

Dehydration of Ethanol into Ethylene over H-MOR: A Quantum Chemical Investigation of Possible Reaction Mechanisms in the Presence of Water

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ABSTRACT

The conversion of ethanol to ethylene, which is one of the most important feed stocks for the petrochemical industry, is of particular commercial interest. Two mechanisms, stepwise and concerted, of the ethanol dehydration to ethylene in the presence of water have been investigated by the ONIOM model (14T/120T) with B3LYP/6-31g(d,p):UFF method. In the stepwise mechanism, the coadsorbed water assists the protonation of ethanol by the acidic zeolite proton to form an ethoxonium ion ($\text{CH}_3\text{CH}_2\text{OH}_2^+$). After that, the cation is dehydrated to form a surface ethoxide intermediate. The dehydration is found to be the rate-determining step with an activation barrier of 41.4 kcal/mol. The ethoxide is then deprotonated with a water molecule which results in the formation of the product of ethylene. The activation energy of the deprotonation is calculated to be 22.2 kcal/mol. The concerted mechanism differs in that the dehydration and the deprotonation occur simultaneously without the formation of the intermediate. In this mechanism, the activation barrier is higher at 54.7 kcal/mol. Therefore, we conclude that the stepwise mechanism should be the dominating one in hydrous ethanol dehydration.

Keywords: dehydration of hydrous ethanol to ethylene, H-MOR zeolite, confinement effects, ONIOM

1 INTRODUCTION

Petroleum has been and still is debatably the most important energy resource of the world. It and its derivatives certainly are still needed for transportation (gasoline, diesel, jet fuel, etc.), and also have an important role in producing electricity. Of equal importance is its role as a raw material for many chemical products. Petroleum resources are inevitably becoming increasingly depleted and more expensive as consumption still continues to increase. The certainty of ever increasing scarcity of petroleum has in recent years resulted in concerted attention, efforts and research to develop alternative hydrocarbon resources.

Biomass, defined as the biological material of living organisms such as animals and plants, is becoming one such increasingly attractive alternative. Conversion of biomass can produce more valuable chemical compounds. A significant and important example of this is bio-ethanol,

which is produced through the microbial fermentation of agricultural feedstock such as corn, sugarcane and cassava. Bio-ethanol has now become a highly attractive product in many countries with abundant agricultural resources.

Ethanol, in turn, used not only as a fuel, can be used also to produce more valuable hydrocarbon compounds, especially ethylene. This hydrocarbon compound is extremely important and is used industrially to synthesize a wide range of organic compounds. More than 200 years ago, acidic solution was used to be a catalyst for this reaction. Solid acid catalysts such as silica-alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) and zeolites have also been used industrially, even before the twentieth century [10]. Zeolite has the advantage that it is environmentally friendly and can be reused and reactivated. Mordenite (H-MOR) and H-ZSM5 zeolite types are frequently used in ethanol dehydration [1,3,5,7,10-12]. Inaba *et al.* [6] found that H-MOR has a high selectivity for ethylene formation by intramolecular dehydration at temperatures of 400 °C, while H-ZSM-5 is effective for the formation of aromatics, paraffins and C3+olefins. These results would indicate that H-ZSM-5 zeolite with a low Si/Al₂ ratio is more suitable to produce higher hydrocarbons from ethanol and, consequently, H-MOR is a more appropriate zeolite for the dehydration of ethanol into ethylene [11].

Generally, the dehydration of alcohol over zeolite is considered to start with the direct interaction of the hydroxyl group of alcohol with the Brønsted acid sites of zeolite [1-3,5,8,12]. Density functional theory (DFT) calculations with small quantum clusters were employed to study this mechanism and it is reported that ethanol dehydration proceeds via an intermediate ethoxide surface species [2]. This finding is in line with recent experimental results which confirm the presence of a stable ethoxy intermediate in this reaction [1,7]. Here, we use a 120T cluster representing the H-MOR framework and use the ONIOM (our Own N-layered-Integrated molecular Orbital and molecular Mechanics) method which recent theoretical studies [6,9,13] have shown that this method can be efficiently used for characterizing the reactivity of active sites inside zeolites.

Two different mechanisms for the dehydration of ethanol into ethylene reaction are considered. One is a concerted mechanism and the other proceeds in two steps. Moreover, we propose here that water is allowed to assist the reaction due to the fact that bio-ethanol or hydrous ethanol (a mixture of ethanol and water) is almost always used in industry and it is known from experimental studies

adsorption energy of this complex is $-48.8 \text{ kcal mol}^{-1}$. At the TS_C transition state configuration, the C1-O4 bond of the ethoxonium ion begins to break to form one water molecule and the ethyl group. For the formation of the latter, the C2-H2 bond distance changes from 1.09 to 1.42 Å. H2 attaches to O1 with a bond length of 1.24 Å. This transition state has one imaginary frequency at 1161.0 cm^{-1} . The activation barrier and the apparent activation energy for this step are calculated to be 54.8 and $5.9 \text{ kcal mol}^{-1}$, respectively. After forming the transition state, the proton (H2) of the ethyl group transfers completely from C2 to O1 to restore the acid site of zeolite and a double bond (1.38 Å) between C1-C2 is formed. The ethylene molecule remains adsorbed via the π -interaction while a water dimer is formed on the basic site of the zeolite (PRD_C). The adsorption energy of this complex is calculated to be $-11.6 \text{ kcal mol}^{-1}$. The desorption of ethylene and one water molecule is an endothermic process which requires $7.3 \text{ kcal mol}^{-1}$.

3.2 Stepwise Mechanism

Alternatively, the dehydration of ethanol to ethylene can proceed in a stepwise mechanism through the formation of ethoxide intermediates that have also been observed in experiments [1,7]. The two processes involved are the dehydration of ethanol to ethoxide and the deprotonation of ethoxide to ethylene.

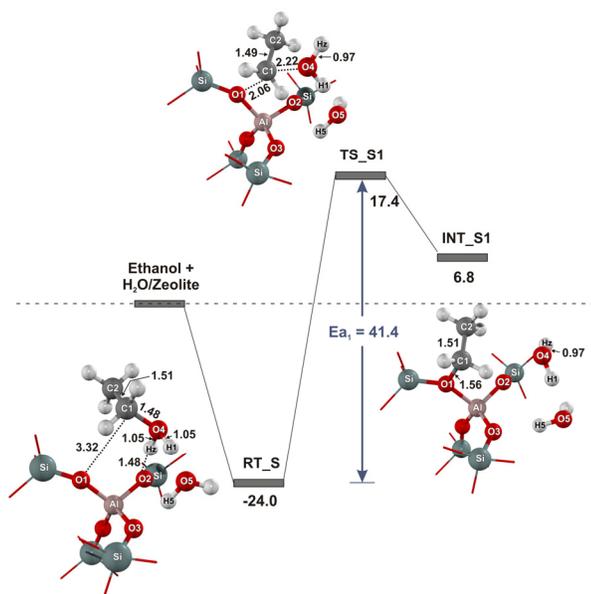


Figure 3: Calculated energy profile for the stepwise mechanism in the dehydration of ethanol to the ethoxide process.

The dehydration of ethanol to the ethoxide process: In this process, the ethanol molecule is dehydrated and an ethyl group is attached to the basic site of the zeolite. From there, the surface ethoxy species is formed within the presence of two water molecules (Eq. 2):



Figure 3 shows the optimized complexes and selected geometric parameters of the reactant, transition state and intermediates. The reaction starts with ethanol and water molecules coadsorbed on the acidic and basic sites of the zeolite, respectively. The adsorption energy of this complex is $-48.8 \text{ kcal mol}^{-1}$. The coadsorbed water molecule facilitates the protonation of the ethanol molecule by the acidic proton of zeolite to form the ethoxonium ion ($\text{CH}_3\text{CH}_2\text{OH}_2^+$). At the TS_S1 transition state, the C1-O4 bond of ethoxonium (2.22 Å) is breaking to form a water molecule (Hz-O3-H1) while the ethyl group gets closer to the basic oxygen of zeolite with an O1-C1 distance of 2.06 Å. The O4-C1-O1 bond angle is 154.4° . The imaginary frequency of this transition state is 366.8 cm^{-1} . The activation barrier and the apparent activation energy for this step are calculated to be 41.5 and $-7.7 \text{ kcal mol}^{-1}$, respectively. After the transition state, the intermediate of ethoxide and two water molecules (INT_S1) are formed. Their adsorption energy is $-18.1 \text{ kcal mol}^{-1}$.

The deprotonation of ethoxide to the ethylene process: The dehydration process produces ethoxide in agreement with the experimental finding from IR spectroscopy [1,7]. In this process, the reaction starts with a surface ethoxy species and a water molecule. Then, the water-assisted deprotonation of ethoxide leads to the formation of ethylene. (Eq. 3):

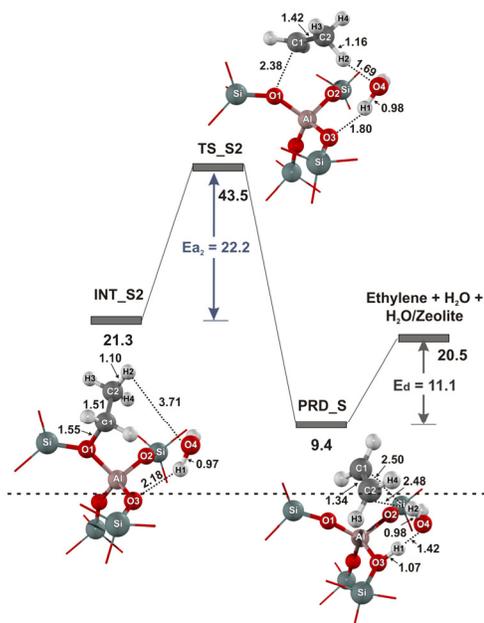


Figure 4: Calculated energy profile for the stepwise mechanism in the deprotonation of ethoxide to the ethylene process.

Figure 4 shows the optimized complexes and selected geometric parameters of the reactant, transition state and products. The reaction starts with ethoxide and water (INT_S2). This complex has an adsorption energy of $-3.5 \text{ kcal mol}^{-1}$. In the transition state (TS_S2), the proton of ethoxide is transferred to the oxygen of the water molecule

that is hydrogen-bound to an oxygen atom of zeolite. The C1-C2 bond distance is slightly shortened by about 0.09 Å and the proton of the water molecule is transferred to the zeolite regenerating the acidic site (O3-H1 bond). This transition state has one imaginary frequency at 248.6 cm⁻¹. The calculated energy barrier and the apparent activation energy are 22.2 and 18.7 kcal mol⁻¹, respectively. The ethylene product is formed by adsorbing the water molecule via the π -interaction (PRD_S). The adsorption energy of this complex is -15.4 kcal mol⁻¹. The desorption of ethylene and water from the pore of H-MOR zeolite requires 37.5 kcal mol⁻¹. The overall reaction energy for the stepwise pathway is endothermic by 22.1 kcal mol⁻¹.

4 CONCLUSIONS

The dehydration of ethanol to ethylene over the mordenite zeolite in the presence of water has been investigated by using the ONIOM2 method. Two reaction mechanisms are considered. The stepwise mechanism occurs through the formation of ethoxide intermediates and can be separated into the dehydration of ethanol to ethoxide and the deprotonation of ethoxide to ethylene. The activation barrier of the first step is 41.5 kcal mol⁻¹, which is much higher than that of the second step (22.2 kcal mol⁻¹), and this is expected to be the rate determining step. For the concerted mechanism, without an ethoxide intermediate, the activation barrier is 54.8 kcal mol⁻¹. This is considerably higher than the barrier of the rate determining step of the stepwise mechanism (41.5 kcal mol⁻¹). On the basis of our calculations it can be concluded, therefore, that the dehydration of hydrous ethanol to ethylene over H-MOR zeolite is proceeding via a stepwise mechanism.

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REFERENCES

- [1] R. Barthos, A. Széchenyi and F. Solymosi, "Decomposition and Aromatization of Ethanol on ZSM-Based Catalysts," *J. Phys. Chem. B.*, 110, 21816-21825, 2006.
- [2] S. R. Blaszkoski and R. A. van Santen, "Theoretical Study of C-C Bond Formation in the Methanol-to-Gasoline Process," *J. Am. Chem. Soc.*, 119, 5020-5027, 1997.
- [3] E. Costa, A. Ugeles, J. Aguado and P. J. Hernández, "Ethanol to Gasoline Process: Effect of Variables, Mechanism, and Kinetics," *Ind. Eng. Chem. Process Des. Dev.*, 24, 239-244, 1985.
- [4] F. Haase and J. Sauer, "Interaction of Methanol with Brønsted Acid sites of Zeolite Catalysts: An ab Initio Study," *J. Am. Chem. Soc.*, 117, 3780-3789, 1995.
- [5] M. Inaba, K. Murata, M. Saito and I. Takahara, "Ethanol Conversion to Aromatic Hydrocarbons over Several Zeolite Catalysis," *React. Kinet. Catal. Lett.*, 88, 135-142, 2006.
- [6] B. Jansang, T. Nanok and J. Limtrakul, "Interaction of Mordenite with an aromatic hydrocarbon: An embedded ONIOM study," *Journal of Molecular Catalysis A.*, 164, 33-39, 2007.
- [7] J. N. Kondo, K. Ito, E. Yoda, F. Wakabayashi and K. Domen, "An Ethoxy Intermediate in Ethanol dehydration on Brønsted Acid Sites in Zeolite," *J. Phys. Chem. B.*, 109, 10969-10972, 2005.
- [8] C. C. Lee and R. J. Gorte, "Calorimetric Study of Alcohol and Nitrile Adsorption Complexes in H-ZSM-5," *J. Phys. Chem. B.*, 101, 3811-3817, 1997.
- [9] P. Pantu, B. Boekfa and J. Limtrakul, "The adsorption of saturated and unsaturated hydrocarbons on nanostructured zeolites (H-MOR and H-FAU): An ONIOM study," *Journal of Molecular Catalysis A.*, 277, 171-179, 2007.
- [10] C. B. Phillips and R. Datta, "Production of Ethylene from Hydrous Ethanol on H-ZSM-5 under Mild Conditions," *Ind. Eng. Chem. Res.*, 36, 4466-4475, 1997.
- [11] I. Takahara, M. Saito, M. Inaba and K. Murata, "Dehydration of ethanol into ethylene over solid acid catalysts," *Catalysis Letters*, 105, 249-252, 2005.
- [12] A. K. Talukdar, K. G. Bhattacharyya and S. Sivasanker, "H-ZSM-5 Catalysed Conversion of Aqueous Ethanol to Hydrocarbons," *Applied Catalysis A*, 148, 357-371, 1997.
- [13] T. Maihom, S. Namuangrak, T. Nanok and J. Limtrakul, "Theoretical Study on Structures and Reaction Mechanisms of Ethylene Oxide Hydration over H-ZSM-5: Ethylene Glycol Formation," *J. Phys. Chem. C.*, 112, 12914-12920, 2008.