

The Theoretical Investigation of Oxidative Dehydrogenation of Ethane to Ethene over Fe-ZSM-5: A QM/MM Study

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ABSTRACT

The complete detailed reaction mechanism for the oxidative dehydrogenation of ethane over Fe-ZSM-5 zeolite has been systematically investigated by means of the ONIOM(MP2/6-31G(d,p):UFF)/ONIOM(B3LYP/6-31G(d,p):UFF) scheme. Two types of reaction mechanisms for the oxidative dehydrogenation of ethane have been suggested: stepwise and concerted. The concerted mechanism, the concurrent abstraction of two hydrogen atoms from ethane was found to be unattainable. Two routes of the stepwise pathway were proposed. The reaction at the straight channel takes place via the alkoxide intermediate, while the key intermediate of the reaction occurring at the sinusoidal channel is an “ethyl radical” one. The activation energies of the reaction observed at the straight channel are 12.4 and 54.9 kcal/mol, which is quantitatively higher than those at the sinusoidal channel (10.3 and 4.8 kcal/mol). The stepwise reaction taking place via the radical intermediate has been proved to be a dominant step in generating the ethene molecule.

Keywords: ethene, Fe-ZSM-5 zeolite, ONIOM, oxidative dehydrogenation, ethane

1 INTRODUCTION

Ethene is one of the most important basic chemicals in the petrochemical industry as a feedstock for the production of ethylene oxide, ethylene dichloride, vinyl acetate, ethyl alcohol and other petrochemical products. Conventionally, ethane is produced in the petrochemical industry by stream cracking. This process occurs at a high temperature (750-950 °C) [1]. Since the conventional production of ethylene has a high-energy consumption, much effort has been devoted to find an efficient route for the selective production of light olefins. Currently, the oxidative dehydrogenation of ethane is an alternative route to produce ethylene. This route carries on at a low temperature which would essentially reduce the formation of coke and also extend the lifetime of catalysts.

A range of heterogeneous catalysts have been used in this reaction for the purpose of achieving energy savings and increasing productivity. These include: metal oxides [3,4], zeolites [5,6], and metal-doped mesoporous materials [7,8].

The iron-modified zeolite of the MFI structure, Fe-ZSM-5, is proven to be one of the potential catalysts for the dehydrogenation of ethane. Held *et al.* [6] found that the ethane oxidation over the iron-modified zeolites; Y, MOR and ZSM-5 zeolites. They found that Fe-ZSM-5 provided the highest selectivity towards ethylene formation (in the range of 55% to 87%), whilst the Fe-MOR and Fe-FAU zeolite provides mainly the complete oxidation process. These results showed that the zeolite structure plays a key role in the catalytic activity of iron species for oxidative dehydrogenation reaction. However, the reaction mechanism of this reaction inside the pore of ZSM-5 zeolite has not been fully investigated.

The purpose of the present study is to analyze the reaction mechanisms of the oxidative dehydrogenation of ethane to ethene over Fe-ZSM-5 zeolite by means of the ONIOM (our-Own-N-layer Integrated molecular Orbital + molecular Mechanics) method. The results of this study may be helpful for understanding the fundamentals of how the oxidative dehydrogenation of ethane over zeolite works.

2 METHOD

The model of ZSM-5 zeolite, the 232T cluster, which covers the 10T active region and three different channel structures (the channel intersection, the straight channel, and the zigzag channel) where the reaction normally takes place, is taken from the lattice structure of the ZSM-5 zeolite [9]. The ONIOM2 scheme, in which the whole model is subdivided into two layers, is adapted. The active region, shown in Figure 1, consists of the 12T cluster, which is considered to be the smallest unit required for representing the reaction site of zeolite and the reactive molecules, is treated with the B3LYP level of theory using the 6-31G(d,p) basis set for H, C, O, Al and Si atoms and the effective core potential basis of Stuttgart and Bonn for the Fe atom [10]. In view of there being several reports that the sextet spin state was the most stable electronic configuration for the theoretical study on Fe-ZSM-5 [11-12], the total spin of the system was maintained at this state throughout all calculations. In order to obtain more reliable interaction energies, the single-point energy calculations at the ONIOM(MP2/6-31G(d,p):UFF)/ONIOM(B3LYP/6-31G(d,p):UFF) level were carried out. The rest of the extended framework is treated with the less demanding UFF force field [13]. It is

considered that these selected models for the ZSM-5 zeolites are large enough to cover all the important framework effects that act on both the active site and on the adsorbates.

All calculations have been performed using the Gaussian 03 code [14]. During the structure optimization, the 5T portion of the active site region and the adsorbate are allowed to relax while the rest of the active region is fixed at the crystallographic coordinates.

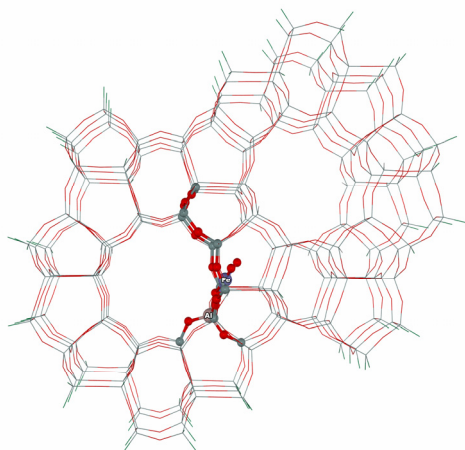


Figure 1: ONIOM2 layer of the 232T cluster model of Fe-ZSM-5. Atoms belonging to the 12T quantum cluster are drawn as balls and sticks.

3 RESULTS AND DISCUSSION

3.1 Stepwise mechanism for ethane oxidative dehydrogenation

Due to the ZSM-5 zeolite consisting of two different types of pore: straight channel and sinusoidal channel, it is of interest to investigate the oxidative dehydrogenation of ethane taking place

in different environments in order to get more insight into the role of the confinement effect of zeolite on the reaction.

Effect of straight channel within the nanoreactor on chemical reactions, Stepwise I: The reaction taking place in the straight channel at the junction of the sinusoidal channel and the straight one, molecular adsorption of ethane on the α -oxygen of Fe-ZSM-5, is observed by the mean of the ONIOM2 scheme. The adsorption complex of ethane (Ads_1) causes the slight lengthening of Fe-O1 and Fe-O2 bond distances by 0.001 Å. The computed adsorption energy is -8.5 kcal/mol. Dunne *et al.* [15] studied the calorimetric heats of adsorption and adsorption isotherm of methane and ethane on the silicalite which has the same crystal structure as ZSM-5 zeolite. The heat of adsorption of methane and ethane on the silicalite zeolite is 5.0 and 7.5 kcal/mol, respectively. This result shows that the difference of the energy is caused by the confinement effect of the zeolitic pore. In comparing the adsorption energy for the interaction of ethane and methane over the Fe-ZSM-5, the difference of values is 2.4 kcal/mol which is consistent with the difference in the adsorption from experimental data [15]. It can be concluded that the adsorption energy of ethane is qualitatively reliable. At the C-H cleavage transition state (TS_1), the activation energy required during the process of the (C1-H1) cleavage is 12.4 kcal/mol lower than the activation energy required during the C-H cleavage of methane over the Fe-ZSM-5 zeolite (15.3 kcal/mol) reported in previous work. The lowering of the activation energy is consistent with the weakening of the C-H bond of methane and ethane. The C-H bonding energy of methane is higher than that of ethane (435 vs. 420 kJ/mol). Therefore, cleavage of the C-H of ethane is preferable. After this step, the ethoxide and hydroxyl groups are formed. The alkoxide intermediate (Ads_2) is located in the intersection space and the H1-O1 bond also points to the direction of the free space in the intersection channel. The obtained ethoxide intermediate is much more stable than the initial state by 75 kcal/mol. The subsequent migration of hydrogen from the alkoxide group to the adjacent hydroxyl group (TS_2) leads to the formation of ethylene and water molecules. These indicate the migrating of

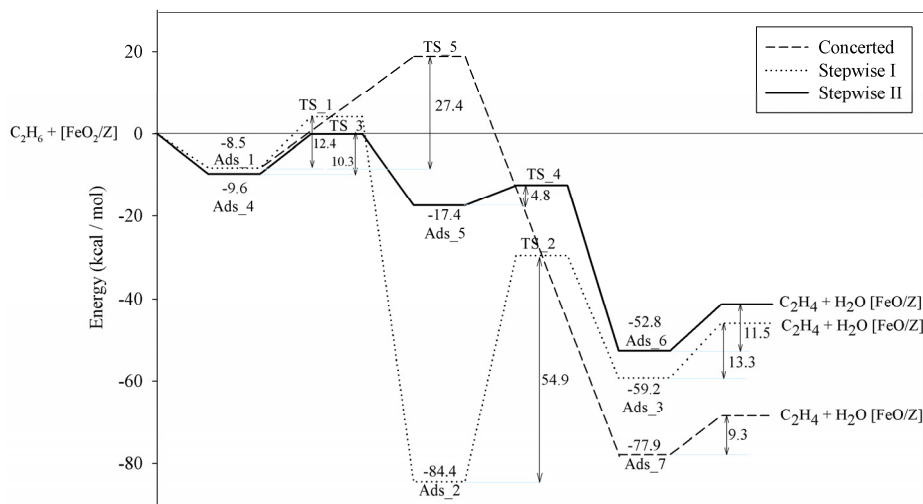


Figure 3: Compared energy profile for stepwise mechanism in the intersection, sinusoidal channel and concerted mechanism.

the C-H bond and the formation of the O-H bond, forming the ethylene and water molecules. This process is exothermic by 59.2 kcal/mol with a high-energy barrier of 54.9 kcal/mol.

Effect of the sinusoidal channel within the nanoreactor on chemical reactions, Stepwise II: The pathway of the oxidative dehydrogenation of ethane inside the sinusoidal channel is similar with that inside the straight channel in general, but their main differences will be highlighted. The reaction is initiated at the O2 site pointing toward the sinusoidal channel. The adsorption energy of ethane (Ads_5) in this channel is -9.6 kcal/mol. At the H abstraction transition state (TS_3), the energy barrier is calculated to be 10.3 kcal/mol, which is slightly lower than that of the C-H cleavage inside the straight channel. Variation of pore dimension at the transition state is shown to affect the direction of the reaction. Obviously, barrier height is decreased by about 30%. Comparison of the TS_1 in the straight channel shows that the form of the intermediate complex is affected by the pore shape. At this channel, the ethyl radical (Ads_6) is stabilized inside the sinusoidal channel. This phenomenon is called “intermediate shape selectivity” [16]. The ethyl radical intermediate is slightly more stable than the initial state by 7 kcal/mol. The formation of ethylene yields via the second H-abstraction by migrating one of the C-H bonds at the methyl site of the ethyl radical to the hydroxyl group bound on the iron site to form a water molecule. The coadsorption between water and ethylene molecules (Ads_6) are reached after the TS_4 requires only 4.8 kcal/mol, which is significantly lower than the activation energy for the corresponding step in the straight channel (TS_2). This result reveals that the ethyl radical is much more active than the alkoxide complex (Ads_2). The Ads_6 has the lowest energy, having the energy difference of about 35 kcal/mol with respect to Ads_5. Removal of water and propene from Ads_6 requires only 11.5 kcal/mol. The rate-limiting step of the reaction is the first H-abstraction step yielding the ethyl radical that reacts with the hydroxyl group attaching to the Fe site (Ads_5).

3.2 Concerted mechanism for ethane oxidative dehydrogenation

In addition to the stepwise mechanism in the formation of ethylene, we consider now the reaction pathway through a cyclic mechanism involving the simultaneous hydrogen abstraction of two hydrogen atoms from ethane to the iron oxygen atoms, yielding the $\text{Fe}(\text{OH})_2$ site and the ethylene molecule. In this hypothesis, the ethane is coordinated on the α -oxygen atoms by a bidentate complex.

Such a TS is expected to involve double hydrogen abstractions with the breaking of the C-H bonds and the making of O-H bonds, leading to the formation of ethylene. However, in spite of intensive search, we were not able to locate the related cyclic minimum whilst the corresponding transition state structure (TS_5) is observed in which two hydrogen atoms are eliminated from the ethane to the α -oxygen atoms of the Fe site. In the bidentate complex, the ethane is twisted into an eclipsed conformation less stable than the minimum form: the staggered conformation, by

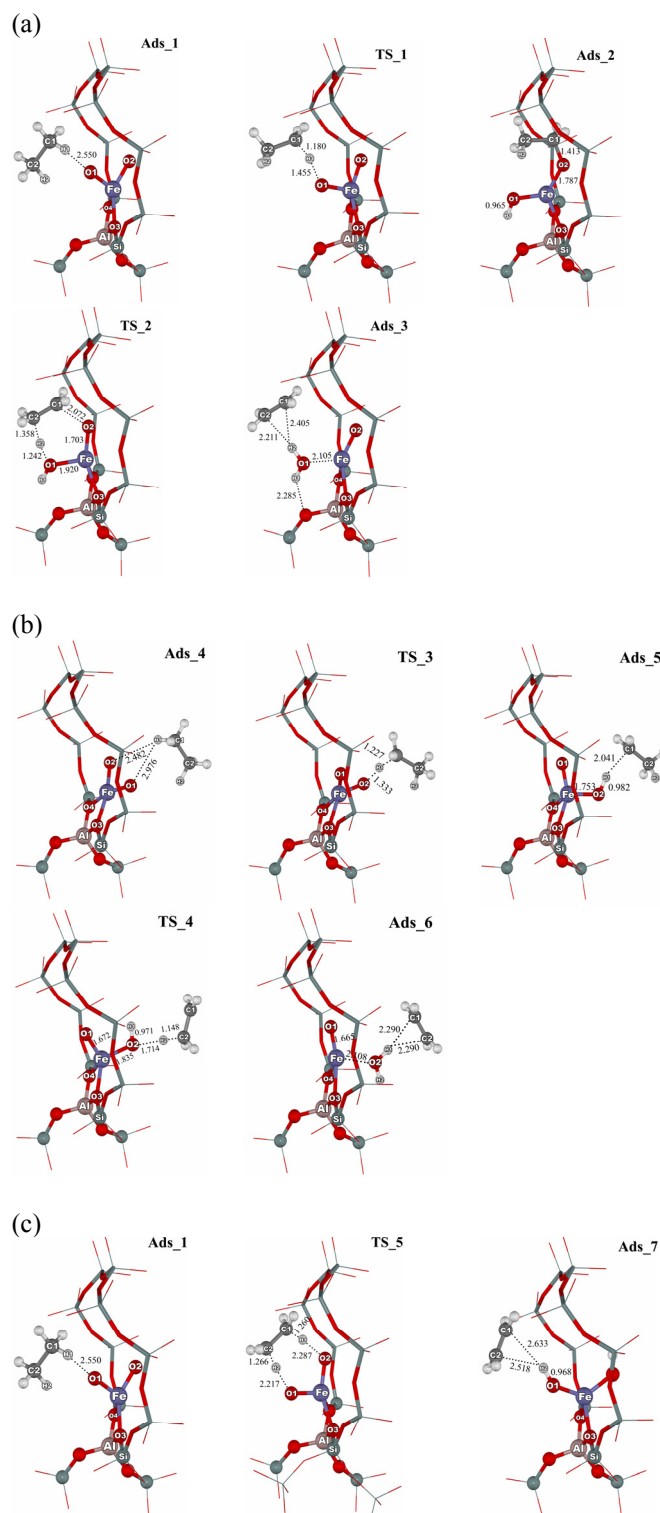


Figure 2: Optimized structures of adsorbed reactants, transition structures and products of (a) the stepwise mechanism in the intersection channel, Stepwise I, (b) the stepwise mechanism in the sinusoidal, Stepwise II, (c) the concerted mechanism.

3 kcal/mol [17]. Due mainly to steric hindrance, the interaction between eclipse-formed ethane and the α -oxygen atoms does not exist. The route via the TS_5 yields ethylene attached to the $\text{Fe}(\text{OH})_2$ site. The exothermicity of the reaction is -77.9 kcal/mol. The subsequent desorption of ethylene is weakly endothermic by 9.3 kcal/mol. These results suggest that only the single site of Fe is not favorable to perform the ethylene via a single step by abstracting two hydrogen atoms from ethane simultaneously. Formation of ethylene should be carried out via the stepwise mechanism.

4 CONCLUSION

The oxidative dehydrogenation reaction of ethane over Fe-ZSM-5 zeolite has been investigated using the ONIOM2 model. Two mechanisms, stepwise and concerted, have been evaluated. The concerted mechanism was found to be unfavorable. Our finding reveals that the stepwise mechanism taking place via the ethyl radical intermediate dominates the overall reaction of the oxidative dehydrogenation of ethane. However, this process competes against another plausible stepwise reaction that can proceed through the "alkoxide intermediate" at the straight channel. For the stepwise reaction with a radical intermediate occurring at the sinusoidal channel, it starts with the hydrogen abstraction of the ethane molecule to form the ethyl radical complex. The ethylene is generated via the second hydrogen abstraction in the second step. The activation energy of the first step is 10.3 kcal/mol, two fold higher than that of the second step (4.8 kcal/mol). These activation energies are quantitatively lower than those of the reaction via the alkoxide intermediate taking place at the straight channel (12.4 and 54.9 kcal/mol for the first and second H-abstractions, respectively). From calculated results, the activity of Fe ions is highly affected by the spaces in the vicinity of the active site. The ethane locating along the narrow channel would be readily dehydrogenated to ethylene faster than that on the open channel.

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