A Mechanistic Investigation on 1,5- to 2,6-Dimethylnaphthalene Isomerization Catalyzed by Acidic Beta Zeolite: An ONIOM Study with a Newly Developed Density Functional Theory

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ABSTRACT

2,6-Dimethylnaphthalene (DMN) is the key intermediate in the synthesis of poly(ethylene naphthalate) (PEN), a high-performance polymer. The detailed reaction mechanism of the catalyzed 1,5- to 2,6-DMN isomerization via 1,6-DMN by acidic beta zeolite is investigated at the ONIOM(M06-L/6-31G(d,p):UFF) level of theory. The M06-L method, a newly developed density functional theory, is applied for the first time to investigate such reaction within the nano-reactor of zeolite. The stepwise mechanism is proposed to proceed with three steps: protonation, methyl shift and proton back-donation. The methyl shift is the rate-determining step with the activation energies of 24.0 and 20.8 kcal/mol for 1,5- to 1,6-DMN and 1,6- to 2,6-DMN steps, respectively. The calculation confirmed the experiment that the 1,6-DMN formation is kinetically controlled. The calculated adsorption and activation energies are in good agreement with experimental data. Our findings demonstrate that the influence of the pore size of the beta zeolite perfectly fit for the enhancement of the isomerization of 1,5- into 2,6-DMN.

Keywords: dimethylnaphthalene, isomerization, density functional theory, zeolite, Beta

1 INTRODUCTION

A high-performance polymeric material, polyethylene naphthalate (PEN), has many more superior properties than common polyethylene terephthalate (PET) [1]. The current production process involves the condensation polymerization of ethylene glycol and dimethyl 2,6-naphthalenedicarboxylate (2,6-NDC). The 2,6-NDC is in turn prepared from 2,6-dimethylnaphthalene (2,6-DMN) [2]. Its present large-scale production (30 kton/yr) is manufactured only by BP-Amoco using their patented process [3], involving four subsequent reactions in four separate reactors: alkylation, cyclization, dehydrogenation, and catalytic isomerization from 1,5- to 2,6-DMN [1, 4]. The final step is thought to be a limiting step which leads to the low availability and the high cost of 2,6-DMN [5]. The isomerization of 1,5- to 2,6-DMN occurs via an intramolecular 1,2-methyl shift [8-10]. This methyl shift is recognized as a key mechanistic step in the rearrangements of alkylbenzenes [8-9], which can be promoted by both Lewis and Bronsted acids.

Zeolite is a unique choice of catalyst for “green chemistry” industrial processes. Recently, Kraikul et al. conducted a catalytic activity test of H-beta, H-mordenite, and H-ZSM-5, on the isomerization of 1,5- to 2,6-DMN [5]. H-beta zeolite was found to provide the highest yield of 2,6-DMN. From further thermodynamic analysis, Kraikul et al. concluded that 1,5- to 1,6-DMN isomerization is the kinetically limiting step for the 1,5- to 2,6-DMN conversion. From the MD simulation to estimate the diffusional energy barrier of DMN in zeolites by Millini et al. [11], the diffusivity of DMN isomer is in the order 2,6-DMN > 1,6-DMN > 1,5-DMN. However, no chemical kinetics parameter is deduced from their study. Later, Sulc and Stuart studied the isomerization kinetics of several alkylbenzenes catalyzed by BF\textsubscript{3}·HF [10]. Although there are some reports concerning the detailed investigation of this limiting step, the information of this reaction at the molecular level has not, to our knowledge, been published [1, 5-7], especially for the activation energy catalyzed by heterogeneous catalysts, zeolite in particular. In addition, although the isomerization from 1,5- into 2,6-DMN over the heterogeneous catalysts is known to occur with two methyl shift steps, the reaction mechanism has not been investigated in detail.

In this work, we report the mechanistic study of 1,5- to 2,6-DMN isomerization catalyzed by acidic beta zeolite by means of the hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) approach, as well as the ONIOM (our-Own-N-layered Integrated molecular Orbital and molecular Mechanics) method [12-18]. Our several reports indicate ONIOM’s good performance on the studies of adsorption and reaction in zeolite [19-29].

2 METHOD

The 120 tetrahedral subunit (120T) cluster, covering the active region, of the H-beta zeolite is used to represent the Bronsted acid site and the framework. This cluster is taken from the crystal lattice structures [30-31]. We focus on the 12T ring representing the main gateway to the intersection of two perpendicular 12T channel systems, where the reactions normally take place (see Fig. 1). A silicon atom at a T5 position in the zeolite is substituted by an aluminum atom. A proton is added to the bridging oxygen bonded.
to the aluminum atom [30], labeled with O1 in this study. In the ONIOM model, an inner layer consists of a 14T cluster including the 12T and two adjacent Si atoms and a reacting molecule. An outer layer consists of the remainder of the extended framework up to 120T to take the confinement effect of the framework into account.

The ONIOM scheme consists of the inner layer of the active region calculated at the M06-L/6-31G(d,p) level and the outer layer of the framework calculated by the universal force field (UFF). M06-L, a DFT method developed by the Minnesota group [32-34]. This functional requires much less computational effort, thus it is practical for the calculation on large systems [34], such as for the interactions of the adsorbates with the acid site of zeolite. The UFF accounts for the van der Waals interaction for the framework [35], which contributes dominantly in adsorption-desorption mechanisms in zeolites [35-38]. During optimization, only the 5T region \((=\text{SiO})_3\text{Al(OH)Si}\) was allowed to relax while the rest was fixed along the crystallographic coordinates. To obtain more reliable energies, single-point calculations at the 120T quantum cluster, i.e. 120T M06-L/6-31G(d,p)/120T ONIOM(M06-L/6-31G(d,p)/UFF) are also computed. All calculations were performed using the Gaussian 03 code [39].

3 RESULTS AND DISCUSSION

3.1 Isomerization of 1,5- to 1,6-DMN

Fig. 2(a) summarizes the reaction mechanism of 1,5- to 1,6-DMN isomerization in the acidic beta zeolite. In this mechanism, a 1,5-DMN molecule is first adsorbed at the Brønsted acid site. Then, the adsorbed 1,5-DMN is protonated to form a \(\alpha\)-complex (Int_1), followed by the intramolecular methyl shift between the C5 and C6 positions. This results in the formation of a new \(\alpha\)-complex (Int_2) which donates proton back to the zeolite yielding a 1,6-DMN (Prod_1).

The adsorption takes place with the C5-C6 double bond interacting with the acidic proton (H1) (see Fig. 3(a)). The 1,5-DMN molecule was slightly perturbed by the zeolite cavity upon the adsorption. The C5-C6 double bond lengths slightly. The adsorption energy of 1,5-DMN is computed to be -22.1 kcal/mol. Even though there is no report of experimental data, this value is in accord with the data of -20.4 kcal/mol for ethylbenzene in H-Y zeolites [40]. Next, the protonation in the adsorption complex, Ads_1, takes place at the C5 position. The protonated molecule is in the form of a carbenium ion in which the positive charge can delocalize over the benzene ring. At the transition state, TS_1, the zeolite proton moves toward the 1,5-DMN. The dimethylphenylenonium ion (Int_1) is then formed and stabilized by the resonance of the intact benzenoid nucleus [10]. The energy barrier for the protonation is 11.7 kcal/mol and the corresponding reaction is endothermic by 5.8 kcal/mol. From Fig. 3(a), the geometry of the transition state (TS_1) is more similar to that of Int_1 than to that of Ads_1. Therefore, the reaction tends to proceed forward to the methyl shift step.

The reversible intramolecular 1,2-methyl shift moves the methyl group from \(\alpha\)-position (C\(_\alpha\)) to the adjacent position (C\(_\beta\)). The TS_2 transition structure shows the shifting methyl group located in-between with C5 and C6 atoms. At this unstable tricentric transition state, the methyl group is moving toward the C6 atom. In the Int_2 structure, the Cm-C6 bond is formed. The calculated binding energy is -15.5 kcal/mol (see Fig. 4(a)). This is slightly less stable than that of Int_1 by 0.8 kcal/mol. Therefore, the reaction is almost thermoneutral. This may be attributed to the reduction of steric hindrance between the methyl group in the naphthalene ring and the zeolitic pore. The activation energy for the DMN methyl migration is 25.7 kcal/mol.

The final stage of the 1,5- to 1,6-DMN isomerization involves the proton (H2) back-donation from the C6 position of Int_2 to the O1 of the zeolite framework to form adsorbed 1,6-DMN (see Fig. 3(a)). This stage occurs very fast as evidenced by the predicted energy barrier of 2.6 kcal/mol (see Fig. 4(a)). The reaction is exothermic by 13.0 kcal/mol. It can be interpreted that the proton prefers to sit on the zeolite. The back transferred proton forms a chemical bond with the O1 atom. The C5-C6 bond resembles a double bond. Finally, 28.4 kcal/mol is required to remove the 1,6-DMN product from the acid site.

The energy profile of the 1,5- to 1,6-DMN isomerization is in Fig. 4(a). The methyl shift was found to be the rate-determining step. It has the highest activation energy of 25.7 kcal/mol compared with 11.7 and 2.6 kcal/mol for the protonation and the back-protonation steps. These results are in good agreement with the experimental observation in which the acid-catalyzed intramolecular 1,2-methyl shift is the rate-determining step for this isomerization with the activation energy of 20.3 kcal/mol [10].

3.2 Isomerization of 1,6- to 2,6-DMN

The reaction mechanism of 1,6- to 2,6-DMN isomerization is outlined in Fig. 2(b).
Figure 2: Reaction mechanism of (a) the 1,5- to 1,6-DMN and (b) the 1,6- to 2,6-DMN isomerization by acidic beta-zeolite. Schematically they consist of protonation, methyl shift and proton back-donation of the adsorbed species.

Figure 3: Optimized geometries of adsorbed reactants, transition states, intermediates and products of (a) 1,5- to 1,6-DMN and (b) 1,6- to 2,6-DMN isomerization over H-beta zeolite (14T/120T).

The energetic profiles for the overall steps of the 1,6- to 2,6-DMN isomerization are virtually similar to 1,5- to 1,6-DMN reaction and also summarized in Fig. 4(b). The methyl shift is found to be the rate-determining step for the isomerization with the energy barrier of 21.0 kcal/mol.

The isomerization from 1,5- to 2,6-DMN is shown in Fig. 2 in which is depicted the successive reactions from 1,5- to 1,6- and finally to 2,6-DMN. Comparison between the energy profiles of the 1,5- to 1,6-DMN and 1,6- to 2,6-DMN isomerizations can be made from Fig. 4. The methyl migration is the rate determining step in both reactions. The activation energy of the 1,5- to 1,6-DMN reaction is 25.7 kcal/mol, which is greater than 21.0 kcal/mol of 1,6- to 2,6-DMN reaction. This indicates that the former reaction proceeds more slowly than in the latter. The conclusion is in line with the thermodynamic observed by Krijik et al. that the isomerization occurs rapidly with a higher isomerization rate [5] according to the ratio of 2,6-DMN:1,6-DMN of greater than 1. Our calculation also suggests the same trend. Although only the 14T cluster representing the active site of zeolite and the adsorbate are allowed to relax in M06-L/6-31G(d,p)/ONIOM(M06-L/6-31G(d,p):UFF) model, the information of the reaction such as adsorption and activation energies, are rational and compared well with the experimental data reports in the literature [5, 8, 10-11, 40-41].
4 CONCLUSION

The isomerization of 1,5- into 2,6-DMN over the acidic beta zeolite is investigated at the molecular level by using the 120T M06-L/6-31G(dp)/120T ONIOM(M06-L/6-31G(dp):UFF) method. This reaction involves two consecutive methyl shift processes through the conversion of 1,5- into 1,6-DMN and of 1,6- into 2,6- DMN, respectively. The reaction mechanism begins with the adsorption of the reactant on a Bronsted acid site of the zeolite followed by the protonation, 1,2-methyl shift and proton back-donation steps and the product desorption. The methyl shift is shown to be the rate-determining step with the 1,5- to 1,6-DMN isomerization reaction expected to be the main product of the isomerization.

ACKNOWLEDGEMENTS

The present work was supported in part by grants from the National Science and Technology Development Agency (NSTDA Chair Professor to JL), Thailand Research Fund (TRF), Kasetsart University Research and Development Institute (KURDI), the National Nanotechnology Center (NANOTEC Center of Excellence and Computational Nanoscience Consortium), the Commission on Higher Education, Ministry of Education, under the Excellence and Computational Nanoscience Consortium, the National Nanotechnology Center (NANOTEC Center of Excellence and Computational Nanoscience Consortium), the Commission on Higher Education, Ministry of Education, under the Postgraduate Education and Research Programs in Petroleum and Petrochemicals, and Advanced Materials as well as the Sandwich Postgraduate Education and Research Programs in Petroleum and Petrochemicals, and Advanced Materials as well as the Sandwich Research Network (CHE-PhD-SW-INDV to CK and CHE-PhD-SW-SUPV to SC). The authors are grateful to Donald G. Truhlar and Yan Zhao for supporting them with the M06-L functional. The Kasetsart University Graduate School is also acknowledged.

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