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, $-180-181 \pm 1$ 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

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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- $1-H_2O_2$ -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 $TS-1/H_2O_2$ 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).



FIG. 1. Model clusters used in quantum chemical calculations.

Two types of model clusters for the titanosilicate structural unit were used for the calculations (Fig. 1). In the smaller cluster, the structure includes only the nearest neighbour Si atoms (structure I), while the larger cluster also includes the next neighbouring oxygen atoms (structure II). In both cases, the unsaturated bonds are saturated by hydrogen atoms. Such an approximation was found to be reasonable in other zeolite reactivity studies (24–26). In order to account for the sterical restrictions caused by the rest of the framework, both unconstrained and partially constrained optimisations were performed. For the initial Ti(OSiH₃)₄ clusters, the constrained optimisation was performed by fixing the angles in the structure to the crystallographic values for the chosen T-atom position according to Ref. (27) and optimisation of the interatomic distances. Thereafter, the hydrogen atoms which saturated the cluster remained fixed at their optimised positions, simulating the presence of the zeolite lattice. In the further calculations for hydrogen peroxide adsorption at such a constrained cluster, the positions of all the other atoms in the adsorption complex were optimised (except for the saturating H shell).

3. RESULTS AND DISCUSSION

3.1. Structure of Titanium Site

The structural parameters obtained after optimisation of the model clusters are given in Table 1. In addition to the completely optimised structure, three other structures, corresponding to T6, T8, and T12 crystallographic positions, were calculated. The choice of these positions was based

TABLE 1

Relative Energies in kJ/mol and Bond Lengths in pm of the Optimised Model Clusters

Parameters	Cluster I					Cluster II
Position	T6	T8	T12	Free	T6(np) ^a	T6-OH
Relative energy ^b Ti-O distance O-Si distance	0.94 183 169-70	0.35 183 169	1.07 183-4 169	0.0 183 169	 182-3 174-6	 182-4 170-3

^a Optimisation at T6 position without polarisation functions.

^b Relative energies of the optimised constrained clusters with respect to unconstrained optimisation.

on published data (10-12). The energy of the four clusters and the optimised structural parameters vary within very narrow limits -1.07 kJ/mol for the energy and less than 1 pm for bond lengths. The interatomic distances are 183 pm for Ti–O, 169 pm for O–Si, and 150 pm for Si–H. The much larger energy differences between Ti in the different positions as found by Millini et al. (11) are due to the way in which titanium incorporation is modelled at each T-atom position. They calculated single-point energies instead of performing partial geometry optimisation. In our calculations, the clusters can relax by changing O-Si and Si-H bond lengths. The computed Ti-O distance is about 1% longer than the experimental distances, the opposite of the result of HF calculations (14). Similar to the crystallographic T-O distances in the MFI structure, the optimised clusters show small alterations in Ti-O bond lengths; two of the oxygens are at 182.6 pm and the rest at 183.4 pm.

The basis set effects (extension of the frozen core to 3p and exclusion of the polarisation d-orbitals for Si and O and the p-orbitals for H atoms) were tested for Ti at the T6 position. The extension of the frozen core gives longer Ti–O distances of 1–2 pm, while in calculations without polarisation this distance is 182 pm. Inclusion of polarisation d-functions is reasonable for Si, because the occupation of its d-orbitals is 0.41. For oxygen atoms the occupation is only 0.02 and does not increase for more complicated clusters, as discussed in the following sections. On the contrary, the hydrogen p orbital occupation is about 0.04 in titanium clusters but increases up to 0.12 in the following cyclic structures.

Calculations for the larger clusters **II**, containing an additional oxygen coordination sphere, give results similar to those for the clusters **I**. The results show larger alterations in the Ti–O bond length for different oxygens in the range 182–184 pm and for O–Si in the range 171–173 pm.

3.2. Adsorption of Hydrogen Peroxide

Adsorption of single molecules of water and hydrogen peroxide as well as co-adsorbed H_2O_2/H_2O and H_2O_2/CH_3OH were studied. A stable structure for water adsorption is not found, even when a hydrolysed initial geometry was studied. This may be due to the relatively poor ability of DFT to account for weak van der Waals interactions (26).

Different initial structures for H_2O_2 adsorption were also tested. Simple molecular adsorption of the peroxide leads to weak bonding of the peroxide molecule to the model cluster by coordination of one oxygen to titanium (structures **III**) (Fig. 2). The adsorption distance and energy depend on the constraints applied to the titanium cluster. In the unconstrained geometry optimisation the peroxide is found closer to Ti (structure **IIIa**) and the adsorption energy E_{ads} (the difference between the energy of the optimised adsorption



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—Ti(OSiH₃)₄ and H₂O₂) 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 (H₃SiO)₃Ti-OOH and HO-SiH₃ 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).



b)

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 \mathbf{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 ($E_{ads} = -33 \text{ kJ/mol}$). 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/molas 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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