

Catalytic Activity of Titanium Silicalites—a DFT Study

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A theoretical study of the catalytic activation of hydrogen peroxide on titanium silicalites is presented. Calculations for several peroxide adsorption structures show that the interaction is weak. Formation of cyclic complexes between deprotonated peroxide and solvent molecules or with a silanol group is highly endothermic (more than 90 kJ/mol). The energy barrier of activation for ethene epoxidation with nondissociatively adsorbed peroxide is 83 kJ/mol with hydrogen peroxide over titanium silicalite. This energy is lower than the energy for peroxide deprotonation and implies that O–H bond cleavage during peroxide adsorption on titanium clusters is not necessary. © 1998 Academic Press

1. INTRODUCTION

Titanium silicalite, active in selective oxidation of organic compounds with hydrogen peroxide, has been the subject of a great number of spectroscopic and catalytic studies in recent years (1, 2). Considerable progress in this field has been made with X-ray diffraction and UV and X-ray absorption spectroscopy, all of which confirm that titanium ions occupy a tetrahedral framework position (3–8). An estimate of the Ti–O bond length based on XRD data, 179 pm (9), is very near the average value obtained by EXAFS, $-180\text{--}181 \pm 1$ pm (6–8).

Several theoretical studies on TS-1 have been published in the last couple of years (10–14). They focused on the local structure of the Ti-containing elementary units and the crystallographic position of titanium ions in the MFI structure of TS-1. The values for the Ti–O bond length obtained by quantum chemical calculations using the Hartree–Fock approximation (HF) (14) and the density functional theory (DFT) (11) fall within the limits of the average Ti–O distance as found by EXAFS.

We have less information about the adsorption of molecules and especially of hydrogen peroxide. A number of spectral and catalytic studies showed that water, peroxide, and alcohol molecules interact with Ti incorporated in the silicalite framework, but the structure of the adsorption

complex is not clear (1, 2) because of its instability. Some authors speculate about the structure of the active complex and the reaction mechanism using indirect structural information, correlations with the catalytic activity, and by drawing analogies to similar catalytic systems (2, 15, 16). Initial deprotonation of the adsorbed hydrogen peroxide is generally considered to be an essential step for its activation. In this situation, theoretical studies can give additional information by analysing the structure of the active adsorption complex and the energetics of elementary reaction steps.

In a recent study by Neurock *et al.* (13), a first attempt was made to explain the specific catalytic activity of titanium silicalites in oxidation with hydrogen peroxide. The authors reported geometry optimisation for an initial TS-1-H₂O₂-CH₃OH complex followed by a reaction with an ethene molecule, approaching from different initial positions. The main conclusion is that the ethene was oxidised by the oxygen atom which is directly coordinated to the Ti centre due to the lower negative charge of this oxygen.

The aim of the present work was to consider two problems related to the catalytic activity of titanium silicalites:

- the relative stability of different structures for dissociative and nondissociative hydrogen peroxide adsorption, including structures with co-adsorbed solvent molecules;
- energetics of ethene epoxidation with a TS-1/H₂O₂ adsorption complex.

2. METHOD

All quantum chemical calculations are based on the density functional theory (DFT) (17, 18) at the generalised gradient approximation level (GGA) using the ADF 2.0.1 program (19, 20). The Vosko–Wilk–Nusair exchange–correlation potential (21) was used for the local density. Nonlocal exchange and correlation gradient corrections were calculated according to Becke (22) and Perdew (23), respectively. Slater-type double-zeta basis sets, with polarisation functions (d for Si, O, and C, and p for H), were applied. The frozen core approximation is used for non-hydrogen atoms (2p for Si, 1s for O and C, and both 2p and 3p for Ti).

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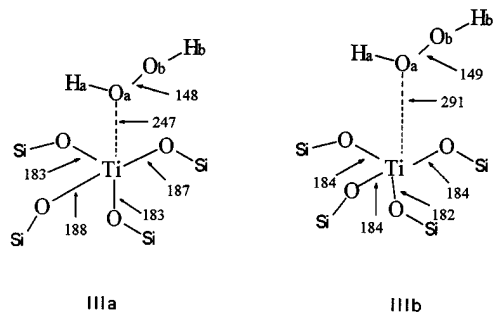


FIG. 2. Molecular adsorption of hydrogen peroxide—unconstrained (a) and constrained (b) optimisation.

complex and the sum of the energies of the optimised separated parts— $\text{Ti}(\text{OSiH}_3)_4$ and H_2O_2 is larger than that for constrained optimisation (-33 kJ/mol versus -3.5 kJ/mol). The reason for this difference is that the free optimisation allows complete relaxation of the titanium cluster, while the fixed positions of the saturating hydrogen atoms in the constrained cluster reduce this ability. Indeed, in the completely relaxed structure **IIIa**, two of Ti–OSi bonds weaken (the distance extends with 4–5 pm) which allows stronger bonding of the peroxide than does the constrained optimisation. In the latter case (structure **IIIb**), titanium cluster expansion is substantially restricted, and Ti–OSi distances change by only 1 pm. The real zeolite framework is not as flexible as in the completely relaxed cluster or as rigid as in the constrained model, but the latter approach is more similar to the actual situation. Despite the different interaction energies, both optimisations with this initial geometry give the same general result—exothermic nondissociative adsorption of hydrogen peroxide at the titanium cluster.

Another geometry optimisation was performed for dissociative adsorption of the peroxide—OOH group end-on adsorbed at Ti and the other peroxide proton bonded to an oxygen atom from the cluster. Both for constrained and unconstrained calculations, the optimisation again gives the adsorption complex, corresponding to molecular adsorption (structures **III**).

Complete hydrolysis of one Ti–OSi bond after hydrogen peroxide adsorption was simulated by separate optimisations of $(\text{H}_3\text{SiO})_3\text{Ti}-\text{OOH}$ and $\text{HO}-\text{SiH}_3$ clusters. In this case the adsorption energy is only -1.3 kJ/mol, but the ad-

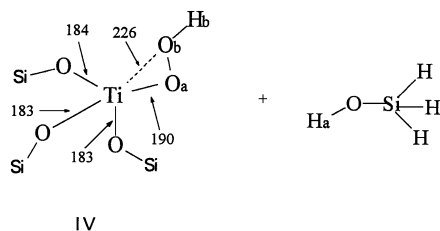


FIG. 3. Simulated complete hydrolysis of one Ti–OSi bond.

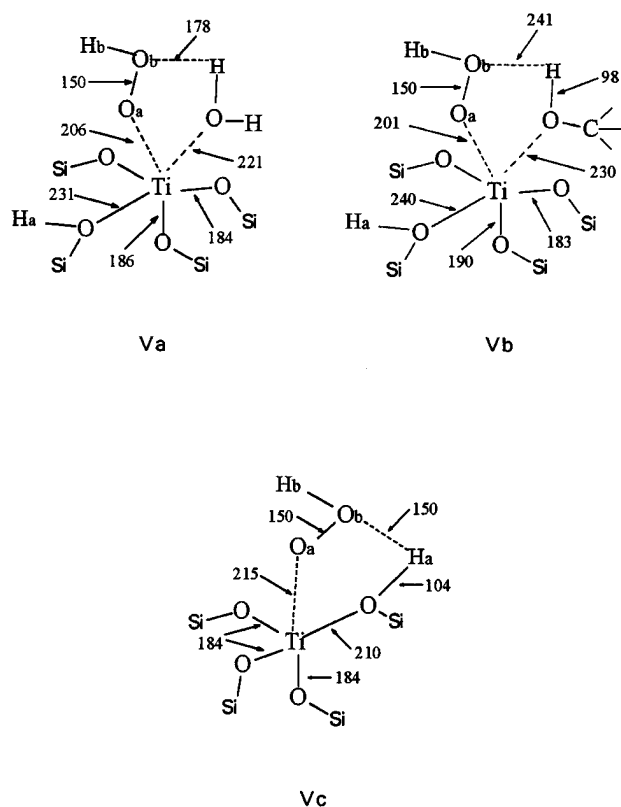


FIG. 4. Optimised cyclic complexes with deprotonated peroxide and water (a), methanol (b), or a silanol group (c).

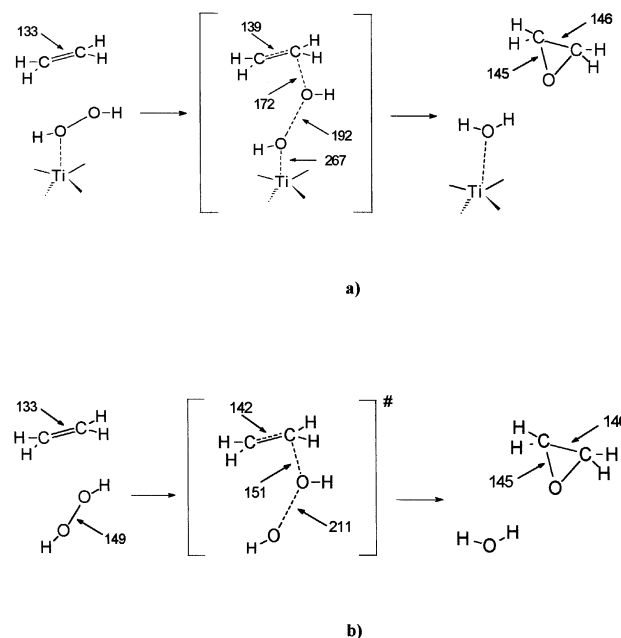


FIG. 5. Reaction path for the epoxidation of ethene with hydrogen peroxide nondissociatively adsorbed to a titanium cluster (a) and without catalyst (b). The distances are in pm.

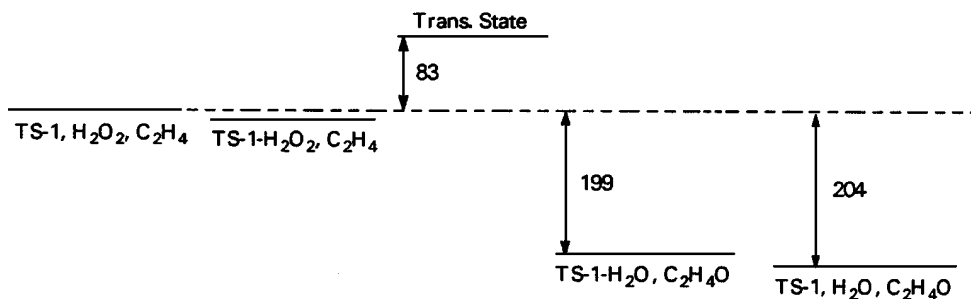


FIG. 6. Reaction energy diagram (in kJ/mol) of ethene epoxidation with an H₂O₂-TS-1 catalytic system.

sorption geometry is quite different. It is a side-bonded hydroperoxo complex with Ti–O bond distances shorter than in the molecular adsorption—190 and 226 pm (structure **IV**) (Fig. 3). This geometry corresponds to the structure proposed for adsorption of alkyl hydroperoxides at Ti(IV) centres (1).

It has been proposed that dissociative adsorption of H₂O₂ is stabilised by the formation of a five-membered cyclic complex with co-adsorbed solvent molecules or with the silanol group (15, 16) and that the deprotonated peroxide is the active species for catalytic oxidation. According to this proposal, we also optimised the geometry of three cyclic adsorption complexes with the participation of water, methanol, or a silanol group (structures **V**) (Fig. 4). Calculations show that the formation of such structures is highly endothermic with adsorption energies +129 kJ/mol for **Va**, +91 kJ/mol for **Vb**, and +104 kJ/mol for **Vc**. Of the three structures, the lowest adsorption energy is found for the cycle with methanol. In both complexes, including solvent molecules, the peroxide is placed closer to the Ti centre than the solvent oxygen. The complete cleavage of a Ti–OSi bond is not observed, and the silanol group remains weakly coordinated as a sixth ligand to the titanium centre at 230–240 pm. The presence of this silanol group generates the differences in the bond distances presented here, as compared with the earlier results reported by Neurock *et al.* for the cycle with co-adsorbed methanol (13). In the third considered structure, **Vc**, the cycle is closed with the silanol group formed after initial deprotonation of the peroxide. The length of the hydrogen bond closing the cycles increases in the order silanol group, water, and methanol, probably due to the decrease in the acidity of the protons in the same order. In summary:

(i) The nondissociative adsorption of hydrogen peroxide at the Ti cluster via one of the oxygen atoms is weakly exothermic ($E_{\text{ads}} = -33$ kJ/mol). Constrained optimisation reduces the interaction energy by 30 kJ/mol.

(ii) Dissociative adsorption is exothermic only when one of Ti–OSi bonds completely cleaves (structure **IV**). Constrained structures with deprotonated peroxide are endothermic with more than 90 kJ/mol.

3.3. Epoxidation of Ethene

In order to understand the mechanism of the reaction of the adsorbed peroxide with ethene catalysed by a titanium centre we analysed a few model situations. The reaction energy of the elementary reaction step, shown in Fig. 5a, is highly exothermic (–199 kJ/mol). The total reaction energy after desorption of the products and restoration of the titanium cluster is –204 kJ/mol (Fig. 6), close to –208 kJ/mol as calculated from the standard enthalpies of formation of the reagents and products (28).

The starting geometry to determine the transition state of elementary reaction (Fig. 5a) is based on the structure **IIIb** which corresponds to the constrained optimisation. The peroxide O–O bond is lengthened to 190 pm, and the ethene molecule is placed near to the second peroxide oxygen Ob. In the transition state (structure **VI**), this oxygen is nearer to the carbon atom of ethene than to the hydroxyl group which remains adsorbed to the Ti cluster. The energy barrier corresponding to this transition state is equal to 83 kJ/mol with respect to the energy of the initial separate reactants (Fig. 6). This is lower than the energy for dissociative adsorption of the peroxide presented in the previous section. We conclude that peroxide deprotonation is not necessary for the catalytic reaction. The energy barrier calculated for elementary reaction step (Fig. 5a) is much lower than the analogous “gas phase” reaction without a catalyst (Fig. 5b). This energy is equal to 221 kJ/mol.

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