

# The Quantum Confinement Effect on the Adsorption and Reaction of Aliphatic Hydrocarbons on 'Nano Reactor' ZSM-5 Zeolite: A Newly Developed Density Functional Theory (DFT) Investigation

B. Boekfa<sup>a,b</sup>, S. Choomwattana<sup>a,b</sup>, P. Maitarad<sup>a,b</sup>, P. Limtrakul<sup>a</sup>, J. Limtrakul<sup>a,b,\*</sup>

<sup>a</sup>Laboratory for Computational and Applied Chemistry, Chemistry Department, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

<sup>b</sup>NANOTEC Center of Excellence, National Nanotechnology Center, Kasetsart University Research and Development Institute, Thailand

\*E-mail: jumras.l@ku.ac.th, Tel: +662-562-5555 ext 2169, Fax: +662-562-5555 ext 2176

## ABSTRACT

Full quantum calculations with a newly developed functional, M06-L, on the ZSM-5 models of 5T, 12T, 34T, 46T and 128T were performed to simulate the nanoporous system. Methane and ethane are chosen to represent saturated hydrocarbons. The calculated adsorption energies are -7.0 kcal/mol for methane and -11.1 kcal/mol for ethane, which agree well with the experimental estimates of -6.7 and -9.1 kcal/mol. The M06-L method is also applied for the first time to systematically investigate the proton exchange reactions of methane and ethane within the nano-reactor of zeolite. The concerted mechanism is proposed for the reaction. The calculated activation energy of methane is 35.3 kcal/mol, which is comparable with the experimental data (33.4 kcal/mol), whereas the energy of ethane is 33.0 kcal/mol. The effect of nano-quantum confinement of the extended zeolite framework on adsorption and reaction mechanisms has been clearly demonstrated not only to better stabilize the adsorption complexes achieving the observed values but also to lower their activation energies to approach experimental benchmarking.

**Keywords:** zeolites, proton exchange reaction, M06-L functional, confinement effect, light alkanes

## 1 INTRODUCTION

In fine-chemical and pharmaceutical manufacture and in petroleum refining, zeolites, which have a combination of high stability with their excellent activity in acid-mediated reactions [1-3], have been applied in the process of heterogeneous catalysis. Especially, ZSM-5, patented in 1975, is widely used in chemical industries such as hydrocarbon cracking, isomerization, alkylation reaction and methanol to olefins (MTO) [4].

To clearly envision the structure, adsorption properties and chemical reaction mechanism, theoretical study can offer a practical tool that provides insight to the reaction mechanism complementing experimental investigations or, in certain cases, offer an understanding that is not possible by experimental investigations. Numerous experimental [5-9] and theoretical [10,11] researches have been devoted to understanding the chemistry of ZSM-5. Attempts have been made to develop the computational methodology that can precisely predict the physical

and chemical properties of the zeolite itself and the reaction inside its nanocavity. The Density Functional Theory (DFT), especially B3LYP, has been widely used to study the interaction of hydrocarbons with zeolites. However, the limitation of the DFT calculations previously employed was that the contribution of dispersion interactions was not taken into account. This interaction contribution in the adsorption has been found to be essential in the chemical adsorptions and reactions inside the zeolite pore [8,12-17]. To overcome the enormous computational resource required for a DFT calculation on a large model, the ONIOM scheme combined with QM/MM calculation [18,19] is applied to such systems. This provides an acceptable balance between the accuracy of the results and the computational cost. The ONIOM scheme provides only an approximation [14,15,18-21] and, therefore, the quest for a more accurate method continues. Recently, the newly developed functional called M06-L was introduced by Zhao and coworkers [22]. It is recommended for transition metal thermochemistry, noncovalent interactions and for when a local functional is required; a local functional has a much lower cost for large systems [23-25]. With the improved combination of the computational method and the realistic model, we hypothesize that this method should be able to represent the interaction within the zeolite system.

The aim of this work is threefold: first, to present a theoretical study on the nature of the H-ZSM-5 adsorption complex of methane and ethane, second, to further describe the proton exchange reaction of methane and ethane catalyzed by the zeolite and third, to present, for the first time, the full quantum calculation application of the 'noncovalent interaction represented' M06-L method on the zeolite framework.

## 2 METHODOLOGY

ZSM-5 structure from the XRD data was trimmed down to become 5T, 12T, 34T, 46T and 128T cluster models (see Fig. 1). The 5T cluster ( $\text{AlSi}_4\text{O}_4\text{H}_{13}$ ) is modeled to represent only the Brønsted active site. The T12 position was selected to be Al due to its being the most energetically favorable [26]. The 12T stands for the 10-membered-ring window of the zigzag nanochannel of the porous structure. The model was extended to 34T to cover the intersection of straight-zigzag channels, including some part of the zigzag channel. Adopted from our previous publications [12,13,20], the 46T model is similar to the 34T, but the framework

is extended surrounding the acid center in the zigzag channel. The largest model, 128T, envelops the whole model of 46T with another shell of tetrahedral subunits. The adsorption and reaction of methane and ethane on different H-ZSM-5 models are fully quantum calculated with the M06-L functional [22], along with the 6-31G(d,p) basis set. During the structure optimization on the 5T, 12T, 34T and 46T systems, the 5T portion of the active site region (AlSi<sub>4</sub>O<sub>4</sub>H) and the reacting molecule are allowed to relax while the rest is fixed at the crystallographic coordinates [27]. The transition states (TS) of the reaction were characterized by the existence of a single imaginary frequency. All calculations were performed using the Gaussian 03 code [28].

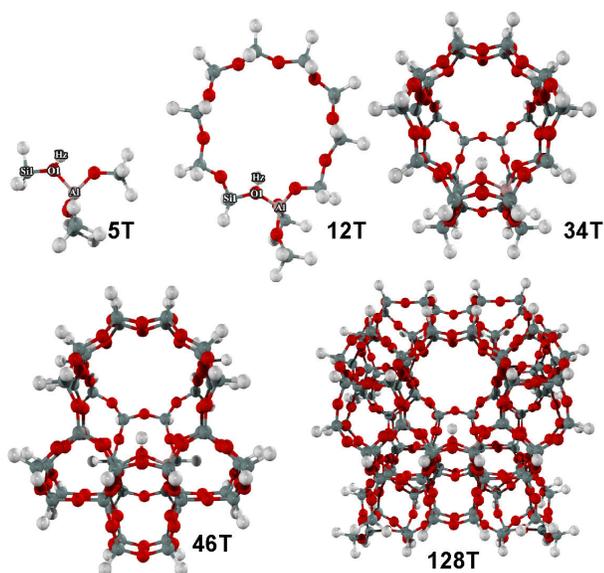


Figure 1: The evolution of H-ZSM-5 models, from the 5T unit to 128T clusters.

### 3 RESULTS AND DISCUSSION

#### 3.1 Molecular Cluster and Nanocluster Models of H-ZSM-5 catalyst

The evolution of our H-ZSM-5 models, from the 5T unit to the 128T framework, is illustrated in Fig. 1. Selected structural parameters of each model are presented in Fig 2.

In the bare zeolite, one can observe the influence of the framework on the effective Brønsted acidity. From Figure 2, the acidity is insignificantly more pronounced in the extended zeolite framework according to the increased O1-Hz bond length by at most 0.2 pm. The calculated Al...H distances in the range of 234.9-237.4 pm are close to the experimental report by Klinoski of 238.0-248.0 pm of H-zeolite [29]. This good agreement confirms the validation of our models.

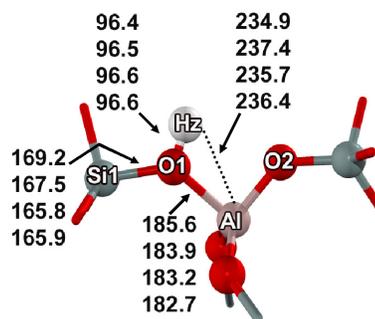


Figure 2: Optimized structure of various H-ZSM-5 models calculated with the M06-L/6-31G(d,p) method.

Distance parameters shown in lines 1-4 are for 5T, 12T, 34T and 46T quantum clusters, respectively.

#### 3.2 Adsorption of Light Alkanes on the Brønsted Acid Site

The adsorption energies of the methane and ethane complexes with various zeolite models are summarized in Table 1. As an underestimated value is expected from a small cluster, we found that the methane is bound by -2.9 kcal/mol to the acid site. This increases slightly and converges to -6.9 and -7.0 kcal/mol for the 34T and 46T, respectively. From the same zeolite models, ethane is bound by -10.8 and -11.1 kcal/mol to the acid site. The larger interaction for ethane than methane is found to agree favorably with the known adsorption trend as the molecular size increases. We also found that the adsorption energies are increased due to the presence of a larger framework effect in larger zeolite models. The experimental observation of methane and ethane adsorbed on H-ZSM-5 are -6.7 and -9.1 kcal/mol, respectively [16,17]. The calculated energies from the 34T and 46T clusters are therefore reasonably close to the experimental data.

| Model             | Methane | Ethane |
|-------------------|---------|--------|
| 5T                | -2.9    | -4.6   |
| 12T               | -5.1    | -7.7   |
| 34T               | -6.9    | -10.8  |
| 46T               | -7.0    | -11.1  |
| 128T <sup>a</sup> | -6.9    | -10.7  |
| Expt              | -6.7    | -9.1   |

<sup>a</sup> The adsorption energies on the 128T cluster were computed with a single point calculation on the optimized structure of the 46T cluster.

Table 1: Interaction energies (kcal/mol) calculated at M06-L/6-31G(d,p) level of theory for the adsorptions of methane and ethane on various H-ZSM-5 models.

To determine the model size of the zeolite that can well represent the adsorption in the real system, the interaction energies from the single point calculation on the large quantum cluster of 128T on the optimized structure of the 46T are used as the energy benchmark. The energies are computed to be -6.9 and -10.7 kcal/mol for methane and ethane, respectively. Since the value from

the 34T model can be considered to be the same as the 128T model, the 34T and 46T models are assumed to be large enough to include the effect of the zeolite pore on chosen nonpolar adsorbates.

From our discussion above, it can be concluded that the full quantum calculation with the M06-L method and the 6-31G(d,p) basis set on the 34T and 46T models of H-ZSM-5 zeolite is the minimal requirement to reproduce the adsorption of methane and ethane within the zeolite pore.

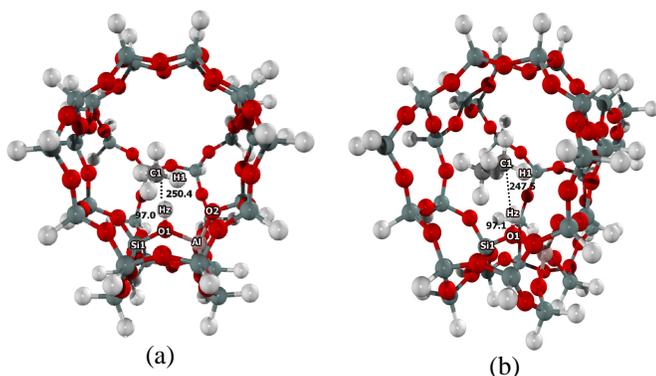


Figure 3: Optimized structure of (a) methane adsorption and (b) ethane adsorption on the 34T cluster model of H-ZSM-5 derived at the M06-L/6-31G(d,p) level of theory. Distances are in pm.

### 3.3 Proton Exchange Reaction of Light Alkanes

Reaction energies of the proton exchange reactions of methane and ethane with various models of H-ZSM-5 zeolite, calculated with the M06L/6-31G(d,p) method are documented in Table 2.

As for the small QM cluster of 5T, the actual activation energy for methane is computed to be 37.2 kcal/mol while the apparent activation energy is 34.3 kcal/mol. The same reaction studied on the small zeolite cluster reported the activation energy in the range of 30-40 kcal/mol [30-36]. Even the activation energies are in good agreement. The adsorption energies from this small quantum cluster are underestimated and found to be less than a half of the experimental data of 6.7 kcal/mol. With a larger zeolite model, the actual activation energies are 36.8, 35.4 and 35.2 kcal/mol, with the 12T, 34T and 46T quantum clusters, respectively. Their corresponding apparent activation energies are 31.7, 28.5, 28.2 kcal/mol. The reaction energies are considered to be 5.9, 11.0 and 10.3 kcal/mol with the 12T, 34T and 46T quantum cluster, respectively. The activation energy obtained from both the 34T and 46T clusters are virtually identical. Similar results are also derived for the single point calculation of the 128T cluster (the energy barrier of 35.2 kcal/mol and the apparent activation energy of 28.3 kcal/mol). Therefore, taking the framework effect into account improves the calculated result by increasing the underestimated adsorption energy and lowering the overestimated activation energy.

With the small quantum cluster (5T), the adsorption energy is -4.6 kcal/mol. The apparent activation energy is 32.5 kcal/mol whereas the actual one is 37.1 kcal/mol. Even though

there is no experimental data for ethane on H-ZSM-5 zeolite, the calculated result is reasonable in that the reaction has a smaller energy barrier and is found to be more endothermic (about 6.5 kcal/mol). As the framework effect is considered in the 46T quantum cluster, the adsorption energy is -11.1 kcal/mol, which agrees well with the experimental data of -9.1 kcal/mol. Their corresponding actual and apparent activation energies are 32.8 and 21.7 kcal/mol, respectively. As expected, the adsorption and reaction energies calculated at the 128T model yield similar results (cf Table 2).

| Model             | Methane |                |      | Ethane |                |       |
|-------------------|---------|----------------|------|--------|----------------|-------|
|                   | AD      | TS             | PR   | AD     | TS             | PR    |
| 5T                | -2.9    | 34.3<br>(37.2) | 0.4  | -4.6   | 32.5<br>(37.1) | -1.9  |
| 12T               | -5.1    | 31.7<br>(36.8) | -0.8 | -7.7   | 28.0<br>(35.7) | -2.7  |
| 34T               | -6.9    | 28.5<br>(35.4) | -4.1 | -10.8  | 22.2<br>(33.0) | -8.3  |
| 46T               | -7.0    | 28.2<br>(35.2) | -3.3 | -11.1  | 21.7<br>(32.8) | -7.7  |
| 128T <sup>a</sup> | -6.9    | 28.3<br>(35.2) | -2.8 | -10.7  | 22.3<br>(33.0) | -10.7 |

<sup>a</sup> The adsorption energies on the 128T cluster were computed with a single point calculation on the optimized structure of the 46T cluster.

Table 2: Reaction energies (kcal/mol) of the proton exchange reactions of methane and ethane with various models of H-ZSM-5 zeolite, calculated with the M06L/6-31G(d,p) method (activation energy in parenthesis).

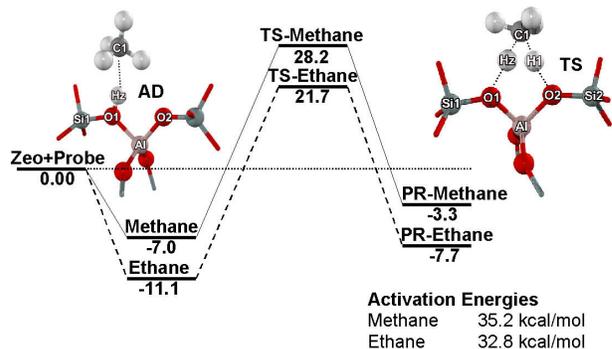


Figure 4: Energy profile for proton exchange reactions of methane and ethane on the 46T quantum cluster of H-ZSM-5, calculated with the M06-L/6-31G(d,p) method.

## 4 CONCLUSION

The chemical investigation on the adsorption and proton exchange reaction of methane and ethane with the H-ZSM-5 zeolite were performed with a newly developed density functional theory, M06-L. Since the dispersion interaction is included in the method, it can well reproduce the experimental estimate of the

adsorption and reaction of the nonpolar molecules, and also predict reliable information for the reactions that have not been experimentally studied. Based on the experimental report, the molecules are placed over the active site to proceed the adsorption and the reaction. With the validated combination of our 46T model and the M06L/6-31G(d,p) approach, the calculated adsorption energies of methane and ethane of -7.0 and -11.1 kcal/mol are in excellent agreement with the experimental observations of -6.7 and -9.1 kcal/mol, respectively. With the activation energy for the methane reaction calculated to be 35.2 kcal/mol, the method gives the apparent activation energy of 28.2 kcal/mol, which compares well with the experimental result. The actual and apparent activation energies for the ethane reaction are predicted to be 32.8 and 21.7 kcal/mol, respectively. To qualify our model for the prediction, we compared both adsorption and reaction results with the single point calculation for the realistic cluster model of 128T. We found that the 46T model gives virtually similar results for the reactions of both methane and ethane. Therefore, the full quantum calculation of the 46T cluster model with the newly developed functional, M06-L functional, is a practical and accurate model to systematically study the adsorption and reaction of hydrocarbons in "nano reactor" ZSM-5 zeolite.

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