygen positions[28,39]. This barrier is 34.2, comparable to the final rate determining step found by Boronat et al in Theta-1 (32.7 kcal/mol)[36].

The tertiary butyl carbenium ion (CARB3) displays C-C distances of approximately 1.46 Å. Due to the unique pore dimensions, the tertiary butyl carbenium ion can make significant interactions with the zeolite. In fact, all 9 hydrogen atoms are found to make significant interactions with the zeolite. The 9 shortest C-H---O interactions observed (one per alkyl H) were 4*2.3 Å, 2.4 Å, 2.6 Å, 2*2.7 Å and 2.9 Å (Figure 7), which would

explain the very low net change on the molecule compared to CARB1 (Figure 6). This observation is discussed in more detail in the following section.

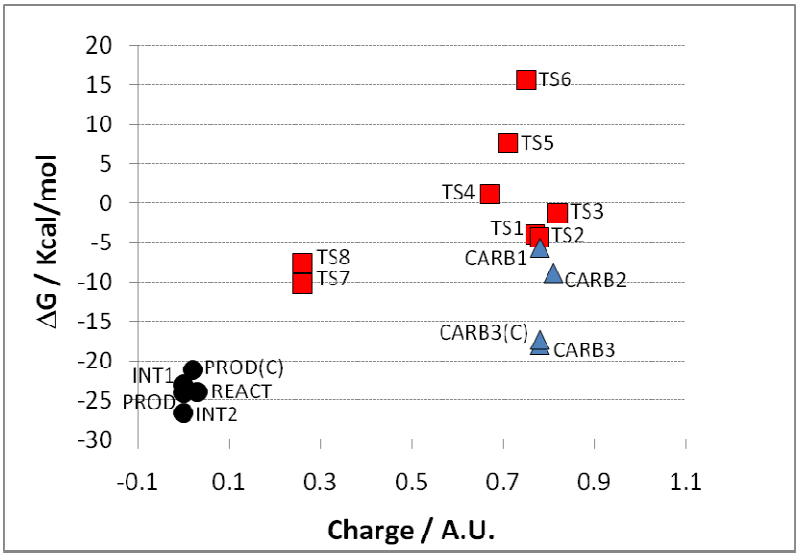


Figure 6 Plot of the zero point corrected single point energies against the Mulliken charge on the alkene. Transition states are denoted by squares (red), carbenium ions by triangles (blue) and other minima using circles (black).

CARB3 is found to be 6 kcal/mol higher in energy than the adsorbed cis-butene and iso-butene molecules. The latter energy is lower than the value reported very recently by Tuma et al (14 kcal/mol for tertiary butyl carbenium – adsorbed isobutene) [42], but it is closer to their earlier reported value of 8.5 kcal mol[43]. Fang et al also report that the tertiary butyl carbenium ion is 14.7 kcal/mol higher in energy compared to adsorbed iso-butene molecules in ZSM5. However, in this case the larger 12T pore of ZSM5 is unlikely to provide the same level of stabilization to the carbenium ion of the smaller FER pore as discussed above.

Transition state 7 (TS7) connects CARB3 with the adsorbed iso-butene molecule. The C1-Hz distance in TS7 is 1.36 Å, the O2-Hz distance is found to be 1.35 Å and the C1-C3 distance is 1.38 Å. The barrier to reaction is considerably higher than that observed for CARB1 due to the inherent stability of the structure. The stabilization provided by the zeolite leads to a forward barrier to reaction of 8.2 kcal/mol (11.4 kcal/mol in the reverse direction). This value is somewhat higher than in the similar study of tert-butyl

carbenium ions in FER (3.3 kcal/mol) reported by Tuma et al[42] but might be a reflection of the different models and methodologies used.

The adsorbed iso-butene molecule is of equivalent energy to the adsorbed cis-butene molecule in line with that found in Theta-1[51]. Unlike the adsorbed cis-butene molecule, the interaction between the acidic site and the alkene double of iso-butene molecule is not approximately symmetric. In the latter case, the C1---Hz distance is found to be 2.20 Á and the C3---Hz distance 2.57 Á. However the symmetric nature of the iso-butene molecule, and the location of the O1 acidic atom at a less restricted part of the pore mean that the somewhat poorer interaction of iso-butene is somewhat compensated for by reduced steric repulsion.

**4.2 Carbenium based mechanism**

The the skeletal isomerision of cis-butene to iso-butene can proceed in a manner somewhat similar to that reported to Boronat et al in Theta-1. The key difference is that the very first, and very final steps, which are reported to be concerted in Theta-1, are found to be stepwise in FER, involving 2 stable carbenium ions. Nevertheless, the reported rate determining barrier for the alkoxide based mechanism found in FER is 34.2 kcal/mol, very close to that reported for Theta-1 at 32.7 kcal/mol.

The observation here that the skeletal isomerisation of linear butenes in FER will proceed in a concerted fashion, via carbenium ion intermediates, is perhaps not surprising given the recent work by Tuma et al on iso-butene carbenium ions in FER[42]. It has not however been reported if the skeletal isomeration of linear butenes in FER can occur via a purely carbenium ion based process or at least now energetically favourable or not such a mechanism would be in comparison to one that proceeds via stable alkoxide intermediates. This is now discussed.

CARB1, formed by the transfer or the acidic proton to the C2 atom of cis-butene, can also react to form an additional carbenium ion, termed CARB2 here. For CARB2 to form, the C1-C2-C3-C4 dihedral angle must rotate from 7.0$^{o}$ in CARB1, to 44.8$^{o}$ in the transition state (TS3), before reaching a minima at.94.8$^{o}$ in CARB2. The barrier to this process is 4.3 kcal/mol. The minimum energy structure formed has a corresponding angle of 94.8$^{o}$, and is 3.2 kcal/mol lower than CARB1 and 18.3 kcal/mol higher in

energy than the adsorbed iso-butene molecule. In this structure the methyl group lies intermediate between the C2 and C3 atoms and is akin to TS4 discussed before. The key difference between the two structures is that CARB2 makes two strong interactions between the migrating methyl group and the Al polarized O2 and O3 atoms. The interactions of 2.28 and 2.09 Å are observed indicating the interaction is particularly strong.

CARB2 can decompose to form CARB3* (related to CARB3 in terms of their symmetry perpendicular to the 001 axis in FER) by completing the migration of the C1 methyl to the C3 position and the simultaneous migration of the C3 hydrogen atom across the C2=C3 bond as it increases in strength. In TS6 the methyl group has completely migrated. The C3-H distance is 1.16 Å, the C2-C3-H angle is 99.7$^{o}$ , and the C2=C3 distance is 1.40 Å. TS6 is found to be higher in energy than the related TS5 due to the fact that in the latter structure the breaking C2-O2 bond (coming from INT2) helps stabilize the structure, as can be seen by the considerably larger net Mulliken charge on the alkene (0.71 vs 0.75 respectively, Figure 6).

CARB3* is slightly higher in energy than CARB3 (-17.4 vs -18.0 kcal/mol). This can be rationalized based on its slightly reduced interaction with the zeolite lattice, as can be seen from the marginally higher net Mulliken charge on the two alkenes (0.75 vs 0.71 respectively). CARB3* reacts via TS8 to form the adsorbed iso-butene complex in a similar fashion to CARB3. The barrier is found to be 10.2 kcal/mol, 2.5 kcal/mol higher than TS7 which is associated with the CARB3. Again the less effective stabilization provided by the zeolite lattice explains the marginally higher barrier between these two related barriers (Figure 6). The adsorbed iso-butene molecule from this step is ~3 kcal/mol less well adsorbed than that arising from the alkoxide based mechanism (product*). These subtle differences are in line with the accessibility of atoms reported by other researchers[28,40,41,51].

The predicted rate determining energy barrier for the carbenium ion mediated process is 24.5 kcal/mol in FER, considerably lower than the 34.2 kcal/mol value obtained for the alkoxide based pathway. In fact, the key reason for the high energy barrier in the latter process is the inherent stability of alkoxide intermediates in acidic zeolites which explains why they are experimentally observed. In FER, the reverse barrier going from

INT2 to INT1 is just 27.7 kcal/mol, lower than the final rate determining step in the alkozide mediated process (34.2 kcal/mol), suggesting that the formation of iso-butene could still occur via a carbenuium based route even though INT2 is highly likely to form given its low energy.

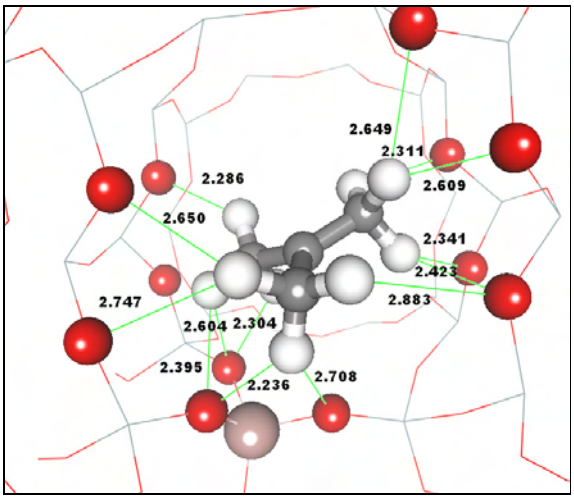


Figure 7 The tertiary butyl carbenium ion obtained in this study (CARB3). The key O---HC interactions are displayed to show the significant stabilizing effect the extended zeolite framework has on this stationary point.

Finally, the relationship between the relative energy of the stationary points obtained here and the net Mulliken charge observed on the alkene/alkane molecule is discussed. Fang et al reported that the stability of carbenium ions is proportional to the proton affinity or pKa of the molecule in question. In line with these finding, here it is found that the transition states that can most effectively delocalize the positive charge on proton transfer are generally of lower energy. TS7 and TS8 are not directly bonded to the proton explaining why the overall mulliken charge on this system is low. TS1, TS2 and TS3 are clustered together in terms of their energies and net Mulliken charges since they all contain secondary carbenium ion centers which are closely related to CARB1. TS4, TS5 and TS6 are related to INT1, INT2 and CARB2 respectively and their stability is correlated to their ability to delocalize their significant net positive charge. TS5 and TS6 both contain primary carbenium ion centers, but the latter interacts more favourably with the acidic center explaining its lower net change and energy (see previous discussion). TS4 contains a ~secondary/tertairy carbenium center which has

two short C---O interactions with the acidic center explaining its lower positive charge than the other fully protonated transition states and even the carbenium stationary points.

This general trend between the ability to delocalize net positive charge and the relative energy does not hold for the carbenium ions. The energy is primarily dictated by whether the carbenium ion is located on a primary, secondary or tertiary center. Also important are the presence of rather stronger interactions with the oxygen atoms of the zeolite lattice which can lower the overall energy, even if this is not reflected in the Mulliken charges (Figure 7). CARB3 and CARB3* are the lowest in energy since they are tertiary carbenium centers, followed by the secondary carbenium ions CARB2 and CARB1. As discussed earlier, CARB2 is lower in energy than CARB1 due to the more effective interactions it can make with the zeolite lattice oxygen atoms (even though its net Mulliken charge is higher).

These results confirm the findings of others that the accessibility of zeolite is very important for determining the stability of intermediates and carbenium ions formed with their pores. These results also suggest that QM models that employ relatively small flexible regions around the acidic center but fixed extended zeolite frameworks may miss a considerable amount of stabilization provided by oxygen atoms in the surrounding pore. These oxygen atoms here were found to move up to 0.3 A in some cases over the course of the reaction pathways simulated.

# บทที่ 5
# สรุปผลการทดลอง

In this study the results from a systematic analysis of two different mechanisms for the skeletal isomeristion of cis-butene to iso-butene have been presented. One involves a conventional mechanism that proceeds via stable alkoxide intermediates and the other is one which proceeds via carbenium ions only.

A 27T cluster model has been used here for this purpose using the M062X DFT functional. Atoms in the 6T region have been treated using the 6-31G(d) basis set and those in the remainder of the cluster treated using the 3-21G basis set. All stationary structures have been confirmed as minima or transition states using the full model and basis set used for optimization. More accurate energies were obtained by taking single point energies (M062X with the 6T region treated using 6-311+G(2df,dp) and the remainder using 6-31G(d)) of the optimized coordinates and correcting for zero point energy effects.

The results obtained here are in good agreement with related reports in the literature where comparison are possible, giving confidence in the models used. The traditional concerted alkoxide based mechanism reported by Boronat et al[36] is not found in FER. In this study the mechanism is found to proceeds in a stepwise manner with proton transfer and nucleophilic attack occurring in separate steps, consistent with recent proposals by Tuma et al[42]. The rate determining step for this mechanism is found to be very close (~34 kcal/mol) to that reported by Boronat et al.

A purely carbenium based mechanism was also investigated, which did not require the formation of any alkoxide intermediates. Although the carbenium ion structures formed over the pathway are inherently less stable than the alkoxide intermediates formed in the more conventional mechanism, the rate determining step is predicted to be almost 10 kcal/mol lower in energy. The higher barrier for the conventional process is due to the inherent stability of the intermediates formed within the FER pore. This could suggest that while these intermediates are formed over the course of a reaction, the skeletal isomerisation of butenes in FER only occurs via the carbenium based mechanism. This proposal is consistent with experimental results that alkoside intermediates are experimentally observed species.

With regards to the skeletal isomerisation of linear butene in larger zeolites such as ZSM-5, Rosenbach et al report that the tertiary butyl carbenium ion is 14 kcal/mol higher in energy than the adsorbed iso-butyl zeolite complex[44]. This is ~8 kcal/mol higher in energy than that observed here but it might suggest that a carbenium based mechanism in ZSM-5 might be close to isoenergetic with the more conventional alkoxide based mechanism. This proposal is currently under investigation.

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## ภาคผนวก

## OUTPUT จากโครงการวิจัยที่ได้รับทุนจาก สกว.

### ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1. Gleeson, D. Skeletal Isomerization of butene in Ferrierite. Assessing the energetic and structural differences between carbenium and alkoxide based pathways. J. Phys. Chem. C, 2011, Submitted.

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# Skeletal Isomerization of butene in Ferrierite. Assessing the energetic and structural differences between carbenium and alkoxide based pathways.



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# SKELETAL ISOMERIZATION OF BUTENE IN FERRIERI

# THE ENERGETIC AND STRUCTURAL DIFFERENCES BE

# AND ALKOXIDE BASED PATHWAYS.

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KEYWORDS: SKELETAL ISOMERIZATION, ZEOLITE CATALYSIS, BUTENE, DFT, M06-2X, FE

**Abstract**

IN THIS STUDY THE RESULTS FROM A SYSTEMATIC ANALYSIS OF TWO DIFFERENT MECH
ISOMERISATION OF CIS-BUTENE TO ISO-BUTENE IN FERRIERITE ARE PRESENTED. ONE INVOLVES
THAT PROCEEDS VIA STABLE ALKOXIDE INTERMEDIATES AND THE OTHER IS ONE WHICH PROCE
A 27T QM CLUSTER MODEL HAS BEEN USED HERE FOR THIS PURPOSE, WHICH IS DESCRIBED US
FUNCTIONAL. ALTHOUGH THE CARBENIUM ION STRUCTURES FORMED OVER THE PATHWAY AR
THE ALKOXIDE INTERMEDIATES FORMED IN THE CONVENTIONAL MECHANISM, THE RATE DETE
BE ALMOST 10 KCAL/MOL LOWER IN ENERGY. THE HIGHER BARRIER FOR THE LATTER PROC
STABILITY OF THE INTERMEDIATES FORMED WITHIN THE PORE. THIS APPEARS TO SUGGEST THA
ARE FORMED OVER THE COURSE OF A REACTION, THE SKELETAL ISOMERISATION OF BUTENE
CARBENIUM BASED MECHANISM. THIS PROPOSAL IS CONSISTENT WITH EXPERIMENTAL
INTERMEDIATES ARE EXPERIMENTALLY OBSERVED SPECIES.

## 1.0 Introduction

ZEOLITES ARE IMPORTANT SILICON BASED CATALYSTS EMPLOYED IN THE PETROCHEMICAL I
MATERIALS INTO REFINED PRODUCTS.[1,2] THE DESIRABLE CATALYTIC ACTIVITY OF THESE MATERIALS MAINL
THE REPLACEMENT OF INDIVIDUAL SILICON ATOMS IN THE 3D LATTICE STRUCTURE WITH ALUM
ACIDIC CENTER AND/OR (B) THE PRESENCE OF ADDITIONAL HEAVY METALS INCORPORATED WITHIN THE P
DIVERSE RANGE OF THREE DIMENSIONAL PORE STRUCTURES THAT, AS A CONSEQUENCE, CAN EXHIBIT SHA
REACTIONS CAN BE CATALYZED BY THESE MATERIALS.[3-5] ONE APPLICATION WHERE SUCH MATERIALS HAV
PARTICULARLY USEFUL IS IN THE CATALYTIC CRACKING AND SKELETAL ISOMERISATION OF H
PETROCHEMICAL INDUSTRY.[2,6-9] THE SKELETAL ISOMERISATION OF LINEAR BUTENES TO ISOBUTENE
EXTENSIVELY STUDIED EXPERIMENTALLY[10-14] AND THEORETICALLY[15-18] DUE TO THE FACT THAT THE LATTER IS AN IMPORTANT CHEMICAL PRECURS

IN THIS STUDY THE RELATED CATALYTIC CONVERSION OF CIS-BUTENE TO ISO-BUTENE IN TH
INVESTIGATED. THIS ZEOLITE IS OF SIGNIFICANT INTEREST FROM THE POINT OF VIEW OF BUTE
HIGH SELECTIVITY IT DISPLAYS FOR ISO-BUTENE COMPARED TO LARGER PORE ZEOLITES S[19-21]
DIFFERENCES ARISE DUE TO THE SO CALLED CONFINEMENT EFFECT OF THE UNIQUE ZEOLITE
ACIDITIES.[6-8] THERE ARE STILL A NUMBER OF UNCERTAINTIES REGARDING THE ORIGIN OF THE CA
THIS REACTION, INCLUDING WHETHER IT OCCURS VIA A MONO-MOLECULAR[2] OR PSEUDO BI-MOL

EXTENSIVE EXPERIMENTATION HAS BEEN UNDERTAKEN ON ZEOLITES USING TECHNIQUES SU
AND EPR SPECTROSCOPY.[22-24] IN ADDITION EXTENSIVE USE OF THEORETICAL METHODS HAVE BEE
LITERATURE. QUANTUM MECHANICAL (QM) CALCULATIONS OF VARIOUS TYPES HAVE BEEN EM
OF ZEOLITE CATALYSIS INCLUDING QM CLUSTER,[5,13,25] HYBRID QUANTUM MECHANICAL/MOL
MECHANICAL (QM/MM)[14,26] AND ONIOM METHODS,[27-29] AS WELL AS PERIODIC DFT SIMULATIONS.[30,31] IN THIS STUDY,
A RELATIVELY LARGE DFT CLUSTER MODEL OF FER IS EMPLOYED TO STUDY THE LOCAL EFFEC
THE SKELETAL ISOMERISATION OF CIS-BUTENE IN THE ZEOLITE (FIGURE 1) SINCE REPORTS FRO
SUCH A SIZED CLUSTER IS NEEDED TO ENABLE THE LOCATIONS OF HIGH ENERGY CATIONIC[32] TRANSI
IMPROVED M062X DFT FUNCTIONAL[33-35] IS EMPLOYED HERE AS IT HAS BEEN USED QUITE EXTENSIVELY T
OF ZEOLITE CATALYSIS RECENTLY[7,13,28,35]

THE INVESTIGATIONS OF BORONAT[36] ET AL IN THE MEDIUM PORE ZEOLITE THETA-1 SHOWED THAT T ISOMERISATION REACTION OF LINEAR BUTENES PROCEEDS VIA TWO ALKOXIDE INTERMEDIA BUTYL) TO THE ISO-BUTENE PRODUCT. THE RATE DETERMINING BARRIER IS 22 KCAL/MOL A MIGRATION. NO CARBENIUM ION STATIONARY POINTS WERE REPORTED IN THETA-1 OR BY A REL[37] THIS AUTHOR. DEMUTH ET AL INVESTIGATED THE RELATED SKELETAL ISOMERISATION OF 2-PE THE MOST LIKELY PATHWAY INVOLVED THE FORMATION OF HIGH ENERGY, BUT STABLE SEC TRANSIENT INTERMEDIATES.[38] THIS DIFFERING RESULT MAY BE DUE TO DIFFERENCES IN THE ZEOLITE PO INVESTIGATION IN THE DIFFERENT STUDIES SINCE THESE ARE KNOWN TO HAVE A DRAMATI CARBENIUM IONS.[39,40] NIEMENAN ET AL[41] HAS ALSO ASSESSED ASPECTS OF ALKOXIDE SPECIES STABILITI ALKENES BETWEEN 3 TO 5 CARBONS IN LENGTH. THEY SHOWED THAT THE STABILITY OF THE SENSITIVE TO THE STERIC BULK OF THE ALKENE IN QUESTION. IN ADDITION, A NUMBER OF S IMPORTANCE OF CARBENIUM IONS AND THEIR RELEVANCE IN SKELETAL ISOMERISATION OF[28,40,42-44] RUSAT AL[42,43], FOLLOWED BY BORONAT ET AL[40], CONCLUDED THAT CARBENIUM IONS SHOULD EXIST AS TRUE, A REACTION INTERMEDIATES.

THIS STUDY CONSIDERS THE SKELETAL ISOMERISATION OF LINEAR BUTENES TO ISO-BUTENE I RECENT PUBLICATIONS IN THE AREA. BOTH A CONVENTIONAL MECHANISM AKIN TO THAT PRO[36,40] THAT PROCEEDS VIA ALKOXIDE INTERMEDIATES, AND ONE THAT PROCEEDS VIA CARBENIUM[39] INVESTIGATED. THE ZEOLITE FER HAS BEEN CHOSEN FOR THIS STUDY DUE TO ITS WIDES ISOMERISATION REACTIONS[15-18] (B) DUE TO ITS RATHER SMALL PORE CAVITY WHICH PRESUMABLY ION FORMATION MORE LIKELY WHEN COMPARED TO LARGER PORE ZEOLITES SUCH AS ZSM CONTRASTED WITH RELATED THEORETICAL STUDIES WHICH HAVE BEEN PERFORMED IN EITHE SIMILAR ALKENES: THETA-1[40], ZSM-22[36,38], ZSM-5[37] AND FER[28,41,42] OR GENERIC ZEOLITE MODELS[45]

## 2.0 Models and Methods

RECENT CALCULATIONS ON FER HAVE USED THE CLUSTER APPROACH[7,28] AND PERIODIC METHODS[42,46] TO GOOD EFFECT TO ELUCIDATE ASPECTS OF ITS CATALYTIC FUNCTION. DUE TO THE CLUSTER APPROACH, AND THE ABILITY OF RELATIVELY LARGE CLUSTERS TO DESCRIBE HIGH

WITHIN ZEOLITE SYSTEMS[32], THE CLUSTER METHOD WAS CHOSEN FOR THIS STUDY. THE CLUSTER M
GENERATED USING THE X-RAY DIFFRACTION DATA OF HEULANDITE[47]. THIS HAS A 2 DIMENSIONAL PORE STRUCTU
A LARGE MAIN 10T CHANNEL BISECTED BY SMALLER 8T CHANNELS. A 27T CLUSTER MODEL WA
COORDINATES, ENCOMPASSING 2 COMPLETE PORES EITHER SIDE OF THE 10T CENTRAL RING. TH
CREATED BY REPLACING A SILICON ATOM LOCATED AT THE T2 POSITION OF THE 10T RING[7,41] WIT
THE 6T REGION OF THE CLUSTER MODEL SURROUNDING THE T2 SITE AND ACIDIC OXYGEN USIN
AND MORE DISTANT ATOMS USING THE 3-21G BASIS SET (FIGURE 1). THIS APPROACH HAS BEE
ALLOW A LARGE QM CLUSTER OF A ZEOLITE TO BE SIMULATED IN A REASONABLE AMOUNT OF T[48,49]. THE 3-21G BASIS SET
DOES APPEAR TO BE SUFFICIENT TO DESCRIBE LONGER RANGE EFFECTS BASED ON THE REPO[49]
RESULTED IN A MODEL SYSTEM WITH A TOTAL OF 1226 BASIS FUNCTIONS.

THE 6T REGION SURROUNDING THE T2 SITE AND ACIDIC OXYGEN WAS EXCISED FROM THE ORI
WITH BONDS CUT ACROSS THE O-SI BOND. TO AVOID ISSUES DUE TO OVERLY STRONG POLARIZA
OH GROUPS, BONDS WERE CUT ACROSS THE SI-O BONDS FOR THE MORE REMAINING 2 OF AT[46]. THIS TYPE
APPROACH IS SIMILAR TO THAT EMPLOYED TO ZHAO ET AL IN THEIR VALIDATION OF THE M0
BASED APPLICATIONS[35]. IONS MAINTAIN THE OVERALL SHAPE OF THE ZEOLITE ALL TERMINAL HYDRO
REGION WERE FIXED WHILE ONLY SILICON ATOMS BEYOND THIS REGION WERE FIXED. THIS AL
OXYGEN ATOMS, WHICH ARE DIRECTED INTO THE FER PORE, TO SUBTLY ALTER THEIR POSITI
SIMULATED REACTION, THEREBY ALLOWING BETTER STABILIZATION OF THE REACTIVE SPECI
THAT THE LACK OF FLEXIBILITY IN THE ZEOLITE LATTICE IS ONE OF THE KEY ISSUES IN E
INTERMEDIATES IN QM MODELS OF ZEOLITES[40].

ALL GEOMETRY OPTIMIZATIONS WERE PERFORMED USING M06-2X FUNCTIONAL[50] IN GAUSSIAN
THE MINNESOTA DENSITY FUNCTIONALS MODULE 3.1 BY ZHAO AND TRUHLAR[32]. MINIMA AND TRANSITION STATES
FULLY CHARACTERIZED AS STATIONARY POINTS IN THE COMPLETE 27T MODEL, IN ALL CASE
SINGLE NEGATIVE FREQUENTLY, RESPECTIVELY. ZERO POINT ENERGY CORRECTIONS TO TH
POSSIBLE. SINGLE POINT ENERGIES OF OPTIMIZED COORDINATES WERE SUBSEQUENTLY OBT
FUNCTIONAL WITH THE 6-311+G(2DF,DP) BASIS SET USED FOR THE 6T REGION AND 6-31G* FOR TH

WITH REGARDS TO MODEL VALIDITY, THE SKELETAL ISOMERIZATION OF LINEAR BUTENES T
BEEN STUDIED BY BORONAT ET AL IN THETA-1 USING A 20T MODEL.[36] THE AUTHORS REPORTED THA
RESULTS WERE IN AGREEMENT WITH PERIODIC MODELS THAT INCLUDE LONGER RANGE EFFE[36,40]
THIS FINDING SHOULD MEAN THAT THE RESULTS OBTAINED HERE FROM A LARGER 27T MODEL
REASONABLY ACCURACY.

### 3.0 Results and Discussion

THE ENERGETIC RESULTS OBTAINED FROM THE CALCULATIONS ARE REPORTED IN TABLE 1 A
PARAMETERS OF THE OPTIMIZED GEOMETRIES ARE DISPLAYED IN FIGURE 2 FOR MINIMA AND
STATES. THE ENERGIES OF THE OPTIMIZED COMPLEXES ARE GIVEN IN TABLE 2 ALONG WITH T
POINT CORRECTION AND THE SINGLE POINT ENERGIES. THE SINGLE POINT AND ZPE CORRECTEI
IN GOOD AGREEMENT WITH THE ENERGIES OBTAINED AT THE ORIGINAL LEVEL OR THEOR
HENCEFORTH CORRESPOND TO THE SINGLE POINT ENERGIES (M062X WITH 6-311+G(2DF,DP) FOR C
REGION AND 6-31G(D) FOR 21T REGION) INCLUDING ZERO POINT ENERGY CORRECTIONS, AND A
THE ISOLATED REAGENTS UNLESS OTHERWISE STATED.

THE SKELETAL ISOMERISATION OF CIS-BUTENE IS FIRST DISCUSSED IN THE CONTEXT OF THE M
BASED MECHANISM FOLLOWED BY A DISCUSSION ON THE RELATIVE LIKELIHOOD OF A CARI
EXISTING IN THIS ZEOLITE.

### 3.1 Alkoxide based mechanism

THE TRADITIONAL UNI-MOLECULAR MECHANISM OF BUTENE ISOMERISATION BEGINS WIT
ADSORBED ALKENE-FER COMPLEX. THE ESTIMATED ADSORPTION ENERGY OF 1-BUTENE[51] IS -18.9
AND -18.4 KCAL/MOL FOR ISO-BUTENE.[42] THUS, THE VALUE OF -23.8 KCAL/MOL OBTAINED HERE FO
ADSORBED TO FER APPEARS REASONABLE ESPECIALLY GIVEN THAT IT IS LESS STERICALLY HI
π-COMPLEX DISPLAYS SHORT C---HZ INTERACTIONS AS EXPECTED (2.11 Å) WHILE THE C=C BOND DISTANCE
ONLY SLIGHTLY ELONGATED COMPARED TO THE ISOLATED GASPHASE VALUE (1.34 VS 1.33 Å)

THE SKELETAL ISOMERISATION IN THETA-1 BEGINS WITH THE FORMATION OF A SECONDA
CONCERTED MECHANISM WITH SIMULTANEOUS TRANSFER OF A PROTON FROM THE ZEOLITE TO
A C-O BOND[36,40]. THE NEXT STEP REQUIRES A METHYL GROUP SHIFT, LEADING TO THE FORMATION
INTERMEDIATE. THE CARBON ATOM FROM WHICH THE METHYL GROUP MIGRATES FORMS A C-
NUCLEOPHILIC OXYGEN, WHILE THE MIGRATING METHYL SATISFIES THE VALENCE OF THE CA
MUST BREAK. THE SECONDARY ALKOXIDE IS FOUND TO BE 6.9 KCAL/MOL HIGHER IN ENERGY TH
COMPARED TO THE PRIMARY ALKOXIDE WHICH IS -2.9 KCAL/MOL LOWER. THE RATE DETERMINI
DECOMPOSITION OF THE PRIMARY ALKOXIDE TO GIVE ADSORBED ISO-BUTENE. THIS FINAL STEP
THE PRIMARY ALKOXIDE TO BREAK AND THE TRANSFER OF A PROTON TO THE ZEOLITE WHICH
OF 32.7 KCAL/MOL. ISO-BUTENE IS FOUND TO BE ADSORBED TO THETA-1 ONLY 0.7 KCAL/MOL H
BUTENE. BORONAT ET AL NOTE THAT THESE ENERGIES ARE LIKELY TO BE UPPER LIMITS GI
OPTIMIZED (A 5T OPTIMIZED MODEL WAS INSERTED INTO THE LARGER MODEL AND A SINGLE
PERFORMED)[36].

IN FER, IT IS FOUND THAT THE FORMATION OF THE INITIAL ALKOXIDE INTERMEDIATE DOES
MANNER, IN CONTRAST TO THAN WITHIN THETHETA-1 PORE. PROTON TRANSFER FROM THE O2 A
OF CIS-BUTENE VIA TRANSITION STATE ONE (TS1) LEADS TO A STABLE CARBENIUM ION 18.3 KC
THAN THE ADSORBED COMPLEX, WITH A BARRIER OF 19.9 KCAL/MOL. THE C2-C3 DISTANCE OF T
INCREASES TO 1.45 Å IN CARBENIUM ION 1 (CARB1), INTERMEDIATE BETWEEN THE DOUBLE AND SIN
EXPECTED FOR CIS-BUTENE IN THE GASPHASE (1.33 VS 1.50 Å RESPECTIVELY). TS1 IS CONSIDERABLY CLOSER IN
TO THE CORRESPONDING CARBENIUM ION THAN ADSORBED CIS-BUTENE AS MIGHT BE EXPE
DIFFERENCES. TS1 HAS A C2-C3 DISTANCE THAT IS VERY CLOSE TO THAT OF CARB1 (1.43 VS 1.45 Å), AS WELL AS THE
C2-HZ DISTANCE OF (1.14 VS 1.13 Å). THE PRINCIPAL DIFFERENCE BEING THE TWO IS THE C1-C2-C3-C
ANGLE, WHICH IS 7° IN CARB1 BUT 46.6° IN TS1, FACILITATING THE INDUCTIVE STABILIZATION OF T
CHARGED CARBON CENTER IN THE FORMER. CARB1 IS STABILIZED BY A SINGLE STRONG INTE
C4 HYDROGEN ATOM AND THE O3 OXYGEN ATOM (1.93 Å), SIMILAR TO THOSE REPORTED BY FANG ET AL[38].

CARB1 CAN DECOMPOSE IN THE FORWARD DIRECTION TO A SECONDARY ALKOXIDE INTERM
BARRIER OF JUST 1.2 KCAL/MOL. THE C3-O1 DISTANCE INCREASES FROM 2.57 Å, IN TS2 TO 1.56 Å IN THE ALKOXIDE

INTERMEDIATE (INT1). THIS STRUCTURE IS ~ 1KCAL/MOL LOWER IN ENERGY THAN THE ADSORB
THAT REPORTED BY BORONAT ET AL IN THETA-1 (6.9 KCAL/MOL). THIS DIFFERENCE IS NOT SURP
AUTHORS SHOW THAT ALKOXIDES FORMED IN MORDENITE WERE SHOWN TO BE HEAVILY DEPEN
DO OTHERS[41]

INTERMEDIATE 2 (INT2) IS FORMED WHEN THE METHYL GROUP (C1) MIGRATES FROM C2 TO TO
O1-C3 BOND TO BREAK AND THE O1-C3 BOND TO FORM IN THE PROCESS. THE TRANSITION STATE
C2=C3 DOUBLE BOND AS OBSERVED BY THE 1.43 Å DISTANCE. THIS FACILITATES THE MIGRATION OF THE
BETWEEN THESE TWO ATOMS. THE C1-C2 DISTANCE IS 2.03 Å AND THE C3-C1 DISTANCE IS 1.83 Å WHILE THE C2-O2
AND O1-C3 DISTANCES ARE 2.20 Å AND 2.99 Å RESPECTIVELY. THE BARRIER OF 24 KCAL/MOL IS CONSIST
OBSERVED BY BORONAT ET AL IN THETA-1 (25.8 KCAL/MOL). THE SECONDARY ALKOXIDE IS 2 KC
THAN THE ADSORBED ISOBUTENE IN FER FROM THE WORK OF TUMANOV ET AL[42], WHICH IS CONSISTENT WITH WHAT IS
HERE (2.5 KCAL/MOL).

TS5 SEPARATES INT2 FROM CARBENIUM ION 3, AND NOT THE PRODUCT AS IS FOUND IN THETA-
O2-C2 BOND SEES THE MIGRATION OF THE HYDROGEN ATOM ATTACHED TO C3 TO C2 AS THE
FORM. PROTON TRANSFER FROM THIS TERTIARY CENTER TO THE ZEOLITE WAS NOT OBSERVE
PRIMARY CARBENIUM CENTER THAT FORMS AT C2. TS5 THEREFORE DISPLAYS A C2-H2 DISTANC
DISTANCE IS 1.15 Å THE C2-C3 DISTANCE IS 1.42 Å. CRUCIALLY, THE C2-C3-H ANGLE IS 90.0° INDICATING THAT TH
PROTON IS IN THE PROCESS OF MIGRATING ACROSS THE C2-C3 BOND. THIS FINDING IS CONSIST
CARBENIUM IONS ARE DEPENDENT ON THE ACCESSIBILITY OF THE ACIDIC PROTON TO THE ZEOLITE[28,29], THIS BARRIER IS 34.2 KCAL/MOL, CONS
COMPARABLE TO THE FINAL RATE DETERMINING STEP FOUND BY BORONAT ET AL IN THETA-1 (3[36]

THE TERTIARY BUTYL CARBENIUM ION (CARB3) DISPLAYS C-C DISTANCES OF APPROXIMATE
UNIQUE PORE DIMENSIONS, THE TERTIARY BUTYL CARBENIUM ION CAN MAKE SIGNIFICANT IN
IN FACT, ALL 9 HYDROGEN ATOMS ARE FOUND TO MAKE SIGNIFICANT INTERACTIONS WITH THE
-O INTERACTIONS OBSERVED (ONE PER ALKYL H), WITH DISTANCES OF 2.4 Å, 2.64 Å, 2.7 Å AND 2.9 Å (FIGURE 6), WHICH
WOULD EXPLAIN THE VERY LOW NET CHANGE ON THE MOLECULE COMPARED TO CARB1 (FIGUR
DISCUSSED IN MORE DETAIL IN THE FOLLOWING SECTION.

CARB3 IS FOUND TO BE 6 KCAL/MOL HIGHER IN ENERGY THAN THE ADSORBED CIS-BUTENE AN
THE LATTER ENERGY IS LOWER THAN THE VALUE REPORTED VERY RECENTLY BY TUMA ET AL [43]
CARBENIUM – ADSORBED ISO-BUTENE) IS CLOSER TO THEIR EARLIER REPORTED VALUE OF 15 KC[43]
AL ALSO REPORT THAT THE TERTIARY BUTYL CARBENIUM ION IS 14.7 KCAL/MOL HIGHER IN EN
ISO-BUTENE MOLECULES IN ZSM5. HOWEVER, IN THIS CASE THE LARGER 12T PORE OF ZSM5 IS UN
SAME LEVEL OF STABILIZATION TO THE CARBENIUM ION OF THE SMALLER FER PORE AS DISCUSS

TRANSITION STATE 7 (TS7) CONNECTS CARB3 WITH THE ADSORBED ISO-BUTENE MOLECULE. T
TS7 IS 1.36 Å, THE O2-HZ DISTANCE IS FOUND TO BE 1.35 Å AND THE C1-C3 DISTANCE AS 1.88 Å. THE BARRIER TO
REACTION IS CONSIDERABLY HIGHER THAN THAT OBSERVED FOR CARB1 DUE TO THE INHEREN
THE STABILIZATION PROVIDED BY THE ZEOLITE LEADS TO A FORWARD BARRIER TO REACTION
IN THE REVERSE DIRECTION). THIS VALUE IS SOMEWHAT HIGHER THAN IN THE SIMILAR STUDY
IN FER (3.3 KCAL/MOL) REPORTED BY TUMA ET AL.[42] WHICH MIGHT BE A REFLECTION OF THE DIFFERENT
METHODOLOGIES USED.

THE ADSORBED ISO-BUTENE MOLECULE IS OF EQUIVALENT ENERGY TO THE ADSORBED CIS-BU
THAT FOUND IN THE TMA.[51] UNLIKE THE ADSORBED CIS-BUTENE MOLECULE, THE INTERACTION BETWE
THE ALKENE DOUBLE OF ISO-BUTENE MOLECULE IS NOT APPROXIMATELY SYMMETRIC. IN TH
DISTANCE IS FOUND TO BE 2.20 Å AND THE C3---HZ DISTANCE 2.57 Å. HOWEVER THE SYMMETRIC NATURE OF
BUTENE MOLECULE, AND THE LOCATION OF THE O1 ACIDIC ATOM AT A LESS RESTRICTED PAR
SOMEWHAT POORER INTERACTION OF ISO-BUTENE IS SOMEWHAT COMPENSATED FOR BY REDUC

### 3.2 Carbenium based mechanism

THE THE SKELETAL ISOMERISION OF CIS-BUTENE TO ISO-BUTENE CAN PROCEED IN A MANNER
REPORTED TO BORONAT ET AL IN THETA-1. THE KEY DIFFERENCE IS THAT THE VERY FIRST, AND
REPORTED TO BE CONCERTED IN THETA-1, ARE FOUND TO BE STEPWISE IN FER, INVOLVING 2
NEVERTHELESS, THE REPORTED RATE DETERMINING BARRIER FOR THE ALKOXIDE BASED MEC
KCAL/MOL, VERY CLOSE TO THAT REPORTED FOR THETA-1 AT 32.7 KCAL/MOL.

THE OBSERVATION HERE THAT THE SKELETAL ISOMERISATION OF LINEAR BUTENES IN FER W
FASHION, VIA CARBENIUM ION INTERMEDIATES, IS PERHAPS NOT SURPRISING GIVEN THE RECE
ISO-BUTENE CARBENIUM IONS IN HAS[42] IT HAS NOT HOWEVER BEEN REPORTED IF THE SKELETAL ISOM
BUTENES IN FER CAN OCCUR VIA A PURELY CARBENIUM ION BASED PROCESS OR AT LEAST NOV
OR NOT SUCH A MECHANISM WOULD BE IN COMPARISON TO ONE THAT PROCEEDS VIA STABL
THIS IS NOW DISCUSSED.

CARB1, FORMED BY THE TRANSFER OR THE ACIDIC PROTON TO THE C2 ATOM OF CIS-BUTENE, C
ADDITIONAL CARBENIUM ION, TERMED CARB2 HERE. FOR CARB2 TO FORM, THE C1-C2-C3-C4 DIH
ROTATE FROM 17.0° IN CARB1, TO 44.8° IN THE TRANSITION STATE (TS3), BEFORE REACHING A MINIM
CARB2. THE BARRIER TO THIS PROCESS IS 4.3 KCAL/MOL. THE MINIMUM ENERGY STRUCT
CORRESPONDING ANGLE OF 94.8°, ON THE 3.2 KCAL/MOL LOWER THAN CARB1 AND 18.3 KCAL/MOL HIGH
THAN THE ADSORBED ISO-BUTENE MOLECULE. IN THIS STRUCTURE THE METHYL GROUP LIES I
AND C3 ATOMS AND IS AKIN TO TS4 DISCUSSED BEFORE. THE KEY DIFFERENCE BETWEEN THE
CARB2 MAKES TWO STRONG INTERACTIONS BETWEEN THE MIGRATING METHYL GROUP AND TH
ATOMS. THE INTERACTIONS OF 2.28 AND 2.35 Å ARE OBSERVED INDICATING THE INTERACTION IS PARTICUL

CARB2 CAN DECOMPOSE TO FORM CARB3* (RELATED TO CARB3 IN TERMS OF THEIR SYMMETR
THE 001 AXIS IN FER) BY COMPLETING THE MIGRATION OF THE C1 METHYL TO THE C3 POSITION
MIGRATION OF THE C3 HYDROGEN ATOM ACROSS THE C2=C3 BOND AS IT INCREASES IN STREN
GROUP HAS COMPLETELY MIGRATED. THE C3-H DISTANCE IS 1.16 Å, THE C2-C3-H ANGLE IS 99.7°, AND THE C2=C3
DISTANCE IS 1.40 Å. TS6 IS FOUND TO BE HIGHER IN ENERGY THAN THE RELATED TS5 DUE TO THE F
STRUCTURE THE BREAKING C2-O2 BOND (COMING FROM INT2) HELPS STABILIZE THE STRUCTUR
CONSIDERABLY LARGER NET MULLIKEN CHARGE ON THE ALKENE (0.71 VS 0.75 RESPECTIVELY, F

CARB3* IS SLIGHTLY HIGHER IN ENERGY THAN CARB3 (-17.4 VS -18.0 KCAL/MOL). THIS CAN
BASED ON ITS SLIGHTLY REDUCED INTERACTION WITH THE ZEOLITE LATTICE, AS CAN BE SEEN
NET MULLIKEN CHARGE ON THE TWO ALKENES (0.75 VS 0.71 RESPECTIVELY). CARB3* REACTS
ADSORBED ISO-BUTENE COMPLEX IN A SIMILAR FASHION TO CARB3. THE BARRIER IS FOUND T
KCAL/MOL HIGHER THAN TS7 WHICH IS ASSOCIATED WITH THE CARB3. AGAIN THE LESS E

PROVIDED BY THE ZEOLITE LATTICE EXPLAINS THE MARGINALLY HIGHER BARRIER BETWEE
(FIGURE 5). THE ADSORBED ISO-BUTENE MOLECULE FROM THIS STEP IS ~3 KCAL/MOL LESS W
ARISING FROM THE ALKOXIDE BASED MECHANISM (PRODUCT*). THESE SUBTLE DIFFERENC
ACCESSIBILITY OF ATOMS REPORTED BY OTHER RESEARCHERS[28,40,41,51]

THE PREDICTED RATE DETERMINING ENERGY BARRIER FOR THE CARBENIUM ION MEDIATED
FER, CONSIDERABLY LOWER THAN THE 34.2 KCAL/MOL VALUE OBTAINED FOR THE ALKOXIDE
KEY REASON FOR THE HIGH ENERGY BARRIER IN THE LATTER PROCESS IS THE INHERENT STAB
IN ACIDIC ZEOLITES WHICH EXPLAINS WHY THEY ARE EXPERIMENTALLY OBSERVED. IN FER, T
FROM INT2 TO INT1 IS JUST 27.7 KCAL/MOL, LOWER THAN THE FINAL RATE DETERMINING STEP I
PROCESS (34.2 KCAL/MOL), SUGGESTING THAT THE FORMATION OF ISO-BUTENE COULD STILL OC
ROUTE EVEN THOUGH INT2 IS HIGHLY LIKELY TO FORM GIVEN ITS LOW ENERGY.

FINALLY, THE RELATIONSHIP BETWEEN THE RELATIVE ENERGY OF THE STATIONARY POINT
MULLIKEN CHARGE OBSERVED ON THE ALKENE/ALKANE MOLECULE IS DISCUSSED. FANG ET A
OF CARBENIUM IONS IS PROPORTIONAL TO THE PROTON AFFINITY OR PKA OF THE MOLECULE IN
FINDING, HERE IT IS FOUND THAT THE TRANSITION STATES THAT CAN MOST EFFECTIVELY DEL
PROTON TRANSFER ARE GENERALLY OF LOWER ENERGY. TS7 AND TS8 ARE NOT DIRECTLY BON
WHY THE OVERALL MULLIKEN CHARGE ON THIS SYSTEM IS LOW. TS1, TS2 AND TS3 ARE CLUSTE
THEIR ENERGIES AND NET MULLIKEN CHARGES SINCE THEY ALL CONTAIN SECONDARY CARB
CLOSELY RELATED TO CARB1. TS4, TS5 AND TS6 ARE RELATED TO INT1, INT2 AND CARB2 RESPE
STABILITY IS CORRELATED TO THEIR ABILITY TO DELOCALIZE THEIR SIGNIFICANT NET POSIT
CONTAIN PRIMARY CARBENIUM ION CENTERS, BUT THE LATTER INTERACTS MORE FAVOUR
EXPLAINING ITS LOWER NET CHANGE AND ENERGY (SEE PREVIOUS DISCUSSION). TS4 CONTAI
CARBENIUM CENTER WHICH HAS TWO SHORT C---O INTERACTIONS WITH THE ACIDIC CENTER EX
CHARGE THAN THE OTHER FULLY PROTONATED TRANSITION STATES AND EVEN THE CARBENIU

THIS GENERAL TREND BETWEEN THE ABILITY TO DELOCALIZE NET POSITIVE CHARGE AND T
HOLD FOR THE CARBENIUM IONS. THE ENERGY IS PRIMARILY DICTATED BY WHETHER THE CA
PRIMARY, SECONDARY OR TERTIARY CENTER. ALSO IMPORTANT ARE THE PRESENCE OF RATHE

OXYGEN ATOMS OF THE ZEOLITE LATTICE WHICH CAN LOWER THE OVERALL ENERGY, EVEN I
MULLIKEN CHARGES (FIGURE 6). CARB3 AND CARB3* ARE THE LOWEST IN ENERGY SINCE
CARBENIUM CENTERS, FOLLOWED BY THE SECONDARY CARBENIUM IONS CARB2 AND CARB1.
CARB2 IS LOWER IN ENERGY THAN CARB1 DUE TO THE MORE EFFECTIVE INTERACTIONS IT CAN
LATTICE OXYGEN ATOMS (EVEN THOUGH ITS NET MULLIKEN CHARGE IS HIGHER).

THESE RESULTS CONFIRM THE FINDINGS OF OTHERS THAT THE ACCESSIBILITY OF ZEOLI
DETERMINING THE STABILITY OF INTERMEDIATES AND CARBENIUM IONS FORMED WITH THEI
SUGGEST THAT QM MODELS THAT EMPLOY RELATIVELY SMALL FLEXIBLE REGIONS AROUND
EXTENDED ZEOLITE FRAMEWORKS MAY MISS A CONSIDERABLE AMOUNT OF STABILIZATION PR
THE SURROUNDING PORE. THESE OXYGEN ATOMS HERE WERE FOUND TO MOVE UP TO 0.3 A I
COURSE OF THE REACTION PATHWAYS SIMULATED.

**4.0 Conclusions**

IN THIS STUDY THE RESULTS FROM A SYSTEMATIC ANALYSIS OF TWO DIFFERENT MECI
ISOMERISTION OF CIS-BUTENE TO ISO-BUTENE HAVE BEEN PRESENTED. ONE INVOLVES A CONV
PROCEEDS VIA STABLE ALKOXIDE INTERMEDIATES AND THE OTHER IS ONE WHICH PROCEEDS VI

A 27T CLUSTER MODEL HAS BEEN USED HERE FOR THIS PURPOSE USING THE M062X DFT FUNC
6T REGION HAVE BEEN TREATED USING THE 6-31G(D) BASIS SET AND THOSE IN THE REMAINDE
USING THE 3-21G BASIS SET. ALL STATIONARY STRUCTURES HAVE BEEN CONFIRMED AS MINIMA
THE FULL MODEL AND BASIS SET USED FOR OPTIMIZATION. MORE ACCURATE ENERGIES WERE
POINT ENERGIES (M062X WITH THE 6T REGION TREATED USING 6-311+G(2DF,DP) AND THE RE
31G(D)) OF THE OPTIMIZED COORDINATES AND CORRECTING FOR ZERO POINT ENERGY EFFECTS.

THE RESULTS OBTAINED HERE ARE IN GOOD AGREEMENT WITH RELATED REPORTS IN THE LITE
POSSIBLE, GIVING CONFIDENCE IN THE MODELS USED. THE TRADITIONAL CONCERTED ALK
REPORTED BY BORONAT[36] ET AL FOUND IN FER. IN THIS STUDY THE MECHANISM IS FOUND TO
STEPWISE MANNER WITH PROTON TRANSFER AND NUCLEOPHILIC ATTACK OCCURRING IN SEP

RECENT PROPOSALS BY TUMANOV ET AL[42] THE RATE DETERMINING STEP FOR THIS MECHANISM IS FOUND TO (~34 KCAL/MOL) TO THAT REPORTED BY BORONAT ET AL.

A PURELY CARBENIUM BASED MECHANISM WAS ALSO INVESTIGATED, WHICH DID NOT REQU ALKOXIDE INTERMEDIATES. ALTHOUGH THE CARBENIUM ION STRUCTURES FORMED OVER THE STABLE THAN THE ALKOXIDE INTERMEDIATES FORMED IN THE MORE CONVENTIONAL MECHA STEP IS PREDICTED TO BE ALMOST 10 KCAL/MOL LOWER IN ENERGY. THE HIGHER BARRIER FOR T DUE TO THE INHERENT STABILITY OF THE INTERMEDIATES FORMED WITHIN THE FER PORE. THI THESE INTERMEDIATES ARE FORMED OVER THE COURSE OF A REACTION, THE SKELETAL ISOM ONLY OCCURS VIA THE CARBENIUM BASED MECHANISM. THIS PROPOSAL IS CONSISTENT WITH ALKOSIDE INTERMEDIATES ARE EXPERIMENTALLY OBSERVED SPECIES.

WITH REGARDS TO THE SKELETAL ISOMERISATION OF LINEAR BUTENE IN LARGER ZEOLITES S AL REPORT THAT THE TERTIARY BUTYL CARBENIUM ION IS 14 KCAL/MOL HIGHER IN ENERGY ZEOLITE COMPLEX[44] THIS IS ~8 KCAL/MOL HIGHER IN ENERGY THAN THAT OBSERVED HERE BUT IT I CARBENIUM BASED MECHANISM IN ZSM-5 MIGHT BE CLOSE TO ISOENERGETIC WITH THE MORE BASED MECHANISM. THIS PROPOSAL IS CURRENTLY UNDER INVESTIGATION.

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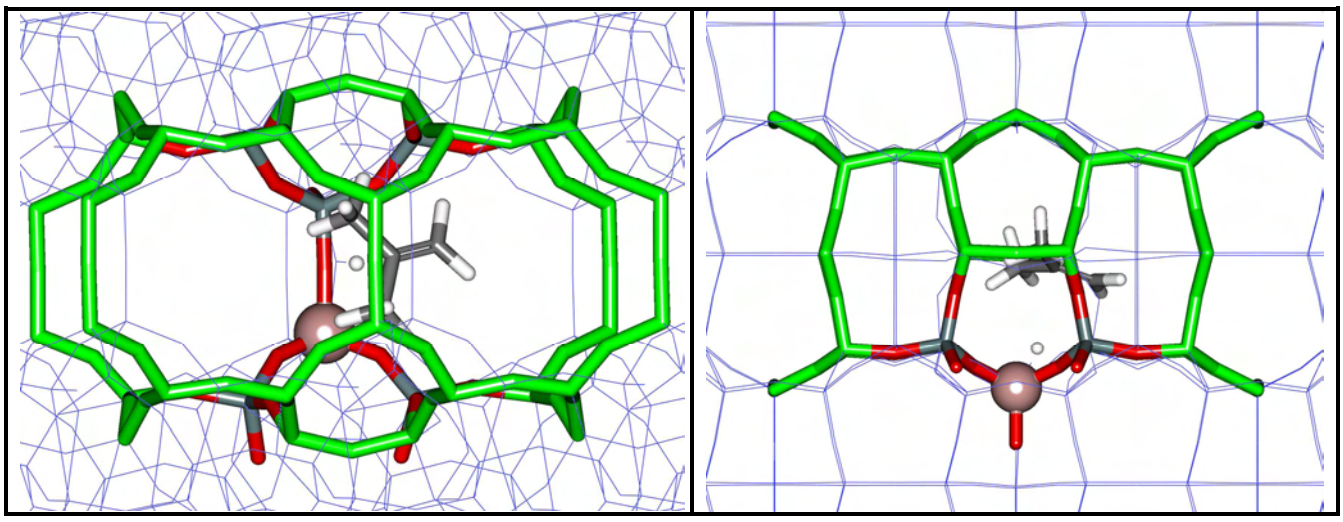

**Figure 1 An illustration of the 27T model used in this study (illustrated using a stick representation). The 6T region surrounding the the T2 Al atom and acidic center are described using the 6-31G(d) basis set (O atoms coloured red and Si grey). To include the confinement effect of the zeolite, the two pores that bisect the main 10T ring are also included in the calculation at using the 3-21G basis set (stick representation with all atoms coloured green).**

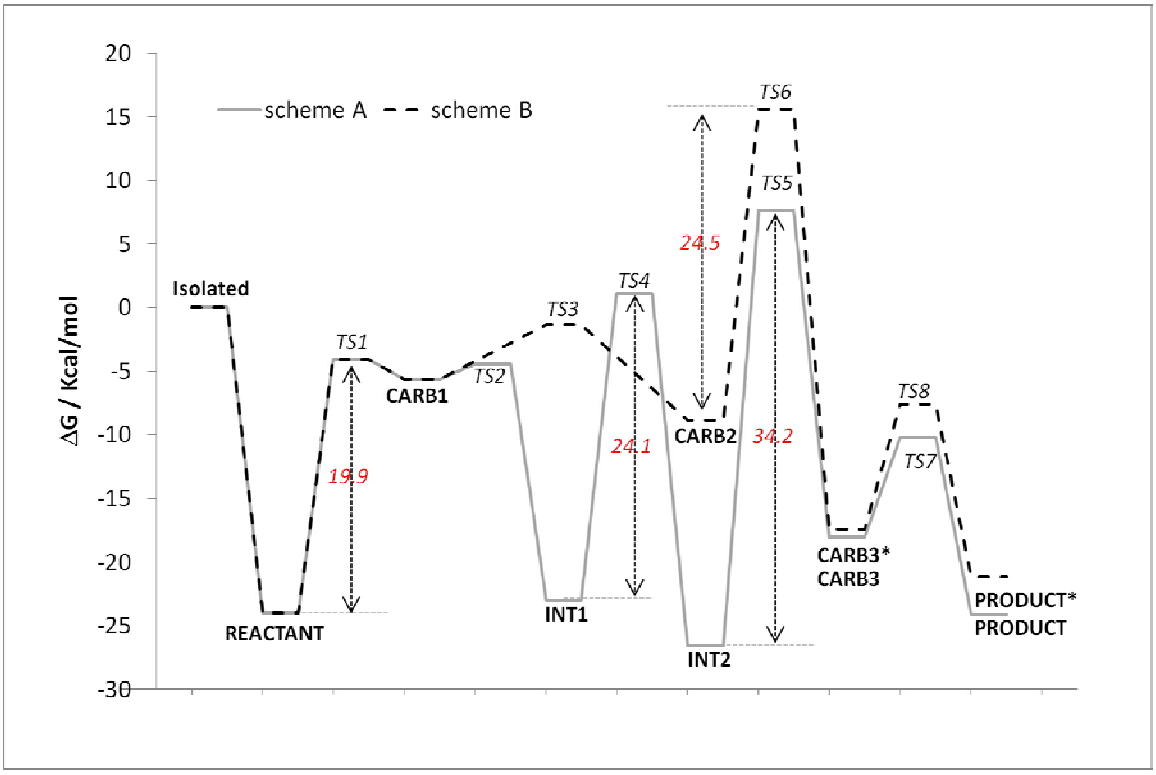


**Figure 2 A graphical illustration of the energetic associated with the alkoxide (Scheme A, grey solid line) and carbenium (Scheme B, dashed black line) based mechanisms. The stationary points found on the two pathways are illustrated in Figure 3 and Figure 4.**

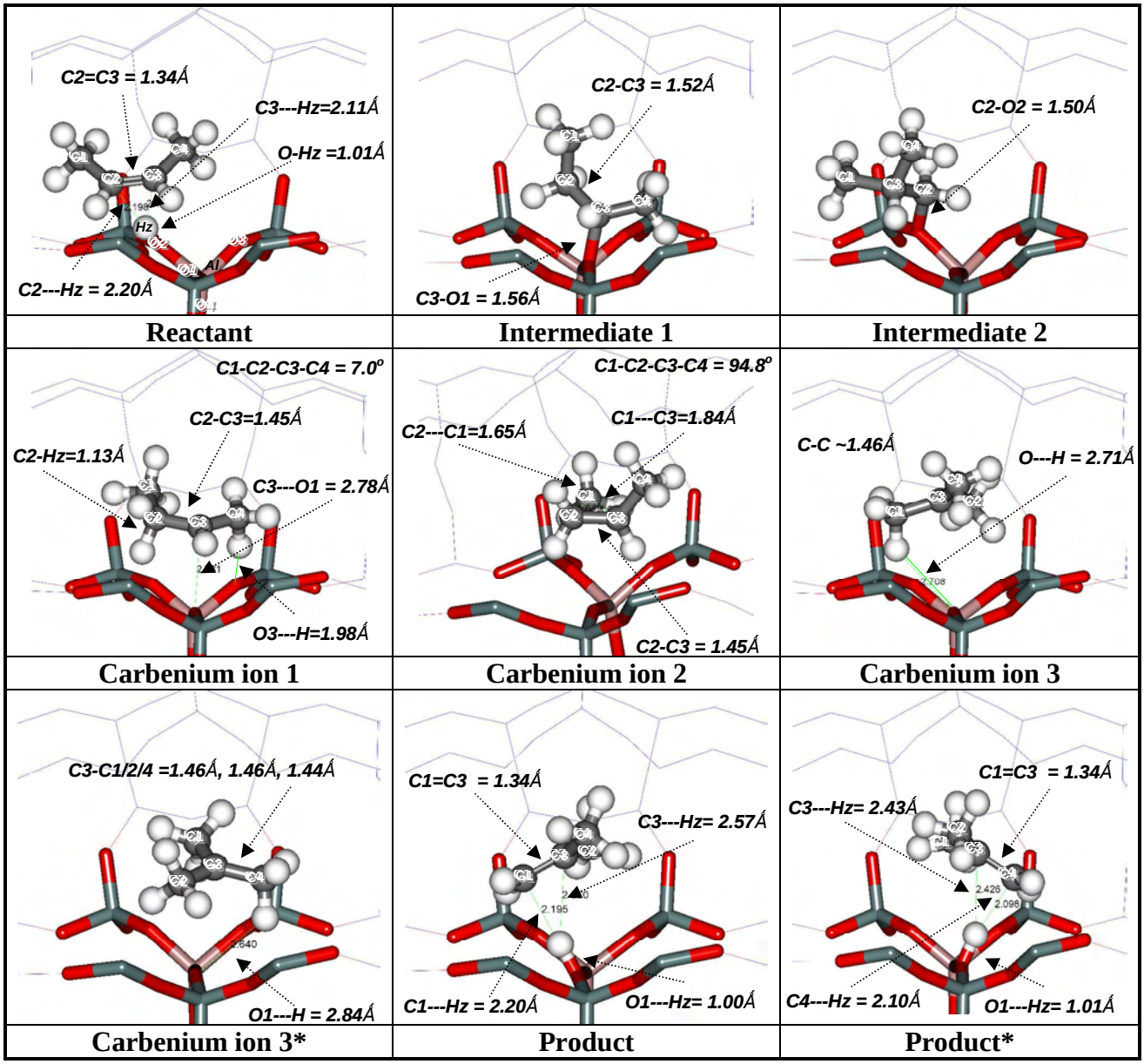


**Figure 3 Minima obtained in this study. 6T region denoted using a stick representation and the 21T region using wireframe. Atoms in the foreground have been removed to aid visualisation. Carbon atoms are numbered 1 to 4 to facilitate interpretation. Only the key zeolite atoms are numbered in the top left panel. Key distances and angles are illustrated.**

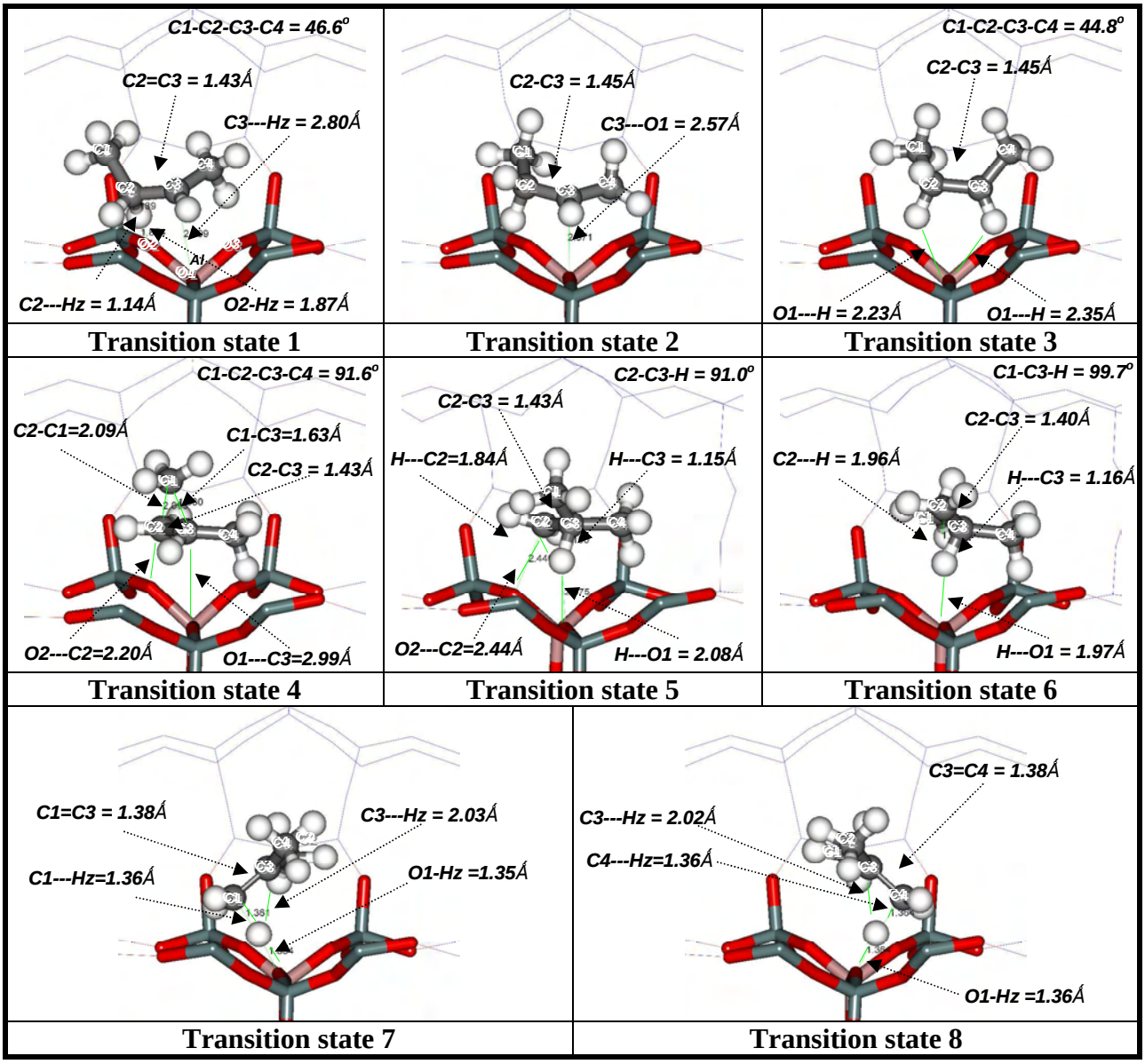


**Figure 4 Transition states obtained in this study. See Figure 3 caption for additional details.**

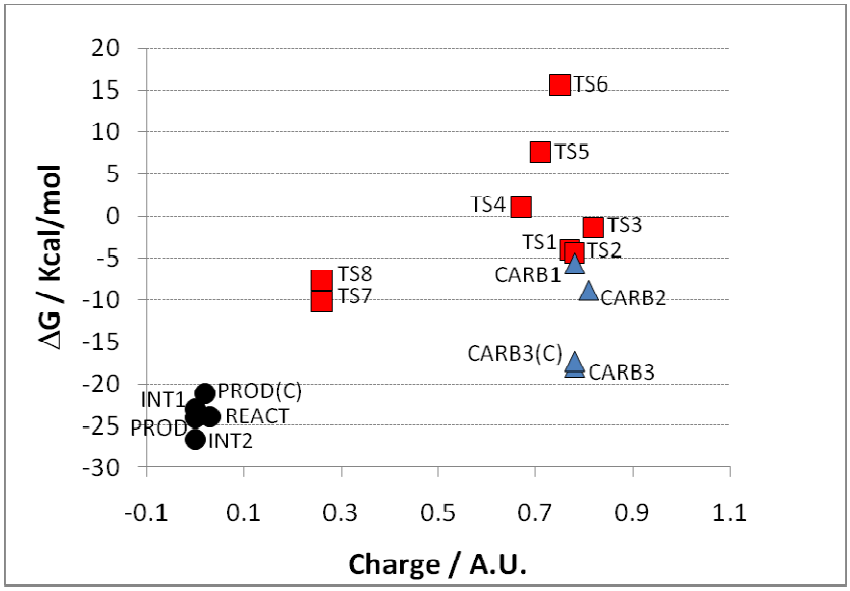


**Figure 5 Plot of the zero point corrected single point energies against the Mulliken charge on the alkene. Transition states are denoted by squares (red), carbenium ions by triangles (blue) and other minima using circles (black).**

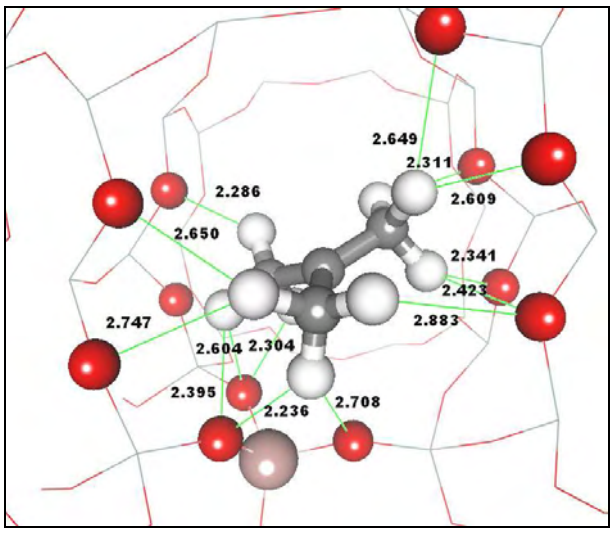


**Figure 6 The tertiary butyl carbenium ion obtained in this study (CARB3). The key O---HC interactions are displayed to show the significant stabilizing effect the extended zeolite framework has on this stationary point.**

## List of Tables

**Table 1 The energies of the stationary points obtained in this study. All energies are relative to the isolated energies of the zeolite model and cis-butene in the gasphase. ΔH corresponds to the energy of optimized complexes using the default basis set (M062X with cis-butene and zeolite 6T described by 6-31G(d) and 21T atoms using 3-21G). ZPE corresponds to the zero point correction energy for the optimized stationary points at the default level of theory. DH SP corresponds to the single point energy of the optimized stationary point performed as follows: M062X with cis-butene and zeolite 6T described by 6-311+G(2df,dp) and 21T atoms using 6-31G(d). The ΔG (SP+ZPE) value corresponds to the ΔH SP plus the ZPE correction obtained using the default basis set calculation. All values are reported in Kcal/mol.**

| Scheme-A | ΔH | ZPE | ΔH SP | ΔG (SP+ZPE) |
|---|---|---|---|---|
| REACTANT | -22.82 | -0.72 | -23.25 | -23.96 |
| TS1 | -4.51 | 0.44 | -4.50 | -4.06 |
| CARB1 | -6.91 | 0.42 | -6.05 | -5.63 |
| TS2 | -4.97 | 0.02 | -4.45 | -4.43 |
| INT1 | -21.65 | -3.98 | -19.03 | -23.01 |
| TS4 | -1.31 | -1.01 | 2.08 | 1.07 |
| INT2 | -29.80 | -3.18 | -23.41 | -26.60 |
| TS5 | 5.39 | 0.85 | 6.78 | 7.63 |
| CARB3 | -19.68 | 0.24 | -18.29 | -18.04 |
| TS7 | -11.38 | 1.42 | -11.62 | -10.21 |
| PRODUCT | -20.34 | -1.61 | -22.50 | -24.11 |

| Scheme-B | ΔH | ZPE | ΔH SP | ΔG (SP+ZPE) |
|---|---|---|---|---|
| REACT | -22.82 | -0.72 | -23.25 | -23.96 |
| TS1 | -4.51 | 0.44 | -4.50 | -4.06 |
| CARB1 | -6.91 | 0.42 | -6.05 | -5.63 |
| TS3 | -1.46 | -0.38 | -0.94 | -1.32 |
| CARB2 | -7.96 | -0.36 | -8.50 | -8.87 |
| TS6 | 13.36 | 2.11 | 13.48 | 15.59 |
| CARB3 (C) | -19.16 | 0.68 | -18.06 | -17.38 |
| TS8 | -9.72 | 1.76 | -9.38 | -7.62 |
| PRODUCT (C) | -18.62 | -2.21 | -18.94 | -21.15 |

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