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Titanium–silicalite catalyzed epoxidation of ethylene with hydrogen peroxide A theoretical study

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Abstract

Active sites in titanium silicalite (TS-1) for selective oxidation of ethylene with H_2O_2 were studied by using ab initio quantum chemical methods. Models of the active sites were energy optimised and the interaction with H_2O and H_2O_2 calculated. The binding situation of the resulting titanium hydroperoxo compounds were explained and transition states and activation energy for the epoxidation of ethylene were computed. The transition states were characterised by calculating the vibrational frequencies.

Keywords: TS-1; Epoxidation; Theoretical study; Mechanism

1. Introduction

During the last years catalytic systems based on titanium silicalite (TS-1) as the catalyst and hydrogen peroxide as the oxidant have been developed for the selective oxidation of organic substrates. The catalyst shows a high selectivity to the partially oxidised products, with total hydrogen peroxide conversion. TS-1 represents a stable heterogeneous catalyst with small susceptibility to poisoning. Despite extensive experimental studies, there is only a limited understanding of the mechanism of the oxidation reaction. The present work will focus on the mechanism of the TS-1/H_2O_2 catalysed epoxidation of ethylene using ab initio quantum mechanical methods which are being more frequently applied to study the structure and reactivity of zeolites [1].

2. Methodology

First principle electronic structure calculations using different levels of theory were performed. Restricted Hartree–Fock (RHF) calculations, using the program-package SPARTAN [2] with a double zeta basis set augmented with polarization functions (DZP), were carried out for geometry optimisations. Calculations at density functional theory (DFT) level have also been performed, using Becke's 88 non-local exchange functional [3] and the Lee–Yang–Parr

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non-local correlation functional [4]. Geometry optimisations were carried out with a DNP basis set and using the grid mesh "FINE". DFT calculations were done with the DMol program [5].

3. Structure of the catalyst

Previous experimental results give no indication of Ti–O–Ti bonds in the framework of the zeolite TS-1. The active centers seem more likely to be isolated Ti atoms surrounded by –O–Si groups [6]. Theoretical work carried out by Jentys and Catlow clearly show that the substitution of titanium in the silicalite lattice is preferred over the formation of species with tetrahedral coordinated titanium atoms in edge-sharing or bridging positions [7]. This has been recently confirmed by high level ab initio calculations [8]. Theoretical work carried out Millini et al. [9] showed no clear evidence for the existence of preferential substitution sites for Ti among the twelve crystallographic different substitution sites in silicalite. The IR-spectrum of TS-1 shows a band at 960 cm^{-1} which some authors associate with a perturbed Si–O stretch in the close presence of the more positive polarised Ti atom [10].

4. Results and discussion

4.1. Structure of the active sites

Two different structures of the active site have been suggested (Fig. 1), the titanyl form and the tetrahedral coordinated form 6. However, in the work by Boccuti et al. it was concluded that the titanyl form is unlikely [11]. Therefore, the active site models $Ti(OH)_4$, $Ti(OSiH_3)_4$ (Fig. 2 and Fig. 3) are considered.

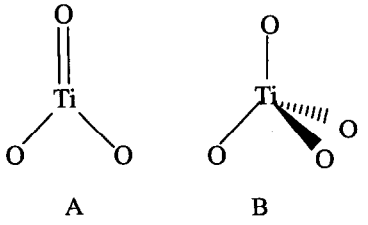

Fig. 1. Suggested structures of the active site; the titanyl form (A) and the tetrahedral coordinated form (B).

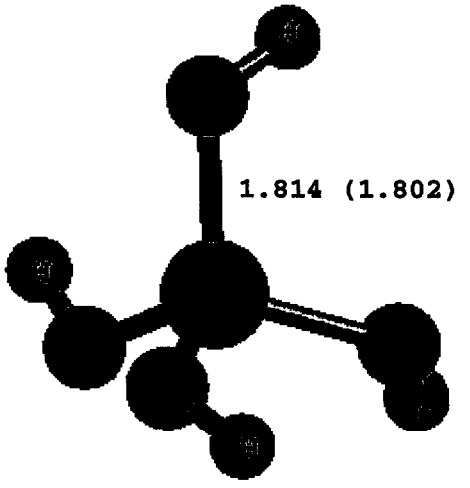

Fig. 2. Optimised Ti–O bond length (Å) in $Ti(OH)_4$ at HF/DZP and DFT/DNP levels of theory. Results in parentheses are at DFT/DNP level of theory. Experimental value of d(Ti–O) is 1.79–1.81Å [1].

Both structures were fully geometrically optimised without symmetry constrains. A tetrahedral structure at the Ti center is found for the

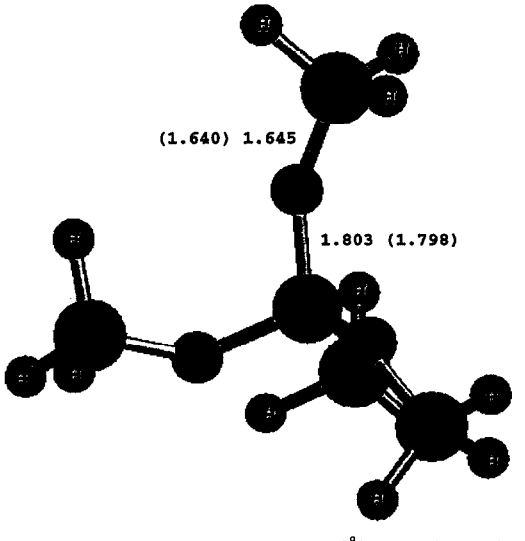

Fig. 3. Optimised Ti–O bond length (Å) in $Ti(OSiH_3)_4$ at HF/DZP and DFT/DNP levels of theory. Results in parentheses are at DFT/DNP level of theory. Experimental value of d(Ti–O) and d(Si–O) are 1.79–1.81 Å and 1.58–1.60 Å, respectively [1].

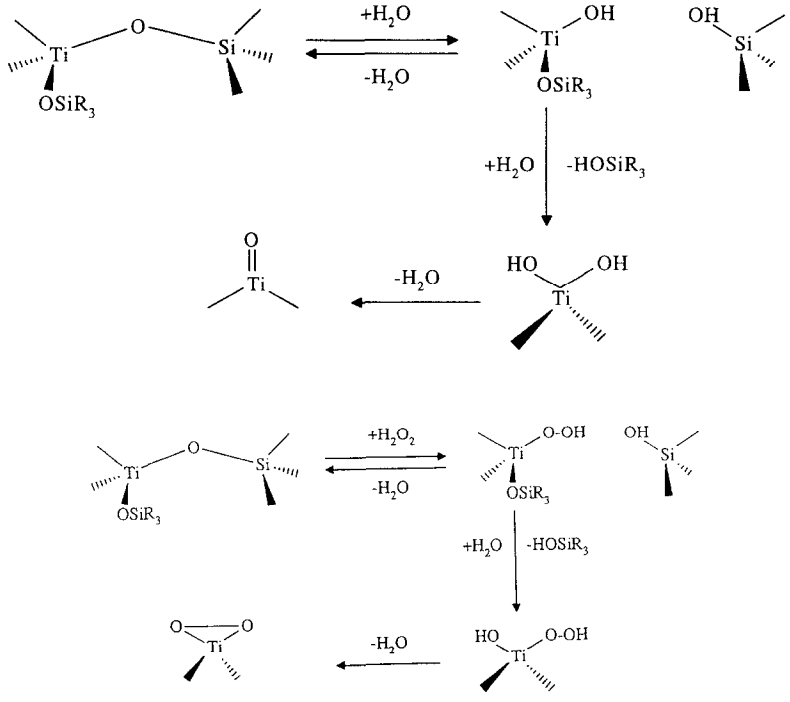

Fig. 4. Possible interactions of H_2O and H_2O_2 with Ti–O–Si site.

two models. The calculated Ti–O bond length in $Ti(OH)_4$ is 1.802Å at HF/DZP level of theory and 1.814 Å at DFT/DNP level of theory. This is in good agreement with experimental result (1.79–1.81Å), see Fig. 2. For the larger model $Ti(OSiH_3)_4$, the calculated Ti–O bond lengths at HF/DZP and DFT/DNP level are slightly shorter (1.798Å and 1.803Å, respectively) compared to the simpler model (Fig. 3).

4.2. Interaction with hydrogen peroxide

Experimental results indicate that peroxy or hydroperoxy groups are formed when H_2O_2 interacts with TS-1 [12–14]. Possible interactions between the Ti–O–Si site and H_2O_2 are given in Fig. 4. The $(OH)_3Ti–O–Si(OH)_3$ model is used for calculating reaction energies at the DFT/DNP level of theory for the reaction with H_2O_2 and H_2O. The results are given in Fig. 5. The reaction with H_2O is slightly endothermic whereas the reaction with H_2O_2 is exothermic by 6.2 kcal/mol. The results also show that the formation of Si–OOH groups is unlikely (endotherm by 19.1 kcal/mol). The formation of the peroxo compound from the hydroperoxo compound is endothermic (21.5 kcal/mol), suggesting that this reaction is not favourable.

$(OH)_3Ti–O–Si(OH)_3 + H_2O \longrightarrow Ti(OH)_4 + Si(OH)_4$ $\Delta E = +2.8$ Kcal/mol

$(OH)_3Ti–O–Si(OH)_3 + H_2O_2 \longrightarrow Ti(OH)_3OOH + Si(OH)_4$ $\Delta E = -6.2$ Kcal/mol

$(OH)_3Ti–O–Si(OH)_3 + H_2O_2 \longrightarrow Ti(OH)_4 + Si(OH)_3OOH$ $\Delta E = +19.1$ Kcal/mol

$Ti(OH)_3OOH \longrightarrow Ti(OH)_2OO + H_2O$ $\Delta E = +21.5$ Kcal/mol

Fig. 5. Calculated reaction energies (kcal/mol) at DFT/DNP level of theory for $(OH)_3Ti–O–Si(OH)_3$ interaction with H_2O and H_2O_2.

For the metal hydroperoxides, the binding of the peroxide to titanium is known to take place via the terminal oxygen. The question raised is if the other oxygen is also involved in the coordination to the titanium leading to bidental (η^2) coordinated peroxide complex (Fig. 6). In a recent density functional study by Wu and Lai, a η^1 structure for the titanium hydroperoxide was found [15]. In our study

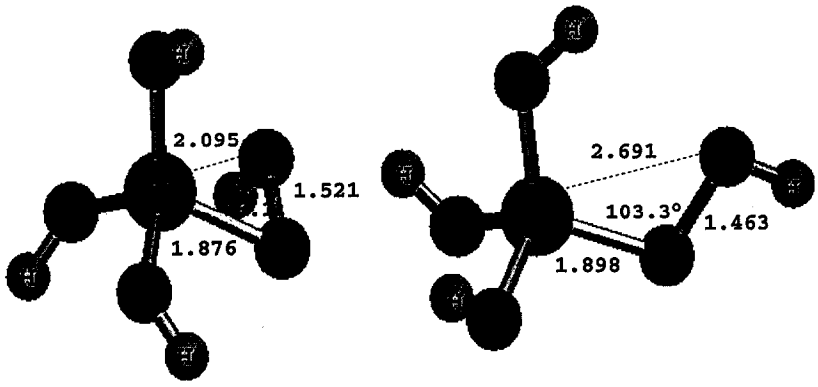

Fig. 6. Selected bond lengths (Å) and bond angle (deg.) at DFT level of theory for η^1 and η^2 structures of $Ti(OH)_3OOH$.

$Ti(OH)_3OOH$ was fully geometry optimised without symmetry constrain using density functional theory (DFT/DNP). As a results, the hydroperoxo moiety is coordinated to the Ti-atom in a η^2 fashion and not η^1. The calculated Ti–O(OH) bond length is 1.898 Å. The O–O bond length in the complex is 1.521Å which represents a remarkable activation of the oxygen–oxygen bond compared to H_2O_2. The other Ti–O(H) bond is predicted to be 2.095Å and the Ti–O–O(H) angle is calculated to be 76.1 (Fig. 6). The difference in coordination (η^1 instead of η^2) found by Wu and Lai [15], can be explained by the C_s symmetry constrain. DFT/DNP calculations under C_s symmetry constrain gives the same results as those of Wu and Lai [15]. The η^1 structure (Fig. 6) is about 8.0 kcal/mol more unstable than the η^2 structure. In the η^2 coordination (hydrogen is out-of-plane), the lone-pair of the hydroxyl oxygen atom points direct towards the Ti atom and can, therefore, contribute to bonding.

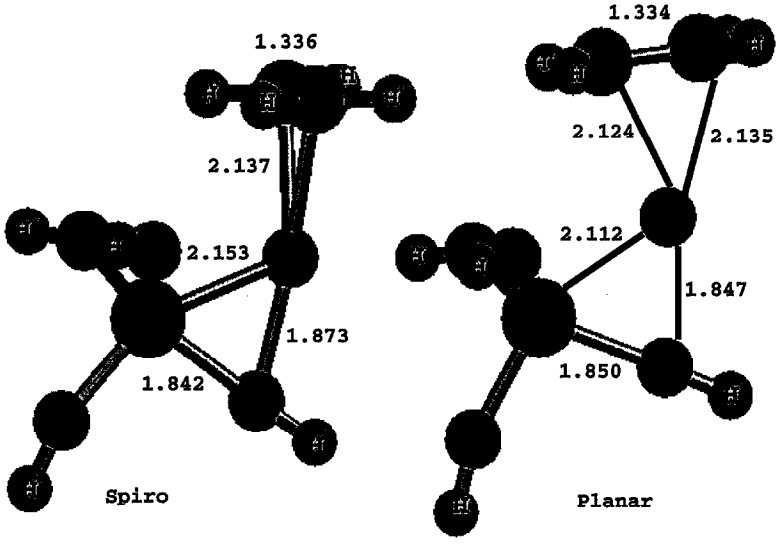

Fig. 7. Selected bond lengths (Å) for the spiro and planar transition state structure.

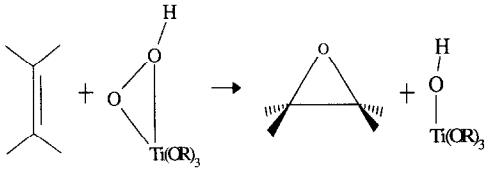

Fig. 8. Calculated reaction energy (kcal/mol) at DFT/DNP level of theory for the epoxidation reaction of ethylene.

4.3. Course of the reaction and the intermediates

Despite experimental efforts, the epoxidation mechanism remains controversial. From front orbital analysis two transition state structures can be considered, a planar and a spiro arrangement (Fig. 7). In a previous theoretical study by Bach et al., where LiOOH and ethylene were used as a model system, a small preference for the spiro structure was observed [16]. In an EHT study of the Sharpless epoxidation, Jørgensen et al. found a preference of about 12 kcal/mol for the spiro transition state structure [17]. Recently, Wu and Lai [15] reported a small preference of the spiro transition state structure. Despite these studies, detailed information about the transition metal-catalysed epoxidation reaction is still not available.

In the following section, a non-local density functional study of the epoxidation reaction of ethylene with trihydroxytitanium hydroperoxide is reported.

Two transition states were found. For both the planar and spiro transition structure, the Ti–(O–OH) part is bound in a η^2 structure, with an increase the Ti–O bond length. This indicates an activation of the oxygen moving towards the alkene. This is also reflected in an

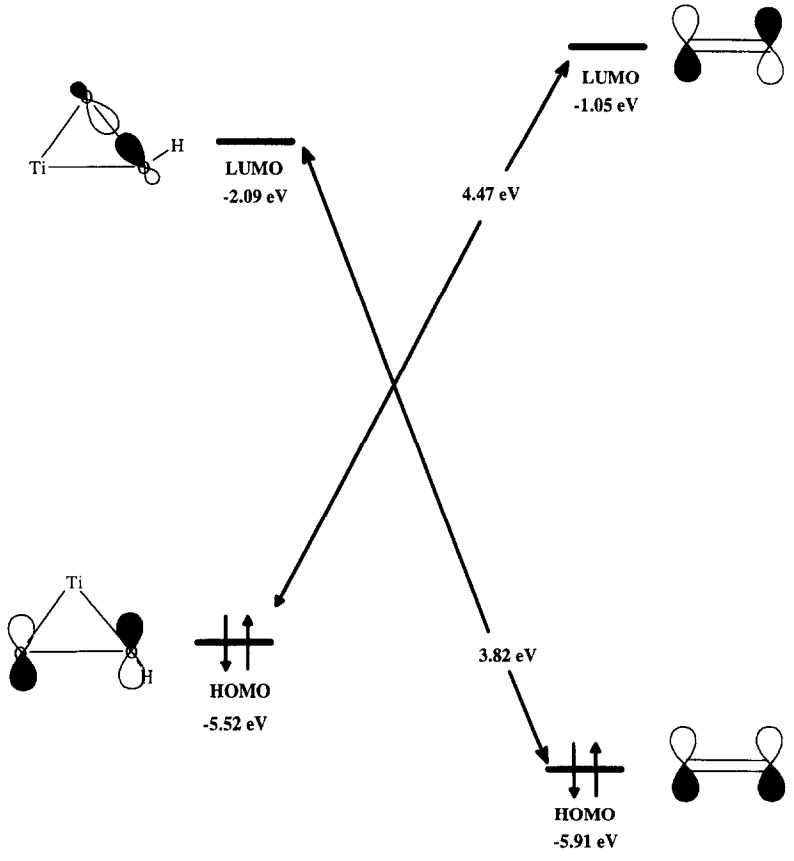

Fig. 9. Schematic diagram of HOMO and LUMO interaction for TiOOH and ethylene.

increased O–O bond distance compared to the free metal hydroperoxo compound. However, since ethylene still has a planar structure and the π-bond is almost intact (the C–C bond distance is typical for C–C double bonds), the transition structures can be described as an early transition states (Fig. 7). For the spiro and planar transition structures, both C–O bond distances are almost equal.

The spiro transition structure is calculated to be slightly more stable than the planar structure. At the DFT/DNP level of theory, this preference is about 3.5 kcal/mol. In contrast to the spiro transition state, two imaginary frequencies were found for the planar transition state (i528 and i61.3 cm^{-1}), which shows that this stationary point resembles a second order saddle point. For the spiro structure, the single imaginary frequency (i533cm^{-1}) corresponds to a stretching mode of the activated oxygen along the path from the ethylene towards ethylene oxide. The epoxidation of ethylene is predicted to be exothermic by 23.5 kcal/mol (Fig. 8).

In order to understand the electronic factors which govern the reaction, it is important to look at the front orbital interactions between ethylene and titanium hydroperoxide.

A schematic diagram of the highest lying MO's of TiOOH and ethylene are given in Fig. 9. According to frontier molecular orbital theory, the HOMO of $Ti(OH)_3OOH$ is mainly a π^* orbital, which has the character of a p type lone pair on the peroxy oxygen atoms. The LUMO is composed mainly of O–O σ^* orbital. When ethylene approaches the Ti complex in a spiro fashion, the best orbital overlap is obtained when ethylene is almost antiperiplanar to the Ti complex (Fig. 10A). There is also a possibility for an interaction between the HOMO of $Ti(OH)_3OOH$ and LUMO of ethylene (Fig. 10C). However, the energy gap between HOMO of ethylene and LUMO of Ti complex is about 0.65 eV smaller than between LUMO of ethylene and HOMO of Ti complex. Furthermore, a relatively high stabilisation energy of the formed MO between HOMO of ethylene and LUMO of

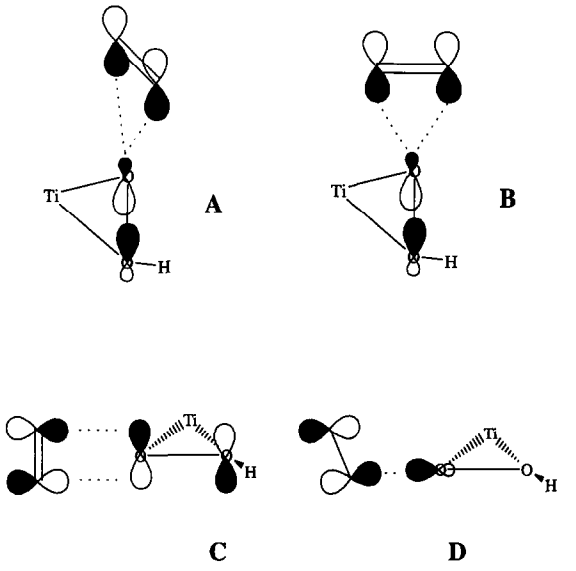

Fig. 10. Interaction of HOMO of ethylene and LUMO of TiOOH (A,B), and interaction of LUMO of ethylene and HOMO of TiOOH (C,D).

the $Ti(OH)_3OOH$ is predicted (about -10 eV). For the formed MO between the LUMO of ethylene and HOMO of the $Ti(OH)_3OOH$, there is even a small increase (about 0.80 eV) in energy compared to HOMO of the $Ti(OH)_3OOH$ reactant. Thus, the dominant interaction seems to be between HOMO of ethylene and LUMO of $Ti(OH)_3OOH$. This is also reflected in the observed electrophilic character of this addition reaction. For both the planar and spiro transition structure, there is an overall electron transfer from the alkene to $Ti(OH)_3OOH$ of about 0.22 electrons. This is in agreement with the fact that metal peroxo and hydroperoxo complexes react faster with more highly alkyl substituted alkenes, which indicates that oxygen transfer is of electrophilic character.

For the planar structure, an antiperiplanar approach will also be possible (Fig. 10B). The formed MO between HOMO of ethylene and LUMO of $Ti(OH)_3OOH$ has almost the same stabilisation energy as the spiro counterpart (-9.90 eV). There is no interaction between the out-of-plane lone pair of the peroxy oxygen atom which is the HOMO of $Ti(OH)_3OOH$ and the LUMO of ethylene. The only interaction

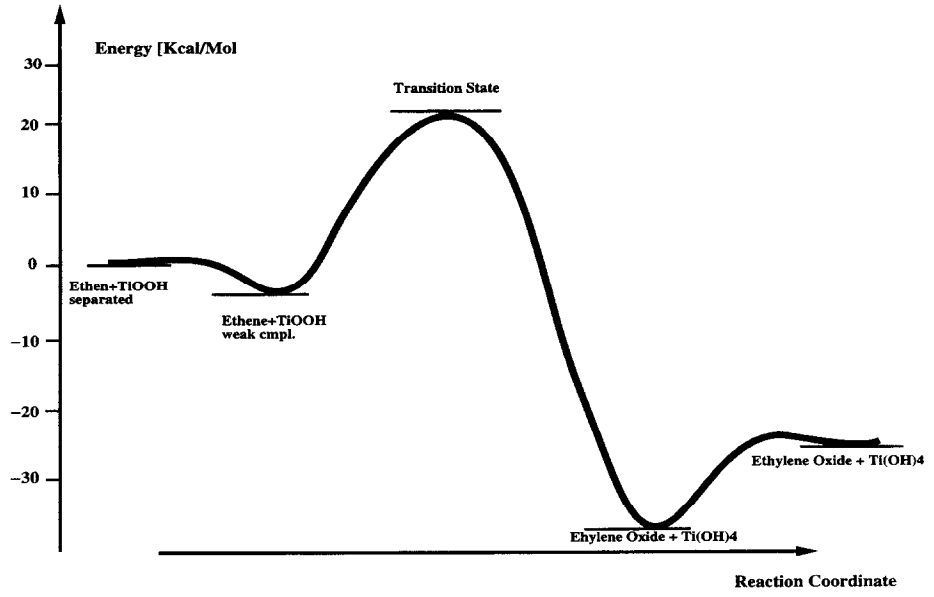

Fig. 11. Potential energy curve for the epoxidation of ethylene with $Ti(OH)_3OOH$.

seems to be between π orbital in-plane of the peroxy oxygen and one of the p orbital on one of the carbon atom (Fig. 10D). However, this unsymmetrical overlap is not as efficient as the symmetrical overlap described above. Thus, the spiro transition state structure seems to have a larger stabilising interaction and should be more favourable.

Intrinsic reaction path following (IRC) was carried out using DFT/DNP level of theory. The potential energy curve is given schematically in Fig. 11. Approaching the reactants results in a weakly physisorbed complex between ethylene and the titanium hydroperoxide ($\Delta E =$ 2 kcal/mol). Further progress in the reaction requires about 23 kcal/mol to reach the transition state, from which a strongly bonded product complex (ethylene oxide + $Ti(OH)_4$) is obtained (exothermic by 56 kcal/mol). Further separation of this strongly bonded complex requires about 10 kcal/mol.

5. Conclusions

Hartree–Fock and density functional theory were used to model the active center in TS-1 and the epoxidation of ethylene in presence of H_2O_2. In this study the optimised Si–O and Ti–O bond distances for two cluster models of the active sites are in good agreement with the experimental results. Calculations of the energies for the reaction of a Ti-site with H_2O_2 show a clear preference for the formation of a Ti–OOH group instead of Si–OOH group. The formation of peroxo compounds from hydroperoxo counterparts is calculated to be endothermic. In the $Ti(OH)_3OOH$ reactant, a η^2 coordination of the hydroperoxo moiety is found. C_s symmetry constrain forces a energetically higher η^1 structure.

There is a preference for a spiro transition state structure which is rationalised by a more favourable interaction between the HOMO of ethylene and LUMO of TiOOH. In addition, the planar structure is calculated to be a second order saddle point. The experimentally observed electrophilic character of epoxidation reaction is reflected in the relative small energy gap between HOMO of ethylene and LUMO of TiOOH and by a negative charge transfer by about 0.2 electrons from ethylene to TiOOH in the transition structure. The activation barrier for the epoxidation is calculated to about 23 kcal/mol.

It is clear that the cluster models employed in the present study are unable to reflect the influence of the zeolite lattice. It can be speculated that only a subset of the twelve different Ti sites are able to accommodate a transition state. The geometry of the transition state will also depend on the zeolite environment, especially when more bulky organic substrates are used. In future studies, it is therefore important to consider embedding methods which describe the active site of the catalyst by a quantum chemical method and treat the lattice for example by a molecular mechanical method. These methods are currently being exploited in our laboratory.

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