Hydrolysis of methoxide species and regeneration of active site in Fe-ZSM-5 catalyst by the ONIOM method

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Abstract

Hydrolysis of methoxide species formed from methane oxidation on Fe-ZSM-5 has been investigated using the ONIOM2 (B3LYP/6-311 + G(3df,2p):UFF) method. The steric constraint of the zeolite nanostructured pores modeled by the ONIOM method plays a vital role in regulating the orientation of reactive species around the active iron center and significantly affects the energetic of the reactive species. Two possible pathways for the hydrolysis of the methoxide species to methanol were investigated. The first pathway proceeds in a stepwise manner through adsorption of water on the iron active center and then the hydrolysis of the methoxide by the adsorbed water and the other pathway proceeds in one step with no initial adsorption of a water molecule. The hydrolysis of the methoxide species is found to preferably proceed via the step-wise mechanism with a small activation energy of 13.7 kcal/mol. The reaction is mildly exothermic by 5.2 kcal/mol. The adsorbed methanol can be desorbed requiring energy of 13.2 kcal/mol. Two pathways for the regeneration of the iron active site were evaluated. One is the direct dehydration, which is found to be energetically unfavorable as it requires high activation energy of 38.5 kcal/mol. The other is the water-assisted condensation of hydroxyl groups. The bridging water molecule can reduce the activation energy for proton transfer between the hydroxyl groups by half to 19.4 kcal/mol. Then, the desorption of waters restores the active form of Fe-ZSM-5 with an energy requirement of 22–23 kcal/mol.

1. Introduction

An Fe-exchanged ZSM-5 has a unique activity in the selective oxidation of methane to methanol at room temperature using nitrous oxide as an oxidant [1,2]. After activation at high temperature under a vacuum or a flow of steam, the active form of iron is formed [3–6], which is generally believed to be highly dispersed iron complexes in the zeolite microporous matrix. This fine iron species has a high affinity toward nitrous oxide and causes the molecule to be decomposed and leave an active surface oxygen species on the iron surface (at a temperature below 300 °C). This highly selective and active surface oxygen is generally called an α-oxygen [1], of which the exact structure is still not clearly understood. Generally, the active iron atoms in Fe-ZSM-5 are found to be highly dispersed iron complexes in the zeolite matrix and could be in the form of isolated ions, or binuclear complexes, or small aggregates of iron atoms [3–14]. According to in situ XANES and Mössbauer studies [6–8], iron atoms at the α-site are in an oxidation state II and after the decomposition of nitrous oxide; the iron atoms are changed to an oxidation state III. EXAFS studies have reported the presence of binuclear iron complexes [9–10] in over exchanged Fe-ZSM-5 catalysts. At low iron loadings (Fe/Al < 1), the iron complexes presence is predominantly in a form of a highly coordinately unsaturated isolated Fe^{II} site located at the Brønsted acid site [12–14].

Several theoretical and experimental studies [3–22] have been devoted to the elucidation of the structure of the active

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site in the Fe-ZSM-5 and the reaction mechanism. It has been theoretically illustrated that the mononuclear and binuclear iron complexes in the ZSM-5 matrix are highly active for nitrous oxide decomposition [15–17] and selective oxidation of methane to methanol [17–20], and also for benzene to phenol [20–22]. For oxidation of methane to methanol, the product obtained is, however, a strongly adsorbed methoxide species. This adsorbed methoxide species is too strongly attached to the active site to be thermally desorbed. Instead, methanol has to be extracted from the surface by hydrolysis with water. Little has been reported about this step. Liang et al. [19] have recently shown theoretically that methane can be converted to methoxide species on the iron-exchanged ZSM-5 and, then, methoxide can be converted to methanol by the reaction with water vapor at 523 K [32]. However, the direct removal of water from the iron active site has a rather high-energy barrier. The authors have shown that the presence of N_2O could reduce the energy barrier significantly.

In this paper, we report the quantum chemical study on the hydrolysis of the methoxide species on the Fe-ZSM-5 using an ONIOM method [23,24]. In our recent study [17], we have reported the oxidation of methane to methanol on the Fe-ZSM-5 using the same ONIOM model, and found that the extended structure of the zeolite has profound effects on the structure and electronic properties and catalytic activity of the iron species. Recently, we have reported that the effects of the extended zeolite framework on the structure and activity of the active site can be properly accounted for by the ONIOM method [17,25,26]. We here investigate the hydrolysis of methoxide and regeneration of the active iron site by

dehydration. Two pathways for the methoxide hydrolysis are investigated: step-wise and concerted mechanisms. We consider that the presence of another water molecule near the active site may play a role in the regeneration of the active iron site. Two pathways for the dehydration of the iron site are considered. One is direct dehydration and the other is water-assisted dehydration.

2. Methods

The structure of the cluster model was taken from the crystal structure of the ZSM-5 lattice [27]. In this study, the Fe-ZSM-5 structure was represented by a 46T ONIOM2 model (Fig. 1). The 46T cluster covers the three different channel structures (the straight channel, the zigzag channel, and the channel intersection), where reactions normally take place. In the ONIOM2 model, the 5T active center was treated quantum chemically at the B3LYP level of theory using the 6-311 + G(3df,2p) basis set for H, C, O Al and Si atoms, and the effective core potential basis of Stuttgart and Bonn [28] for the Fe atom. The rest of the extended framework, up to 46T, was treated at molecular mechanics force field (UFF).

Geometry optimizations and SCF energy calculations were done at the B3LYP/6-311 + G(3df,2p) level of theory. No corrections were made for basis-set superposition errors since the geometry optimizations and energy calculations were already performed at the high basis set. The total spin of the system was kept constant at the sextet state throughout all calculations as it has been reported by Bell and co work-
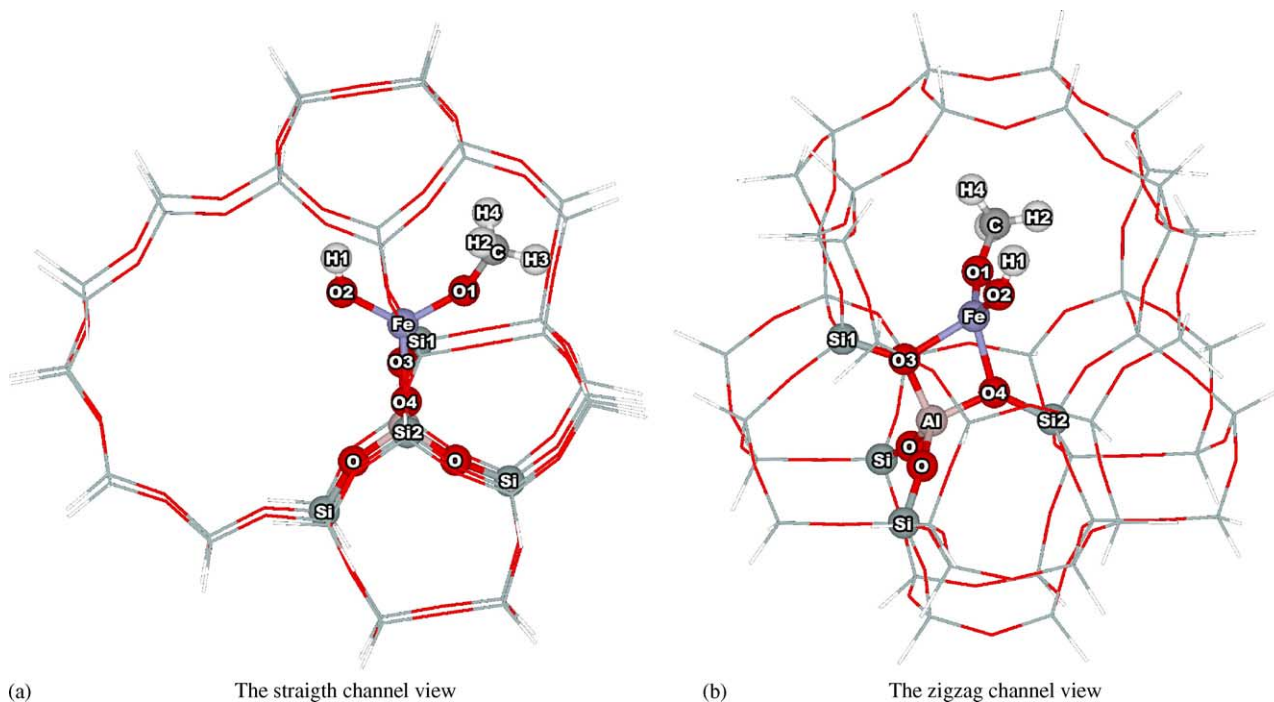

Fig. 1. 46T ONIOM model of the Fe-ZSM-5 zeolite, $AlSi_{45}O_{68}H_{49}$, with methoxide and hydroxide species bonded to the iron atom, atoms belonging to the active region are drawn as spheres: (a) the straight channel view and (b) the zigzag channel view.

ers [16,19,21] that the sextet spin state was the most stable configuration for the nitrous oxide decomposition and partial oxidation of methane and benzene on the mononuclear iron-oxo exchanged ZSM-5. During the structure optimization, only the 5T portion of the active site region and the adsorbates were allowed to relax, while the rest was fixed at the crystallographic coordinates. Normal mode analyses were carried out to verify that the transition states had one imaginary frequency whose mode corresponds to the designated reaction. All calculations have been performed by using the Gaussian03 code [29].

3. Results and discussion

Oxidation of methane on the active site of the Fe-ZSM-5 catalyst leads to the formation of methoxide species being strongly adsorbed on the active site. The structure of the iron–methoxide complex is shown in Fig. 1 and selected structural parameters are presented in Table 1. In the Fig. 1, atoms on the extended framework up to 46T of the ZSM-5, which are theoretically represented by the UFF force field, are drawn with lines while the atoms on to the 5T active region, which are modeled with B3LYP, are drawn with spheres. In Fig. 1a, the active iron center was viewed along the straight channel while it was viewed along the zigzag channel of the zeolite (in Fig. 1b). On the active iron center, which is located on the ion exchange site of the ZSM-5 at the cavity of the intersection of the straight and zigzag pore channels, there are methoxide and hydroxide species covalently bonded to the iron cation (Fe^{III}) with the bond distances of 1.785 and 1.809 Å, respectively. This surface methoxide species is very stable on the active iron site. It was found in our previous study [17] that the formation of this species is exothermic by 91.0 kcal/mol compared to the starting active site and gaseous methane. The conversion to methanol by

direct transfer of proton from the hydroxide to the methoxide would require a high activation energy (∼40 kcal/mol) [17,19]. Experimentally, it is found that attempts to thermally desorb the methoxide species, as a methanol will, however, result in the decomposition of the methoxide to carbon monoxide and hydrogen. Alternatively, hydrolysis of the methoxide will readily result in a methanol at room temperature [1,2].

3.1. Hydrolysis of methoxide species on Fe-ZSM-5

Two possible pathways for the hydrolysis reaction of the methoxide species to methanol are presented in Fig. 2 and selected structural parameters are tabulated in Table 1. In the first pathway (Fig. 2a), the reaction proceeds in a three-step manner, similar to that proposed by Liang et al. [19]. First, a water molecule adsorbs on the iron–methoxide complex via hydrogen bonding with a hydroxyl group of iron complex. Since the space around the iron site is limited by the pore walls and crowded by the hydroxide and the methoxide species, the water molecule can only weakly adsorb on the iron site. The distance between the oxygen atom of the water molecule and the iron site (Fe−O5) is calculated to be 2.247 Å, indicating weak interactions between the water molecule and the iron site. The O2−H5 distance is found to be 1.897 Å, indicating a hydrogen bonding between the water molecule and the hydroxide species on the iron site. The adsorption energy of water is calculated to be −10.5 kcal/mol, which is much lower than the adsorption energy of waters in H-ZSM-5 zeolite (19–24 kcal/mol) [30]. Then, the proton is transferred from the adsorbed water to the methoxide species, leading to the formation of methanol and the addition of a hydroxyl group onto the iron site. The transition state structure demonstrates the proton transfer as the O−H bond of the water molecule being elongated (from 0.964 to 1.215 Å). A new O−H bond is formed on the methoxide (the O1−H6 distance decreased

Table 1
The ONIOM2(B3LYP/6-311 + G(3df,2p):UFF) optimized geometric parameters of the isolated zeolite clusters, reaction intermediates and transition states (TSa, TSb) for hydrolysis of methoxide species on Fe-ZSM-5 (distances in Å and angles in degrees) via the step-wise and the concerted mechanisms

| Parameters	Complexes					
	Z[(HO)Fe(OCH$_3$)]	Z[(HO)Fe(OCH$_3$)(H$_2$O)]	TSa	Z[(HO)$_2$Fe(HOCH$_3$)]	TSb	Z[Fe(H$_2$O)(CH$_3$OH)]
Fe−O1	1.785	1.802	2.026	2.203	1.971	2.040
Fe−O2	1.809	1.877	1.824	1.825	1.723	1.694
Fe−O3	2.042	2.086	2.078	2.151	2.036	2.055
Fe−O4	2.024	2.087	2.063	2.072	2.022	2.059
Fe−O5	–	2.247	2.034	1.872	3.110	3.321
O2−H1	0.931	0.961	0.964	0.966	1.334	1.638
O1−H6	–	3.015	1.204	0.975	1.813	1.005
O2−H5	–	1.897	2.748	2.844	2.801	3.063
O5−H5	–	0.978	0.963	0.963	0.961	0.960
O5−H6	–	0.964	1.215	1.903	1.236	1.651
O5−H1	–	–	–	–	1.094	0.999
∠O1−Fe−O2	119.2	116.8	121.6	132.4	100.2	101.2
∠H1−O2−Fe	129.2	122.6	121.5	118.9	105.2	108.8
∠H1−O5−H5	–	–	–	–	103.5	105.0
∠H5−O5−H6	–	106.3	118.8	142.2	–	–
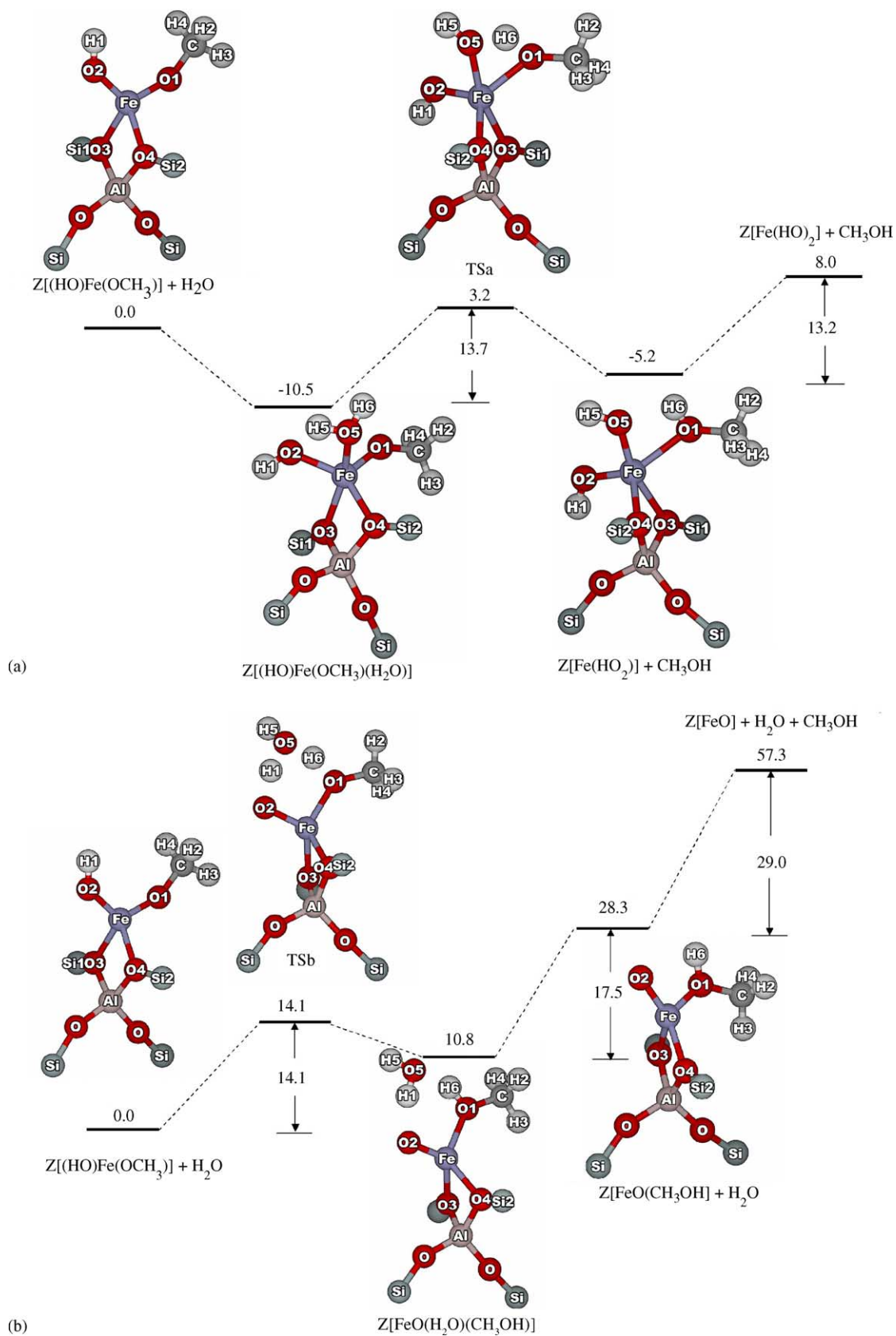
Fig. 2. Energy profile (kcal/mol) for hydrolysis of methoxide species on Fe-ZSM-5: (a) step-wise and (b) concerted mechanisms.

from 3.015 to 1.204 Å). The activation barrier for this step is 13.7 kcal/mol. The addition of another hydroxide species onto the iron site causes an increase of steric interactions. As a result, the produced methanol is moved away from the iron site. The distance between the methanol and the iron site (Fe−O1) is measured at 2.203 Å, indicating weak interactions between the two. While the distance between the hydrogen atom of the methanol and the oxygen atom of the hydroxide O5−H6 distance of 1.903 Å indicates weak hydrogen bonding. Therefore, the weakly adsorbed methanol can be readily desorbed at this stage with a small desorption energy of 13.2 kcal/mol, which is much lower than the desorption of the adsorbed methanol of 28.8 kcal/mol [17] on the iron (II) complex, Z[CH₃OHFeO] where steric repulsion is not as pronounced as in this case.

These results indicate that the steric constraint imposed by the pore confinement of the ZSM-5 zeolite modeled by the ONIOM2 scheme plays a significant role in this process. The confinement of the zeolite pore walls limits the space around the iron complex and causes more steric repulsive interactions between the coordinated ligands. As a result, the adsorbed reactant complex, Z[(HO)Fe(OCH₃)(H₂O)], and the product complex, Z[(HO)₂Fe(CH₃OH)], are less stable than the same complexes modeled by the 3T quantum cluster by Liang et al. [19] where the steric interactions with the zeolite pore walls were not included. Additionally, the product complex is more destabilized by the confinement of the zeolite pores than the adsorbed reactant complex. This may be due to the bulkiness of the product complex which causes more steric repulsion, indicated by the longer distance between the oxygen atom of the methanol and the iron atom than the distance between the oxygen atom of the methoxide and the iron atom (2.203 versus 1.802 Å). The reaction energy for this step is calculated to be slightly endothermic (by 5.3 kcal/mol) whereas Liang et al. [19] reported that the reaction was slightly exothermic (by −0.9 kcal/mol). Consequently, the activation energy in this study (13.7 kcal/mol) is higher than that calculated by the 3T cluster (6.2 kcal/mol) [19] complying with the Bronsted–Evans–Polanyi principle [31,32]. However, with the less steric hindrance of the 3T quantum cluster, the produced methanol interacts more strongly with the iron complex and, hence, requires the high desorption energy of 18.8 kcal/mol (versus 13.2 kcal/mol in this study) and the overall process was limited by the desorption of the adsorbed methanol, which is not the case in our calculations.

The alternative pathway for the hydrolysis of methoxide species on Fe-ZSM-5 in which the methoxide hydrolysis proceeds in one step with no initial adsorption of a water molecule is presented in Fig. 2b and selected structural parameters are tabulated in Table 1. The water molecule assists the proton transfer from the hydroxyl group of Z[(OH)Fe(OCH₃)] to the methoxide forming the adsorbed methanol. The proton (H1) of the hydroxyl group transfers to the bridging water molecule and, simultaneously, the hydrogen atom (H6) of the water molecule shifts to the oxygen

atom (O1) of the methoxide group. The activation energy of this step is calculated to be 14.1 kcal/mol, which is comparable to the activation energy of the step-wise mechanism. This hydrolysis pathway yields the complex of water hydrogen bonded to the Z[FeO(CH₃OH)]. This complex is not stable compared to the initial reactants and the reaction energy is computed to be endothermic by 10.8 kcal/mol. Desorption of the water molecule can proceed with the desorption energy of 17.5 kcal/mol and results in the complex of Z[FeO(CH₃OH)], which is unstable when compared to the initial methoxide complex, Z[(HO)Fe(OCH₃)]. The methanol is attached strongly on the iron complex. It would require energy of 29.0 kcal/mol to desorb the methanol. Although the activation energy for the hydrolysis step is comparable to the stepwise mechanism, the unstable intermediates and the high desorption energy of methanol negate the viability of this pathway.

3.2. Regeneration of the active site of Fe-ZSM-5

After the hydrolysis of methoxide and desorption of methanol, the iron site, Z[Fe(OH)₂], can be converted back by dehydration to the active form Z[FeO] which is the reduced form of the active iron site that can be easily oxidized and restored to the active surface oxygen by nitrous oxide decomposition [1,2]. The dehydration can occur directly via the direct proton transfer between the two-hydroxyl groups. The pathway for the hydrolysis reaction of the regeneration of the active site via direct proton transfer is presented in Fig. 3a and selected structural parameters are tabulated in Table 2. There are two hydroxyl groups covalently bonded to the iron atom of Z[Fe(OH)₂]. The bond distances of Fe−O2 and Fe−O5 of the two-hydroxyl groups are 1.803 and 1.807 Å, respectively, representing the typical Fe−O single bond. The O2−O5 distance is found to be 3.134 Å and the O2−H5 and O5−H1 distances are calculated to be 3.450 and 3.457 Å, respectively, indicating no hydrogen bonding between the

Table 2
The ONIOM2(B3LYP/6-311 + G(3df,2p):UFF) optimized geometric parameters of the isolated zeolite clusters, reaction intermediates and transition state (TSc) for regeneration of the iron active site on Fe-ZSM-5 via direct dehydration (distances in Å and angles in degrees)

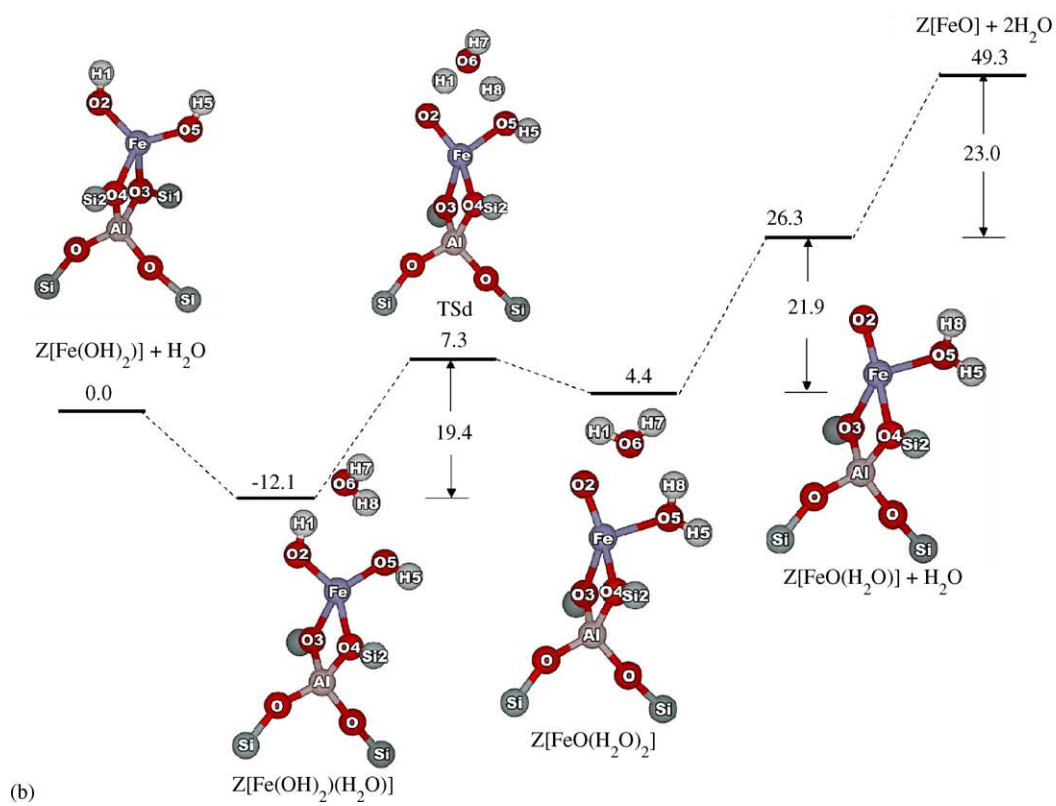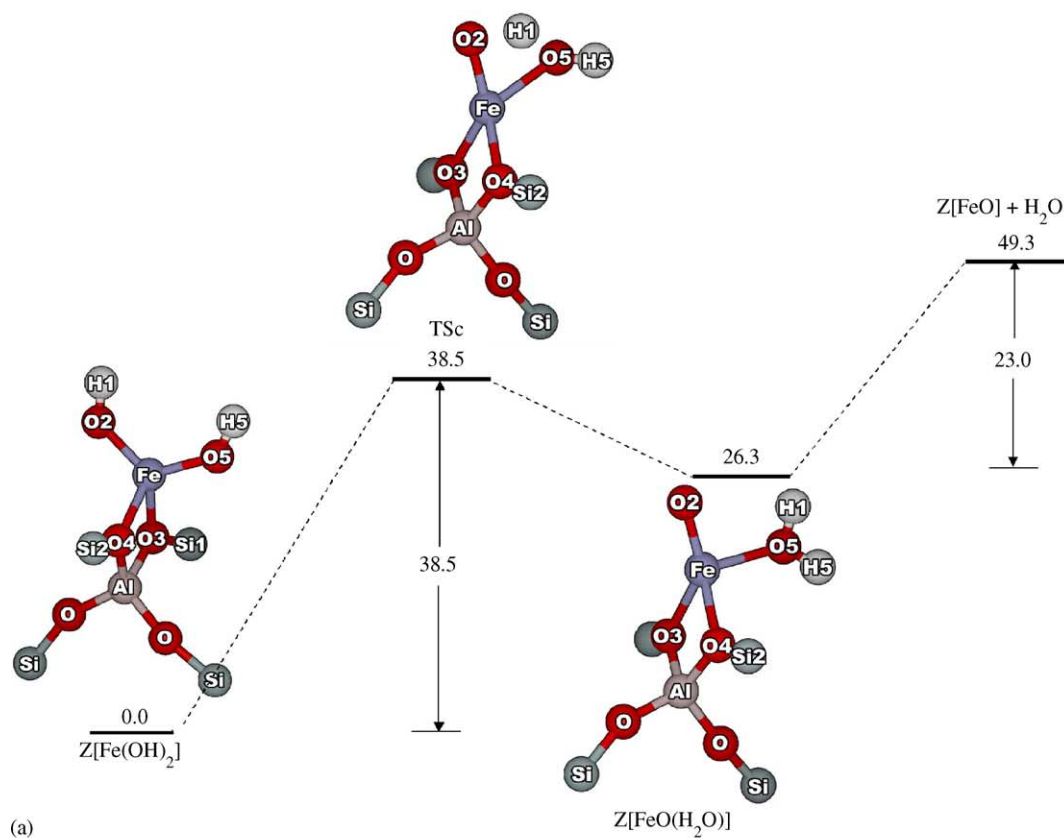| Parameters	Complexes			
	Z[Fe(OH)₂]	TSc	Z[FeO(H₂O)]	Z[FeO]
Fe−O2	1.803	1.737	1.674	1.655
Fe−O3	2.032	2.026	2.067	2.033
Fe−O4	2.014	2.013	2.055	2.021
Fe−O5	1.807	2.057	2.158	–
O2−H1	0.961	1.285	2.793	–
O2−H5	3.450	3.022	3.804	–
O2−O5	3.134	2.326	2.866	–
O5−H1	3.457	1.205	0.965	–
O5−H5	0.961	0.963	0.964	–
∠O2−Fe−O5	120.5	75.1	96.0	–
∠H1−O2−Fe	131.3	78.7	68.0	–
∠H5−O5−Fe	130.8	125.9	135.5	–
∠H1−O5−H5	85.4	117.6	109.4	–

Fig. 3. Energy profile (kcal/mol) for regeneration of the iron active site on Fe-ZSM-5: (a) direct dehydration and (b) water assisted process.

Table 3
The ONIOM2(B3LYP/6-311 + G(3df,2p):UFF) optimized geometric parameters of the isolated zeolite clusters, reaction intermediates and transition state (TSd) for regeneration of the iron active site on Fe-ZSM-5 via water assisted process (distances in Å and angles in degrees)

Parameters	Complexes					
	Z[Fe(OH)$_2$]	Z[Fe(OH)$_2$(H$_2$O)]	TSd	Z[FeO(H$_2$O)$_2$]	Z[FeO(H$_2$O)]	Z[FeO]
Fe—O2	1.803	1.791	1.718	1.691	1.674	1.655
Fe—O3	2.032	1.970	2.011	2.041	2.067	2.033
Fe—O4	2.014	1.980	1.997	2.030	2.055	2.021
Fe—O5	1.807	1.840	1.986	2.074	2.158	–
O2—O5	3.134	3.047	2.794	2.876	2.866	–
O2—H1	0.961	0.979	1.360	1.660	–	–
O6—H1	–	1.893	1.101	0.999	–	–
O6—H7	–	0.960	0.962	0.961	–	–
O6—H8	–	0.974	1.216	1.574	–	–
O5—H8	–	1.906	1.204	1.016	0.965	–
O5—H5	0.961	0.962	0.961	0.962	0.964	–
∠O2—Fe—O5	120.5	114.1	97.6	96.0	96.0	–
∠H7—O6—H8	–	105.4	111.8	80.1	–	–
∠H1—O6—H7	–	111.2	106.9	109.5	–	–
∠H5—O5—H8	–	134.0	120.0	109.4	109.5	–

two hydroxyl groups. At the transition state of proton transfer, the O2 and O5 atoms move closer (O2—O5 distance decreased from 3.134 to 2.326 Å) and the H1 proton is transferred from the O2 to O5 atom (the O2—H1 bond is elongated from 0.961 to 1.285 Å and the O5—H1 distance decreased from 3.457 to 1.205 Å). However, this direct proton transfer has a high activation energy of 38.5 kcal/mol and the produced adsorbed water molecule can be desorbed endothermically by 23.0 kcal/mol. On the other hand, the conversion of the adsorbed product, Z[FeO(H$_2$O)] back to dihydroxy iron species, Z[Fe(OH)$_2$] is relatively easy to achieve and requires a small activation energy of 12.2 kcal/mol as the dihydroxy iron species is more stable than the adsorbed product.

It is well known that water molecules can assist proton transfer in aqueous solution. Therefore, during the regeneration of the active site, another nearby adsorbed water molecule may assist the proton transfer between the two-hydroxyl groups and may significantly reduce the energy barrier. The reaction profile of the water assisted hydroxide condensation is presented in Fig. 3b and selected structural parameters are tabulated in Table 3. In the first step, a water molecule is adsorbed by forming hydrogen bonding to the two-hydroxyl groups on the iron site. The adsorption energy is evaluated to be −12.1 kcal/mol. The proton transfer between two hydroxyl groups of the Z[Fe(OH)$_2$] proceeds through the bridging water molecule. The interatomic distances between the bridging water molecule and the hydroxyl groups of the iron complex O5—H8 and O6—H1 are found to be 1.906 and 1.893 Å, respectively, which indicate a much shorter path of proton transfer than the path for the direct proton transfer which occurs through the O5—H1 distance of 3.457 Å. At the transition state, the proton (H1) from the hydroxyl group is transferred to the bridging water, as reflected by the increase of the O2—H1 distance from 0.979 to 1.360 Å, leading to the breaking of the O2—H1

bond of the hydroxyl group and the decrease of the O6—H1 distance from 1.893 to 1.101 Å, leading to the formation of the O6—H1 bond to the bridging water molecule. Simultaneously, the proton (H8) of the bridging water is deprotonated to the other hydroxyl group, as indicated by the lengthening of the O6—H8 distance from 0.974 to 1.216 Å and the shortening of the O5—H8 distance from 1.906 to 1.204 Å. The proton transfer results in the formation of an active iron site with two adsorbed water molecules, Z[FeO(H$_2$O)$_2$]. The activation energy of this step is 19.4 kcal/mol, which is only about a half of the direct proton transfer. Then, the two water molecules are sequentially desorbed with desorption energies of 21.9 and 23.0 kcal/mol, respectively. The computed desorption energies of waters from the iron complex FeO-ZSM-5 are comparable to the desorption energy of about 19–24 kcal/mol of waters from H-ZSM-5 [30]. After desorption of waters, the initial active form of Fe-ZSM-5, Z[FeO] is recovered.

4. Conclusion

The hydrolysis of methoxide species covalently bonded to the active site in Fe-ZSM-5 and the regeneration of the active iron site has been investigated using the ONIOM approach. The extended structure of the zeolite is found to have profound effects on the structures and relative stabilities of adsorbed reactive intermediates and, therefore, have strong influences on the reaction mechanisms. The hydrolysis of the methoxide species can preferably proceed via the stepwise mechanism forming the adsorbed methanol with a small energy barrier of 13.7 kcal/mol. The adsorbed methanol can then be readily desorbed, requiring a small desorption energy of 13.2 kcal/mol. The regeneration of the active iron site can preferably proceed via the water-assisted condensation of the two hydroxyl groups on the iron site with a relatively

small activation energy of 19.4 kcal/mol. The desorption of adsorbed waters on the Fe-ZSM-5 remains the most difficult step, which requires an energy about 22–23 kcal/mol.

Acknowledgements

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