

Quantum Chemical Prediction of Hydrocarbon Cracking Reactions

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Abstract

For many years, researchers have been developing theoretical methods of estimating reaction rates and energetics when experimental measurements are not available. Recent advances have led to composite energy methods with near chemical accuracy. The performance of these new methods for predicting activation energies and rate constants have not been evaluated for large hydrocarbon cracking reactions.

In this work, *ab initio* methods are used to study the transition state structures and activation energies of ethane cracking, hydrogen exchange and dehydrogenation reactions catalyzed by zeolites. The reactant and transition state structures are optimized by HF and MP2 methods and the final energies are calculated using a Complete Basis Set composite energy method. The computed activation barriers are 71.39 kcal/mol for cracking, 31.39 kcal/mol for hydrogen exchange and 75.95 kcal/mol for dehydrogenation using geometries optimized with the MP2 method. The cluster effect and acidity effect on the reaction barriers are also investigated. The relationship between activation barriers and zeolite deprotonation energies for each reaction are proposed so that accurate activation energies can be obtained when using different zeolites as catalysts.

Keywords: Zeolite, Ethane, Cluster approach, CBS method

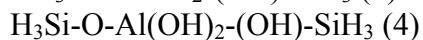
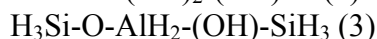
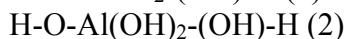
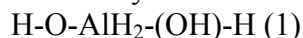
1. Introduction

Zeolites are crystalline aluminosilicates with a three-dimensional framework structure which forms uniformly sized pores of molecular dimension. They are broadly used as catalysts in the oil refining and petroleum industries; the total annual zeolite catalyst consumption rate is 1.4 million to 1.6 million tons [1]. A zeolite has a lattice structure. When all lattice ions are silicon, the zeolite lattice's composition is SiO_2 , a polymorph of quartz. Brønsted acidic sites are formed when a silicon atom, which has a formal valency of four, is replaced by an aluminum atom with a valency of three. A proton is attached to the oxygen atom connecting the silicon and its aluminum atom neighbor, resulting in a chemically stable structure where the oxygen atom becomes a three-coordinated structure. SiO and AlO bonds have considerable covalency, resulting in a relatively weak OH bond. The "onium" type coordination of oxygen is the fundamental reason for the high acidity of the attached proton, which makes a zeolite a good catalyst [2].

The conversion of hydrocarbons by zeolite acid catalysts is essential for the modern oil and chemical industries [3,4]. The heterogeneous catalytic reactions which

occur on zeolite surfaces can be studied with computational methods using either the cluster approach. A cluster model is formed by cutting out a small portion of the catalyst lattice and terminating the open valences with hydroxyl or hydride bonds. The cluster size is chosen so that the reaction can be modeled using quantum methods [5]. The aspects of a catalytic reaction which are only dependent on local properties, such as activation of adsorbates and any bond breaking or forming that may take place, are in the realm of the cluster approach.

When studying heterogeneous zeolite reactions, an important issue is the choice of cluster model to describe the local environment around the zeolitic proton [6]. This Brønsted acidic site is generally modeled by one of the following cluster models:



The major differences among these cluster models lie in the number of tetrahedral (T) molecules (Al and Si) and the termination bonds (-H or -OH). Cluster models (1) and (2) contain only one tetrahedral molecule--aluminum, but no silicon--and are called T1 clusters. Cluster models (3) and (4) contain three tetrahedral structures--one aluminum and two silicons--and are called T3 clusters.

Ab initio quantum chemistry has long been applied as a major tool for investigating the structure, stability, reaction kinetics and mechanisms of different molecular systems. *Ab initio* calculations, which are based on the Schrödinger equation, have the advantage of depending on the fundamental laws of physics and universal constants only. Therefore, no empirical constants are required in the calculations. In recent years, the application of *ab initio* calculations has become an essential approach to the understanding of the chemical features of the zeolite reactions [7].

Blaszkowski *et al.* studied ethane conversion reactions using local density approximation (LDA), a low level density function method [8]. Density function theory and *ab initio* quantum chemical methods have been applied by other researchers to study catalytic reactions quantitatively [9-21]. However, with the best calculations of the B3LYP method, the transition state energies may be underestimated by approximately 10 kcal/mol [22]. Kazansky *et al.* investigated the same reactions using the small 3-21 basis set and a silicon free T1 cluster [20]. The activation energies obtained are very high bringing into question the validity of the results. In this work, a silicon-containing T3 cluster is used to simulate the zeolite surface and *ab initio* methods are implemented to investigate the reaction. The results are then compared with those from previous research.

2. Computational Methods

In this work, the CBS compound model was used to investigate ethane conversion energetics on a zeolite cluster. All of the *ab initio* calculations were performed with the GAUSSIAN98 [23] software package. Geometries were optimized at the HF/6-31g* and MP2(full)/6-31g* levels of calculation. Initial geometries for MP2/6-31g* were obtained using HF/6-31g* optimization results. In some cases, a planar symmetry constraint of two

carbon atoms of the ethane reactant with five cluster atoms (one Al, two O and two Si) was imposed in order to accelerate calculation. All products and reactants were verified with frequency calculations to be stable structures and all transition states were found to be first order saddle points with only one negative eigenvalue. Additionally, intrinsic reaction coordinate (IRC) calculations showed that each reaction linked the correct products with reactants. Zero point vibrational energies (ZPVE) were obtained from harmonic vibrational frequencies calculated at the MP2(full)/6-31g* level with a scaling factor of 0.9661[24]. Frequencies were scaled with a factor of 0.9427 at the MP2(full)/6-31g* level.

In order to verify the computational method used in this work, zeolite cluster $\text{H}_3\text{SiOAlH}_2(\text{OH})\text{SiH}_3$ geometry and frequency calculation results together with the available experimental results are compared and listed in Table 1.

Table 1. Calculated results using MP2/6-31g* and experimental data

	$\text{H}_3\text{SiOAlH}_2(\text{OH})\text{SiH}_3$ ^a	Experimental Data
H-Al distance (Å)	2.39	2.43±0.03, 2.48±0.04 ^b
O-H vibrational frequency (cm^{-1})	3708	3600-3623 ^c

a – calculated results using MP2/6-31g*

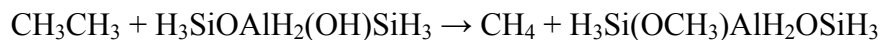
b – ref [25,26]

c – ref [27-29]

By NMR spectroscopic method, the distances between acidic hydrogen and aluminum atom are measured to be 2.43±0.03Å and 2.48±0.04Å respectively by Freude [25] and Kenaston [26]. The calculation results using MP2/6-31g* is 2.39Å, which is in excellent agreement with both experimental data. The vibrational frequency of the acidity H-O bond is 3496 cm^{-1} using same method. Compared with experimental value of 3600-3623 cm^{-1} [27-29], the relative error is within 3%.

3. Results and discussions

3.1 Cracking reaction



The cracking reaction consists of the C-C bond cleavage of ethane by the zeolite Brønsted acid proton. The proton attaches to one methyl group of the ethane reactant and forms methane and a surface oxide. The calculated reaction transition state structure using the MP2/6-31g* method is shown in Figure 1(a). The acid proton has been transferred to the right carbon of ethane and a methane molecule is almost formed. The left methyl group of ethane becomes a planar structure and forms a carbenium ion together with the cluster structure. The zeolite cluster plays an important role in this reaction. The right oxygen of the cluster acts as a Brønsted acid which donates a proton while the left oxygen acts as a Lewis base which receives the methyl group.

The activation energies obtained from the MP2 geometry optimization method and CBS energy calculation is 71.39 kcal/mol. Because there are no experimental

activation energies available, this result is compared with the computational results from other researchers. As listed in Table 2, the activation energy obtained by Blaszkowski *et al.* [8] using LDA density functional method is relatively lower because density function theory has been known to underestimate activation energies. The result from Kazansky [20], 93.38 kcal/mol, is high because of the small T1 cluster used and the fact that MP2 single point energies overestimate barrier heights. Another result from Kazansky [15] used a T3 cluster and the MP2(fc)/6-31++G** energy calculation method. The activation energy obtained, 75.23 kcal/mol, is still high because the MP2 method is known for over-predicting activation energies.

3.2 Hydrogen exchange reaction

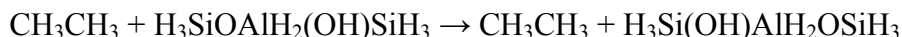
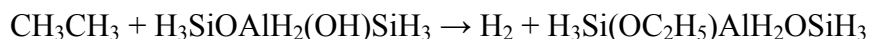


Figure 1(b) shows the calculated transition state structure for the hydrogen exchange reaction of ethane using the MP2 method. It shows clearly the C_s symmetry obtained without any symmetry constraints applied for the optimization step. The carbon in the main plane of zeolite structure, C(15), is protonated and becomes a penta-coordinated structure. The other carbon atom keeps its tetrahedral structure. The two hydrogen atoms, H(14) and H(19), stay in the middle of the carbon and oxygen atoms, indicating the forming of one C-H bond and breaking of the other. The right oxygen of the cluster acts as a Brønsted acid which donates a proton. The left oxygen acts as a Lewis base which receives the hydrogen atom from ethane.

The activation energies obtained from the MP2 geometry optimization method and the CBS energy calculation is 31.39 kcal/mol. The barrier is the lowest among the three ethane conversion reactions, indicating it is the easiest reaction to take place. The activation energy is higher than the result obtained by Blaszkowski *et al.* [8] using density function theory, 28.28 kcal/mol, listed in Table 2. Again, the lower number from the previous work is probably due to the systematic underprediction of activation energies by density functional methods. There are no additional calculated results available for comparison.

3.3 Dehydrogenation reaction



The dehydrogenation reaction consists of cleavage of a C-H bond by the zeolite Brønsted acid proton. The transition state structure of the reaction is shown in Figure 1(c). The carbon atom attached by the acidic proton becomes a planar structure and the other carbon keeps the tetrahedral structure. A six member ring, O(2)-Al(1)-O(3)-H(14)-H(20)-C(15), is formed. With the H(20)-C(15) and H(14)-O(3) distances greatly extended, a dihydrogen molecule is almost formed whereas the C_2H_5 binds to the zeolite oxygen, O(2), which acts as a Lewis base.

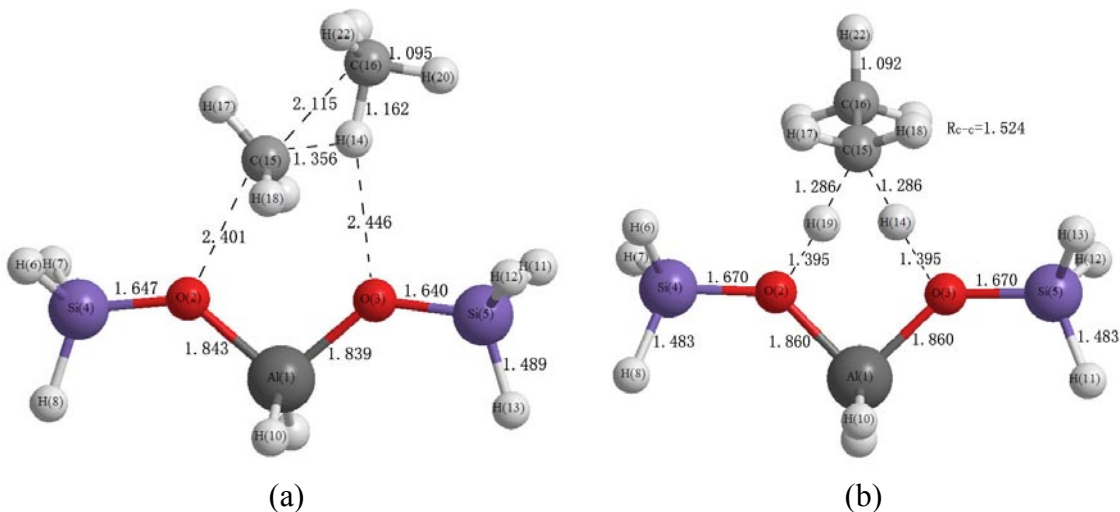
The activation energies obtained from the MP2 geometry optimization method with the CBS energy calculation is 75.95 kcal/mol. The barrier is the highest among all three ethane conversion reactions, indicating it is the most difficult reaction to take place. Compared with other researchers' work, this result is higher than the result obtained by Blaszkowski *et al.* [8] using density function theory and much less than the results obtained by Kazansky [15,20] using the MP2 energy calculation method with HF geometry optimization as listed in Table 2. Systematic effects on activation energies are leading to these discrepancies with the expectation that the complete basis set results are more accurate in general [30].

Table 2. Activation energy calculation results for ethane conversion reactions on zeolites using the CBS method (Units in kcal/mol)

Geometry Optimization Method	This Work		Others' Work	
	HF	MP2	DFT ^a	HF ^b
Cracking	71.29	71.39	69.78	93.38, 75.23
Hydrogen Exchange	31.90	31.39	28.28	-
Dehydrogenation	75.91	75.95	70.98	94.80, 79.53

a – ref. [8]

b – ref. [15,20,21]



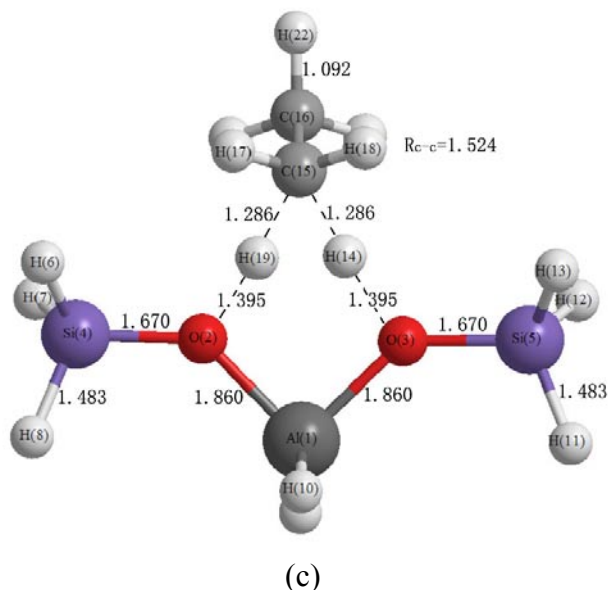


Figure 1. Transition state structures for ethane reactions on zeolite cluster (a) Cracking reaction, (b) Hydrogen exchange reaction, (c) Dehydrogenation reaction (Units in Å)

3.4 Geometry optimization method

In this work, both HF and MP2 optimization methods combined with the same basis set, 6-31G*, were used to obtain the geometries of the reactants and transition states. The energies were then obtained by using the composite CBS method. As shown in Table 2, there is little difference between the activation energies obtained using these two different geometry optimization methods with the maximum difference within 1 kcal/mol. The Hartree-Fock method, the cheapest method in the *ab initio* family, is described by other researchers to fail in describing the motion of the individual electrons, especially for the computation of hydrogen bonds and protonation [6]. However, this was not encountered in this work. Therefore, we find that the calculated activation energies depend greatly on the level of energy calculation method and depend less on the level of geometry optimization method. The CBS energy calculation method is crucial in this situation. Therefore, the geometry optimized using the HF method is adequate for activation barriers as long as the final energy is obtained using a high level method like CBS. Because of the low computational cost of the HF geometry optimization method, it is recommended for studying other zeolite catalytic reactions of large hydrocarbon species.

4. Conclusions

In this work, ethane cracking, hydrogen exchange and dehydrogenation reactions catalyzed by a zeolite were studied using *ab initio* methods. The transition state structures were optimized using HF and MP2 methods, and the energies were obtained using the CBS composite energy method. The effects of zeolite cluster size and acidity on the activation barriers were investigated. Additionally, the choice of HF and MP2 geometry optimization methods and the effects on the barrier heights were also studied.

The activation energies obtained for cracking, hydrogen exchange and dehydrogenation reactions are 71.39, 31.39 and 75.95 kcal/mol respectively using geometries optimized by the MP2 method. This indicates that the hydrogenation exchange reaction has the lowest barrier and is the easiest reaction to happen, while the dehydrogenation reaction has the highest barrier and is the most difficult to happen.

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