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การศึกษากลไกปฏิกิริยาไอโซโพรพิลเลชันของแนฟทาลีนบนตัวเร่งปฏิกิริยาซีโอไลต์ชนิด Faujasite ด้วยระเบียบวิธีเคมีควอนตัม

Reaction mechanism of isopropylation of naphthalene on Faujasite Zeolite: A quantum chemical study

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Abstract

The reaction mechanisms of isopropylation of naphthalene by propene on faujasite zeolite (FAU) has been systematically investigated using the density functional theory with the M06-2X functional. The catalytic cycle of the β, β-selectivity towards the 2-isoproplynaphthalene (2-IPN) and 2,6-diisopropylnaphthalene (2,6-DIPN) is proposed to proceed through the three elementary steps. The reaction is initiated by the protonation of a propene resulting in an isopropoxide species bounded on the FAU framework with the highest activation barrier for overall reaction pathway of 18.1 kcal/mol. The second step is the isopropylation of naphthalene by isopropoxide from the first step leading to the formation of a key intermediate, naphthalynic carbocations, which is subsequently transformed to 2,6-DIPN via the proton back-donation in the final step. It appears that the large 56T cluster including zeolite pore structure is able to stabilize naphthalynic carbocations as a stable intermediate by the confinement effects. The results of this study demonstrate the importance of using a large zeolite cluster for understanding the relationship between

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the steric constraints and van der Waals dispersion induced by the pore structure of FAU and its catalytic activity.

Keywords: Isopropylation, Faujasite zeolite, naphthalene, DFT, M06-2X

1. Introduction

Alkylation of naphthalene by propene is an important reaction in the production of the valuable chemicals such as 2-isopropylnaphthalene (2-IPN) and 2,6-diisopropylnaphthalene (2,6-DIPN) which are the raw materials for the production of polyester fibers and plastics [1]. Traditionally, 2-IPN and 2,6-DIPN are commercially produced by alkylation of naphthalene with alcohols or olefins using Friedel-Crafts catalyst, such as $AlC1_3$ [2]. However, the use of such catalyst provides several drawbacks. In one example, the low selectivity to the desire products in which the alkyl group can be directly substituted either the α or β position of the naphthalene to form the monoalkylnaphthalenes. Dialkyl substitution will then take place at α,α (1,4 and 1,5), α, β (1,6, 1,7 and 1,3) or β, β (2 ,6 and 2,7) positions to form the dialkylnaphthalenes, as shown in Fig. 1.

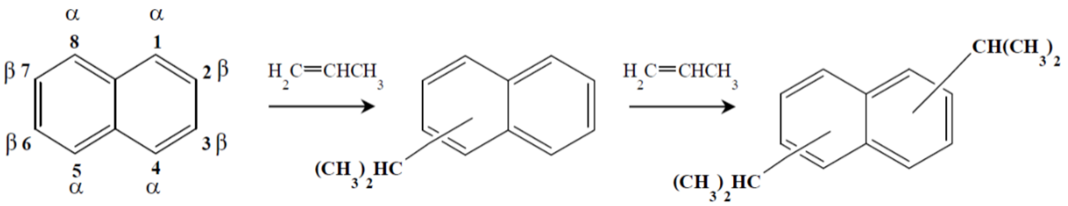
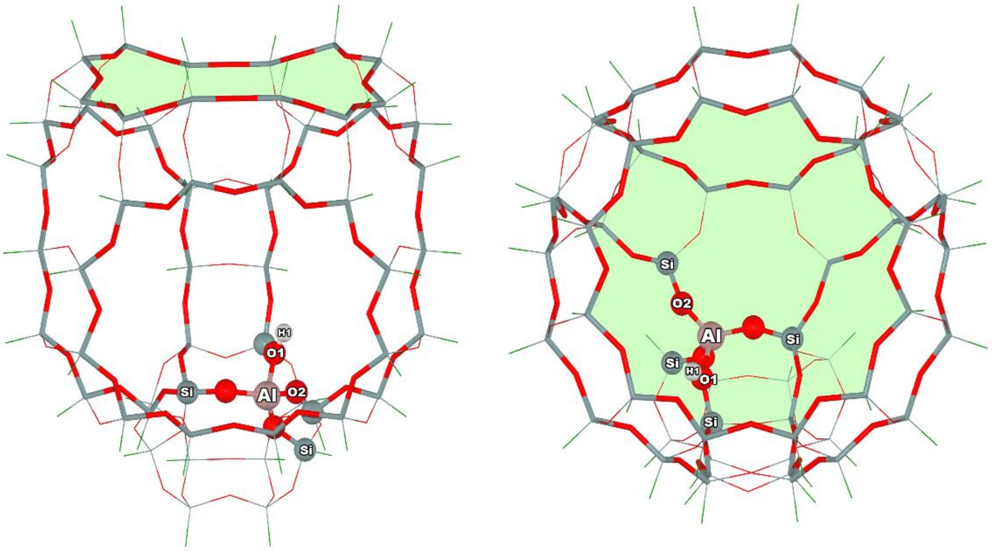


Fig. 1 Positions of carbon atoms in the dialkyl substitution of naphthalene by propene.

Polysubstituted naphthalene will be obtained by further alkylation of substituted groups resulting in more than 10 isomers which can be formed simultaneously. Moreover, the high toxic waste, separation problems as well as corrosion issues restrict the large scale production of 2,6-DIPN. For these reasons, the 2,6-diisopropylnaphthalene synthesis carried out over heterogeneous catalysts such as the large-pore zeolite catalysts has been extensively studied [3-6]. Sugi *et al.*, reported that the formation of the slimmest isomer and thermodynamically stable 2,6-DIPN over faujasite zeolite was increased with the increasing in temperature (200-250 °C) [5]. Brzozowski *et al.* showed that the mono- and di-alkylation were less β-selective on Mordenite zeolite (MOR) than FAU and amorphous aluminosilicate[6]. In spite of this, the intensive study concerning to the reaction mechanisms has not been provided in literature and remain considerable debate. Therefore, in the present study, we perform theoretically mechanistic investigation to address the fundamental questions regarding reaction mechanisms of the isopropylation of naphthalene in model of a large FAU cluster with the newly developed density functional, M06-2X. The results of this study would be useful to extend the scope of applicable alkylation of naphthalene on zeolite-based catalysts.

2. Model and Method

The structure of the 56T cluster (56 Tetrahedral unit), including a supercage as a nanometer-sized chemical reactor where the adsorbates can be trapped inside, was taken from the lattice structure of FAU zeolite [7] (Fig. 2). The 56T cluster of FAU model is large enough to confine the adsorbates and allow the computations to be completed in an affordable time. A silicon atom at window position in FAU was substituted by an aluminum atom. A hydrogen atom was added to one of the bridging oxygen atoms bonded directly to the aluminum atom, conventionally called the O1 position. The M06-2X functional [8] and the 6-31G(d,p) basis sets were applied for all structures. All calculations have been performed using the Gaussian 09 code [9]. Since the Minnesota class functionals are sensitive to the choice of grid for numerical integrations, the ultrafine integration grid of Gaussian 09 was used. During the structure optimization, the 5T portion of the active site region [≡SiO(≡SiO)$_2$AlO(H)OSi≡], and the adsorbates were allowed to relax while the rest of the active region was kept at the crystallographic coordinates. Vibrational analysis was carried out to verify local minima and transition states. All optimized adsorption complexes and intermediates were local minima without imaginary frequencies. All the optimized transition state structures possessed only one imaginary frequency.



Side view

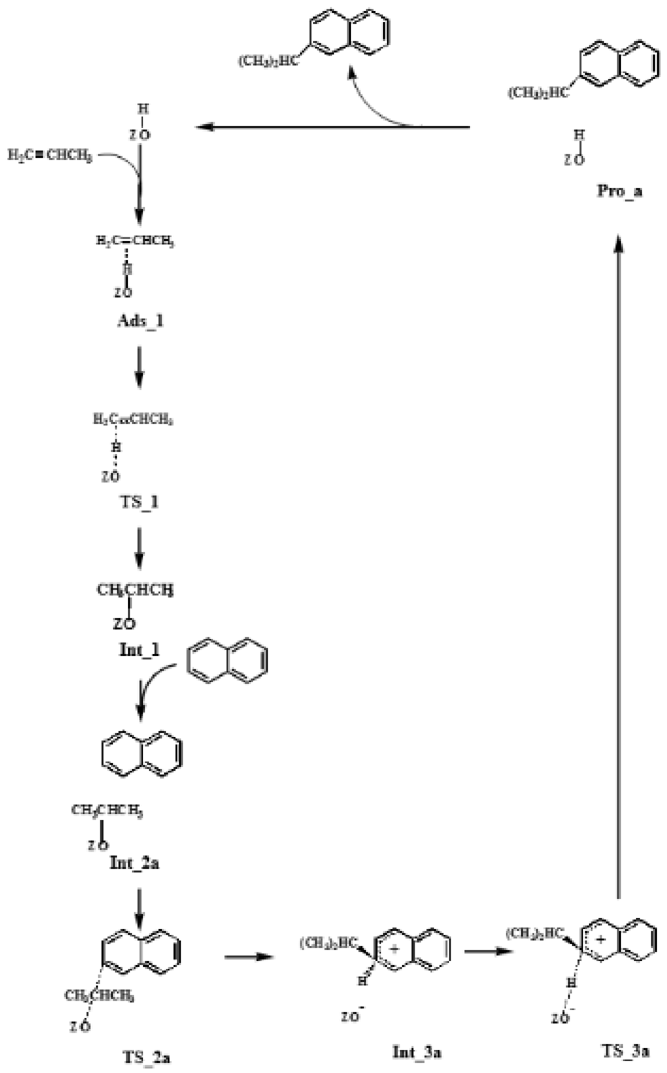
Top view

Fig. 2 The 56T cluster of faujasite zeolite (FAU). The sticks present the 12T pore opening to the supercage of FAU.

3. Results and Discussion

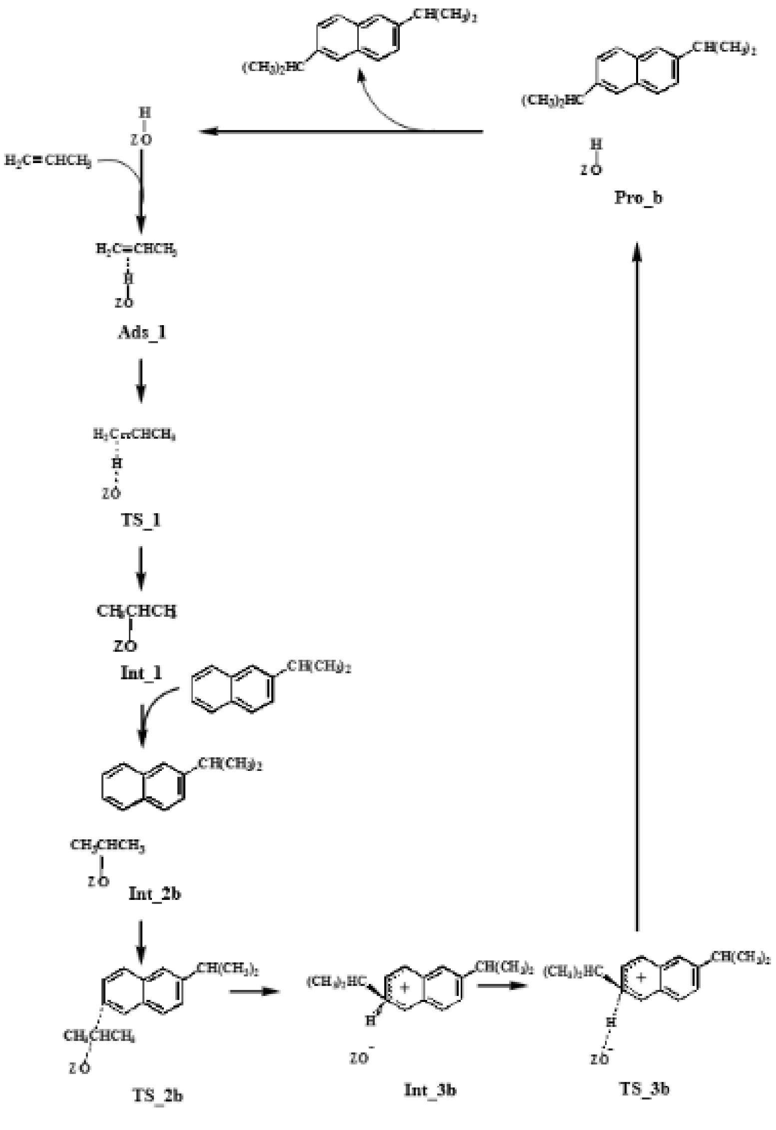
The catalytic schemes including all species involved in this theoretical study are depicted in Scheme 1 and 2. The energy profiles are shown in Fig. 3 and 4. The reaction is initiated by the adsorption of a propene on the Brønsted acidic site of FAU zeolite (denoted Ads_1 in Scheme 1). After the chemisorption of propene is reached (Ads_1), the propene is protonated by Brønsted acidic proton resulting in a propoxide species bounded on FAU framework (Int_1). Subsequently, the incoming naphthalene or 2-isopropylnaphthalene (2-IPN) approaches to the active site forming interaction with the propoxide species (Int_2a or Int_2b). The isopropylation reaction between naphthalene and propoxide species takes place yielding the naphthalynic carbocations (Int_3a or Int_3b). After the key intermediate in this reaction, naphthalynic carbocation, is generated, subsequently converted to 2-IPN or 2,6-DIPN via the proton back-donations from naphthalynic carbocation in the final step (Pro_a or Pro_b).

After the adsorption of propene on active site of FAU takes place, the hydrogen bonding complex of a propylene C=C bond and the Brønsted acidic proton is formed. This results in the lengthening of the O1-H1 and C1=C2 bonds leading to the protonation process (please see Fig. 3). The adsorption of propene is predicted to be -13.8 kcal/mol. Adsorption of propene on Brønsted site of large pore zeolites was previously reported of -12.5 kcal/mol [10]. The calculated adsorption energy in this study therefore seems to be a reliable result. In the protonation step, the propene C=C bond is activated by the hydrogen transfer of the Brønsted acidic proton (H1) to the carbon of propene (C1). We observe the lengthening of the C1-C2 bond and the association of the C2-O2 bond, respectively. The activation energy with respect to the adsorption complex is calculated to be 18.1 kcal/mol, and the reaction energy for isopropoxide formation with respect to the adsorption complex is endothermic by 10.8 kcal/mol. Once propene becomes protonated and converted to isopropoxide, Int_1, it can instantaneously interact with the proximity adsorbing naphthalene (see solid line in Fig. 3) or 2-IPN (see dot line in Fig. 3) to produce the 2-IPN or 2,6- DIPN , respectively. Naphthalene or 2-IPN are physisorbed nearby the isopropoxide and located inside supercage of FAU.



Scheme 1. The catalytic cycle of the isopropylation of propene with naphthalene on FAU zeolite

In the alkylation step, the transition state which is associated to the C-C bond formation between and isopropoxide and naphthalene, TS_2a, (or 2-IPN, TS_2b) at the β -position requires the activation energy of 7.8 kcal/mol (6.7 kcal/mol). Due to the steric hindrance of the bulky transition state structure, therefore, using a small quantum cluster without zeolite framework Constraints, which exclude the confinement effect from zeolite pore, may not be enough to give the reliable results.[11] It is worth to note that the transition state structure is not concerned with proton back-donation to the FAU framework but only C-C bond formation takes place. The propoxide C2 atom forms a single bond with the C3 (or C4) atom of naphthalene (or 2-IPN), respectively yielding the key intermediates, naphthalynic carbocations. These key intermediates have not been previously reported by the study using small zeolite cluster model [12]. This result is in agreement with the results reported by N. Hansen *et al.* [12] and X. Rozanska *et al.* [13]. They found the existence of aromatic cations in the zeolite cavity as a reaction intermediate and concluded that large models of medium and micro-pore zeolites are able to stabilize the benzylic ionic intermediate. At this point, one can expect that the results of the present study demonstrate the importance of using a large zeolite cluster for the theoretical study of chemical transformation of aromatics in zeolite catalyst.



Scheme 2. The catalytic cycle of the isopropylation of propene with 2-isoproplynaphthalene (2-IPN) on FAU zeolite.

2-IPN and 2,6-DIPN can be generated through the direct proton transfer from the tetrahedral carbon center of the naphthalenium carbocations to an oxygen atom attached with the aluminum atom at the active sites (TS_3a and TS_3b in Fig. 4) with the calculated activation barrier of 4.7 and 3.4 kcal/mol. At the transition states TS_3 where the C-H cleavage occurs, the C-H bond distance of naphthalene intermediates are elongated and an H-O bond of active site are regenerated. Finally, the products, 2-IPN and 2,6-DIPN are adsorbed at the acidic active site via a π-bond interaction by -58.2 and -62.1 kcal/mol, respectively. These predicted reactions are exothermic and at the end 2-IPN and 2,6-DIPN require desorption energies of 25.9 and 30.0 kcal/mol, respectively.

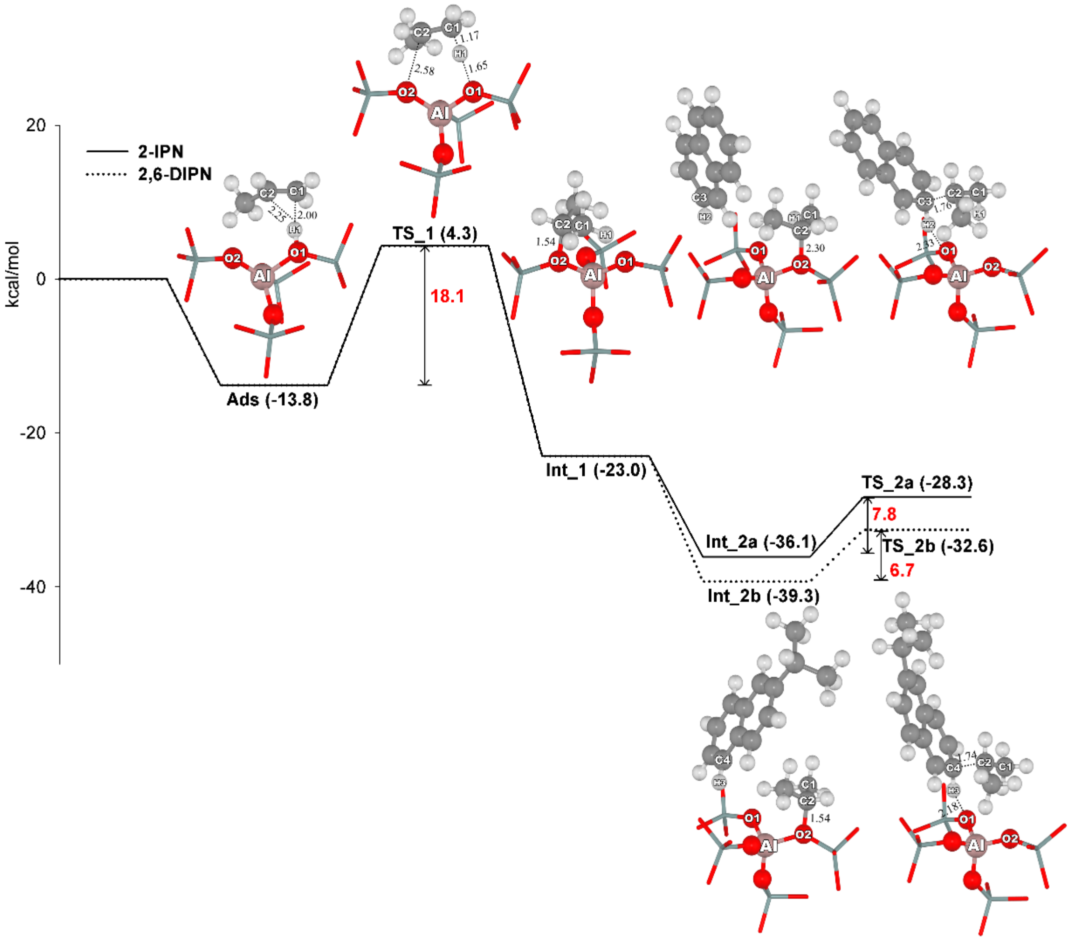


Fig. 3 Calculated energy profile for the first step of isopropylation of naphthalene to 2-IPN (solid line) and 2,6-DIPN (dash-line) on FAU zeolite. Energies are in kcal/mol.

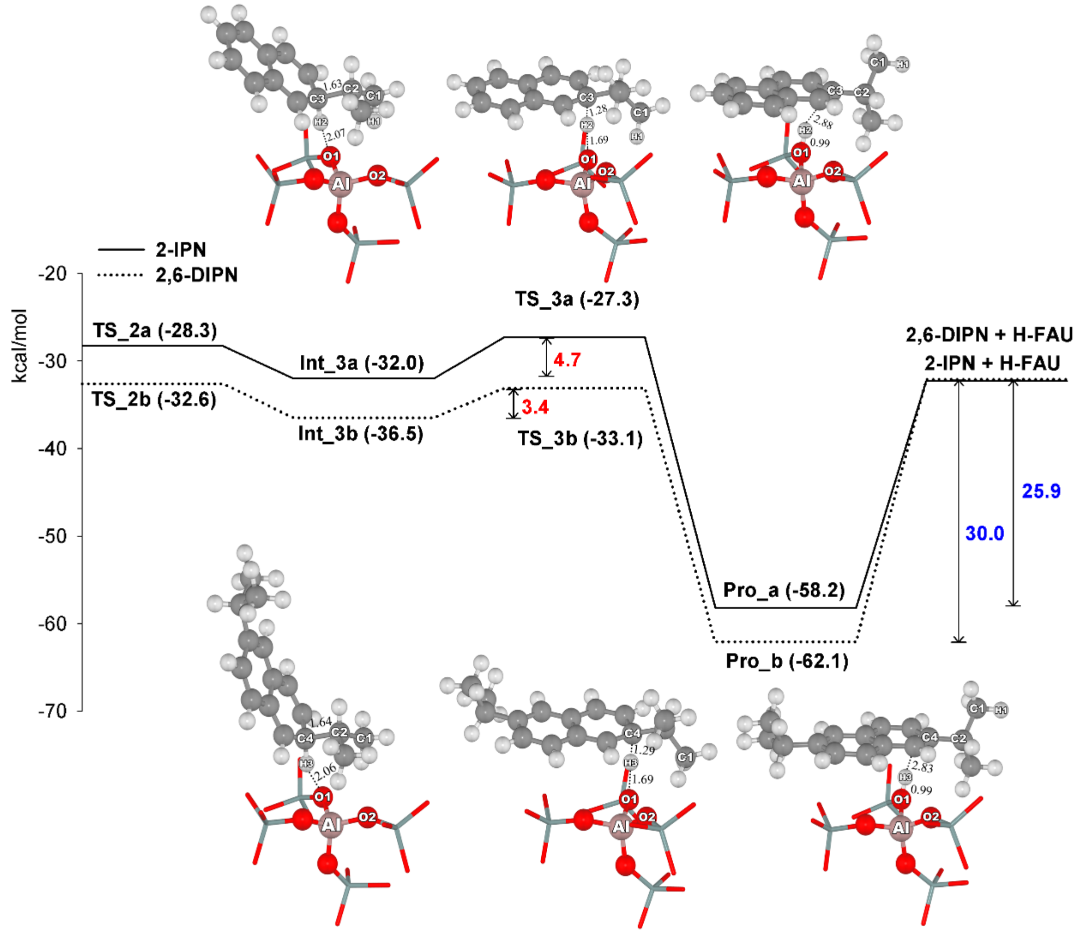


Fig. 4 Calculated energy profile for the second and the third steps of the isopropylation of naphthalene to 2-IPN (solid line) and 2,6-DIPN (dash-line) on FAU zeolite. Energies are in kcal/mol.

4. CONCLUSIONS

In the present article, we have investigated the reaction pathways of isoproplyation of naphthalene by propene in the framework of FAU zeolite pore using large 56T cluster. Our results can be summarized as follows

(1) The isoproplyation of naphthalene by propene to 2,6-DIPN is initiated by the adsorption of the propene on the Brønsted acidic site resulting in the propoxide group attached to the oxygen of the FAU framework. Subsequently, the isopropoxide group from the zeolite framework transfers to naphthalene or 2-IPN at the β-positions yielding as a consequent naphthalenium carbocations. Eventually, 2-IPN and 2,6-DIPN are generated by direct proton transfer from the naphthalenium carbocations to the active site. The desorption of the products, 2-IPN and 2,6-DIPN, are considered as the rate-determining step.

(2) The FAU framework plays an important role in the stabilization of the adsorption complexes, transition states and intermediates which are in good agreement with others theoretical and experimental observations. The 56T cluster used in this work is able to stabilize the key reaction intermediates, the naphthalenium carbocations.

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