

The Catalytic Reaction of Ethanol to Ethylene: A DFT Study

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Abstract

The use of low-cost biomass as starting material for chemical processes is an interesting research issue due to environmental concern. Ethylene, an important raw material for polymer production, can be made from bioethanol via catalytic dehydration reaction. In this work, the conversion of ethanol to ethylene catalyzed by sulfuric acid was studied theoretically by the density functional theory with the M06-2X functional. During the course of reaction, an ethanol molecule in protonated form was found when the number of ethanol had been increased to 3 molecules. The activation energies for the reactions with the ratio of ethanol to sulfuric acid varied from 1 to 3 were determined to be 53.1, 51.3 and 55.2 kcal/mol, respectively. More understanding about the adsorption was achieved by Natural Bond Orbital Analysis.

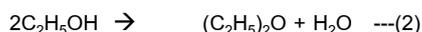
Keywords : Biomass, ethanol, ethylene, M06-2X, NBO analysis

Introduction

Biomass has become an interesting research issues due to the environmental concern. Bio-ethanol produced by fermentation of biomass product such as sugar and wood-wastes is one of the most important renewable energy sources [1], [2]. Thailand, one of the top-three sugar-export country, has a stimulus package to increase value of sugar by converting it to ethanol fuel [3]. Nevertheless, ethanol can be catalytic converted to much more valuable products for chemical industrial. The most important product would be ethylene, which is mainly used as raw materials for the polyvinyl chloride (PVC) production [4]. The dehydration reaction of ethanol to ethylene is shown below:



Several catalysts can be used in this dehydration reaction. The acidic catalysts such as sulfuric acid and phosphoric acid have been widely used in the production of ethylene. At low temperature, the side reaction is possible as shown below:



To understand the reaction mechanism, the computational chemistry is used to describe the adsorption properties and reaction pathway. The post Hartree-Fock methods such as MP2 and CCSD calculations can provide accurate results but they require enormous computational time

[5], [6]. Several density functional theory (DFT) methods have been developed and compared with post Hartree-Fock methods. Among various proposed DFT functionals, the M06 functionals (M06-L, M06 and M06-2X) are quite promising for studying main group thermochemistry, kinetics, noncovalent interactions, excited states, and transition elements [7]. The M06 functionals have been used for the studies of adsorption and reaction on various catalysts such as zeolites, metal catalyst [8], porphyrin [9] and metal organic framework [10]. Recently, the M06 functional have been successfully applied for the coumarin synthesis with H_2SO_4 catalyst [11] and ethylene oxidation with permanganate [12].

In this study the dehydration of ethanol to ethylene was studied at molecular level. The proposed mechanism was examined by density functional theory with the hybrid M06-2X functional. The Natural Bond Orbital (NBO) analysis was applied to understand the adsorption properties [13]. Our results provide more understanding about the adsorption and reaction for the dehydration reaction.

Methodologies

The adsorption and dehydration of ethylene on the sulfuric acid were theoretically studied. Effect of sulfuric concentration has been determined by vary ratio of ethanol to sulfuric acid from

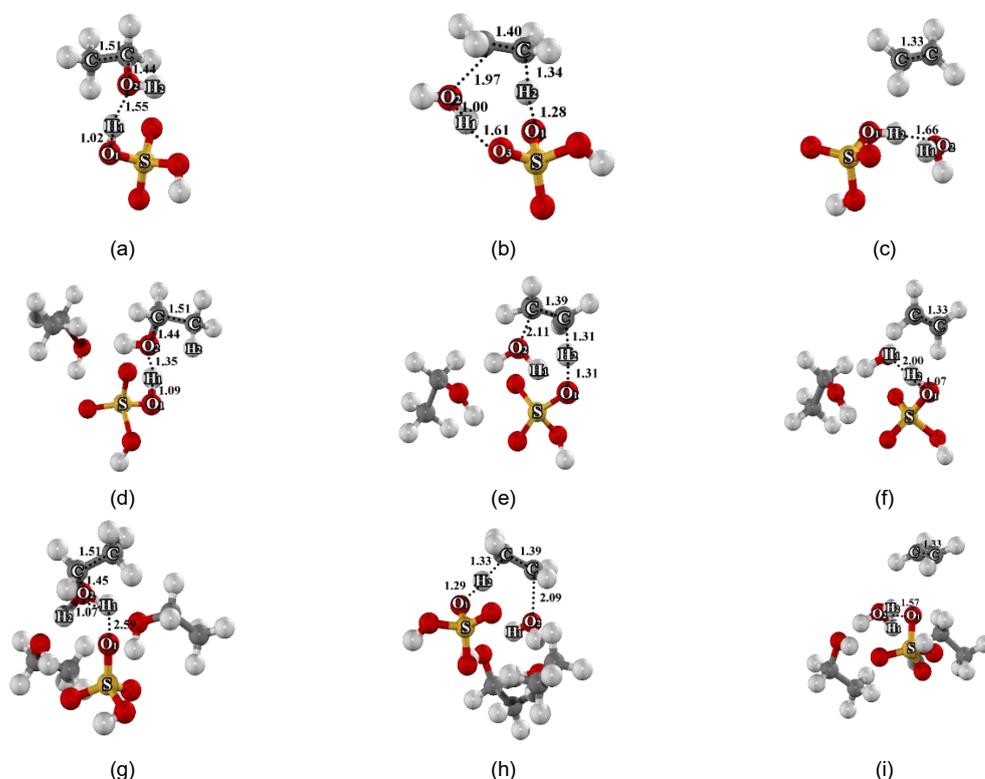
1 to 3. Structures of all related species were optimized by DFT methodology with M06-2X functional and 6-31G(d,p) basis set. The M06-2X functional, a high-nonlocality functional with double the amount of nonlocal exchange (2X), was benchmarked against the MP2 method and was compared with other density functionals for various calculated properties [7]. Recently, our calculated apparent activation energy for the coumarin synthesis with sulfuric acid was agreed well with experimental results [11]. Transition states were located by using the Berny algorithm and each optimized TS calculations was confirmed by its single imaginary frequency corresponding to the reaction pathway. The adsorption structures were analyzed by NBO method [13]. All calculations were performed using Gaussian 09 program [14].

Results and Discussion

The dehydration reaction of ethanol to ethylene catalyzed by sulfuric acid was examined by M06-2X functional. The adsorption, transition state and products with some selected distances are shown in Figures 1. For one ethanol with sulfuric acid, the ethanol adsorbed on the sulfuric via the hydrogen bond between the oxygen of hydroxyl group and the Brønsted

acid of sulfuric (Figures 1a, AD1). The H1...O2 bond distance was 1.55 Å. For the transition state (Figures 1b, TS1), the H1 atom transferred to the O2 of ethanol to form water while the H2 atom of the ethanol transferred back to the sulfuric and the C1-O2 bond was broken. The O1-H1, O2-C1 and H2-O1 bond distances were 1.00, 1.97 and 1.28 Å, respectively. The product was the ethanol and water (Figures 1c, PR1). Water adsorbed with the sulfuric via the hydrogen bond between oxygen and Brønsted acid of sulfuric with H2...O2 bond distance of 1.66 Å.

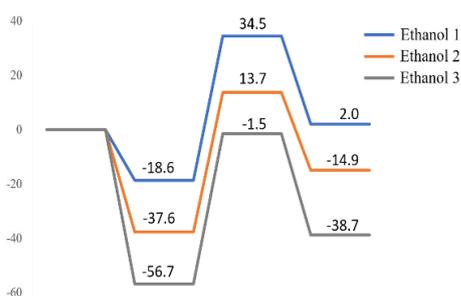
In case of two ethanol molecules, the first ethanol adsorbed on sulfuric acid via the hydrogen bond (Figures 1d, AD2). A shorter H1...O2 bond distance of 1.35 Å and a longer O1-H1 bond distance of 1.09 Å indicated that second ethanol stabilized the adsorption complexes. In case of 3 ethanol molecules, the protonated form of ethanol was found (Figures 1g, AD3). The O1-H1 bond distance of 2.59 Å was found with the ion pair interaction. The transition state and the product were calculated as shown in Figures 1e, 1f, 1h and 1i for TS2, PR2, TS3 and PR3, respectively.



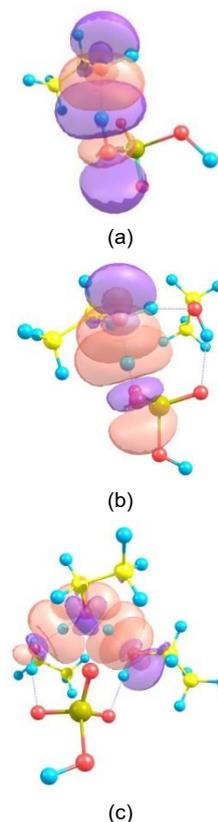
Figures 1. Optimized structures of the AD1 (a), TS1 (b), PR1 (c), AD2 (d), TS2 (e), PR2 (f), AD3 (g), TS3 (h), PR3 (i) complexes over sulfuric acid at M06-2X/6-31G(d,p) level of theory. Distances are in Å.

The calculated energy pathways were illustrated in Figures 2. The apparent activation energies for the reaction with the ratio of ethanol to sulfuric acid varied from 1 to 3 were 34.5, 13.7 and -1.5 kcal/mol, respectively. The total activation energies for the reaction were 53.1, 51.3 and 55.2 kcal/mol, respectively. Comparing with previous experimental study, our calculated activation energies were close to the experimental activation energies of the same reactions on H-MOR, H-ZSM-5 and H-FER zeolites, which were 38.5 ± 1.4 , 43.3 ± 0.5 and 44.9 ± 0.5 kcal/mol, respectively [15].

The Natural Bond Orbital Analysis of adsorption complexes over sulfuric acid was performed as shown in Figures 3. For the one- and two-ethanol cases, electron transfer from the lone pair electron of oxygen of ethanol to the antibonding of O-H bond of sulfuric acid was found to be important ($E_2 = 50.0$ and 100.2 kcal/mol, respectively). In case of 3 ethanol molecules, the electron transfer from the lone pair of oxygen atoms to the antibonding of O-H bond was even more crucial ($E_2 = 98.2$ and 87.3 kcal/mol).



Figures 2. Energy profiles for the dehydration of ethanol to ethylene with different number of ethanol molecules determined by M06-2X/6-31G(d,p) level of theory. Energies are in kcal/mol.



Figures 3. The Natural Bond Orbital Analysis of adsorption complexes over sulfuric acid for (a) one ethanol molecule, (b) two ethanol molecules and (c) three ethanol molecules at M06-2X/6-31G(d,p) level of theory.

Conclusion

The catalytic conversion of ethanol to ethylene with sulfuric acid was studied by the density functional theory. Structures of all related species were optimized with M06-2X/6-31G(d,p) method. The effect of sulfuric concentration was determined by varying ratio of ethanol to sulfuric acid from 1 to 3. The activation energies were calculated to be 53.1, 51.3 and 55.2 kcal/mol, respectively. The protonated form of ethanol were found when the number of ethanol increased up to 3 molecules. The Natural Bond Orbital Analysis (NBO) showed that the electron transfer from the lone pair electron of oxygen of ethanol to the antibonding of Brønsted acid were important.

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