

## The Role of Co-adsorbed Solvent Molecules in the Formation of Ti-OOH Active Site: A Density Functional Theory Study

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### Abstract

The PW91-GGA density functional theory method was used to investigate the role of the co-adsorption of H<sub>2</sub>O molecule in the TS-1/H<sub>2</sub>O<sub>2</sub> system. The results show that the formation of the physisorbed 23T-H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O is more favored than that of 23T-H<sub>2</sub>O<sub>2</sub> by 5.8 kcal/mol, and the formation of chemisorbed 23T-Ti-OOH( $\eta^2$ )/H<sub>2</sub>O is more favored than that of 23T-Ti-OOH( $\eta^2$ ) by 6.8 kcal/mol. These agree well with the cooperative role of H<sub>2</sub>O in stabilizing the Ti-OO intermediate. The calculated Ti-O (H<sub>2</sub>O<sub>2</sub>) and O-O distances in the chemisorbed 23T-Ti-OOH- ( $\eta^2$ )/H<sub>2</sub>O complex agree well with the available experimental data. The electronic structures of the species are also discussed.

## 1 Introduction

Ti-Silicalite (TS-1) is a widely used catalyst in heterogeneous catalysis and has been frequently studied during the last two decades. With aqueous H<sub>2</sub>O<sub>2</sub> as oxidant agent, TS-1 can catalyze numerous oxidation reactions with high activity and selectivity under mild conditions, e.g. the reactions from ammonia to hydroxylamine and from secondary alcohols to ketones, as well as phenol hydroxylation, olefin epoxidation and cyclohexanone ammoximation [1-6]. Therefore, both experimental and theoretical

studies have been done to elucidate the structure of TS-1 [7-11], the nature of the active species for the oxidation reaction with H<sub>2</sub>O<sub>2</sub> [12-21], the effect of the solvent [22-23] and the catalytic reaction mechanisms [24-28]. Most of these work have been summarized in a recent review [29]. However, debates still exist on the reactive intermediates during the catalytic reactions.

It is now accepted that the formed Ti-OO species in TS-1 catalyst with aqueous H<sub>2</sub>O<sub>2</sub> is the active intermediate for partial oxidations [13,21,26-29]. Among the various

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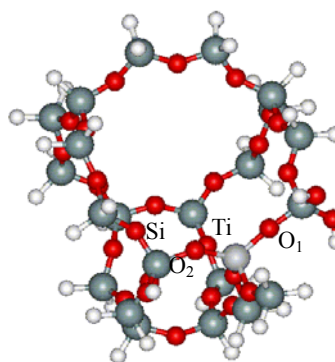
forms of Ti-OO species, the most popular view is the Ti-OOH species either in Ti-OOH( $\eta^1$ ) or in Ti-OOH( $\eta^2$ ) mode. Due to limited experimental conditions, few studies on the formation of this species included H<sub>2</sub>O [21,22,30]. IR spectroscopic studies of TS-1 showed the existence of Ti-OOH( $\eta^1$ ) and Ti(O<sub>2</sub><sup>-</sup>) in the presence of H<sub>2</sub>O<sub>2</sub> [31], while a bidentate species Ti-OOH( $\eta^2$ ) is found in other studies [19]. However, Ti-OOH( $\eta^2$ ) was computed to be more stable than Ti-OOH( $\eta^1$ ) [32], and therefore was considered as the active intermediate in partial oxidations.

Being the oxidant of the oxidation agent for the epoxide reaction, H<sub>2</sub>O<sub>2</sub> is added as its 30% water solution. Therefore, the role of water in this reaction is very important for the elucidation of the reaction mechanisms. In a recent work by Bonino et al, it is found that water as co-reactant in favoring the H<sub>2</sub>O<sub>2</sub> adsorption at the Ti site. However, their theoretical studies did not consider the water molecule for the complicity of the model. In this work PW91-GGA density functional theory method was used to investigate the active species formed in the TS-1/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O system, and the cooperative role of H<sub>2</sub>O molecule on the formation of the Ti-OO reactive intermediates was also considered.

## 2 Models and methods

The zeolite framework was modeled by a 23T cluster (Figure 1) which represents the intersection region of the straight and sinusoidal channels of the MFI framework [33]. In this cluster a Ti atom replaces a Si at the T<sub>12</sub> site, which is proved to be one of the most likely substitution sites for Ti [8] and locates at a special position where it is easily accessible for reactants. The peripheral silicon or oxygen atoms in the clusters were saturated by one or two terminal hydrogen atoms. The Si-H and O-H distance was set to 1.48 and 1.0 Å, respectively, and the

orientation of the Si-H and O-H bonds was along the pre-existing Si-O bonds. All the calculations were carried out by using Dmol3 program as implemented in Material Studio 2.2 package of Accelrys Inc [34]. The doubled numerical basis set with polarization functions (DNP) and the generalized gradient corrected (GGA) functional by Perdew and Wang (PW91) were used. The tolerance of energies, gradient and displacement convergence were  $1 \times 10^{-5}$  au,  $2 \times 10^{-3}$  au/Å, and  $5 \times 10^{-3}$  Å, respectively. The real space cut-off of atomic orbital was set at 5.5 Å. The structure of the zeolite model and the physically and chemically formed species were optimized by constraint only on the terminal hydrogen atoms described above, and the rest of the clusters were free to relax.



23T

**Figure 1.** Structure of 23T cluster representing the intersection region of TS-1 catalyst

## 3 Results and discussion

### 3.1 The structure of the TS-1 model and its adsorption complexes with H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O

The structures of H<sub>2</sub>O<sub>2</sub> adsorbed on 23T cluster with and without the co-adsorption of one H<sub>2</sub>O molecule are shown in Figure 2, and the selected structural parameters are presented in Table 1. It is shown that the calculated Ti-O (Si) average distance in the 23T model of 1.804 Å is in good agreement

**Table 1** Selected bond lengths (Å) and angles (degrees) in the 23T model and its adsorption complexes

	23T	23T-H <sub>2</sub> O <sub>2</sub> (physisorbed)	23T-H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> O (physisorbed)	23T-H <sub>2</sub> O <sub>2</sub> (chemisorbed)	23T-H <sub>2</sub> O <sub>2</sub> /H <sub>2</sub> O (chemisorbed)
Ti-O <sub>1</sub>	1.818	1.857	1.875	2.193	2.237
Ti-O <sub>2</sub>	1.817	1.854	1.850	1.849	1.866
(Ti-O)	1.804	1.831	1.838	1.919	1.938
Ti-O <sub>1</sub> -Si	162.6	159.9	155.3	129.6	123.3
Ti-O <sub>2</sub> -Si	138.1	140.2	139.8	128.6	132.3
O <sub>1</sub> -Ti-O <sub>2</sub>	118.2	126.8	123.5	158.4	165.2
O <sub>1</sub> -Si	1.636	1.621	1.618	1.674	1.677
O <sub>2</sub> -Si	1.632	1.615	1.613	1.611	1.600
Ti-O <sub>a</sub>	--	2.351	2.245	1.961	1.925
Ti-O <sub>b</sub>	--	3.228	3.174	2.256	2.274
O <sub>a</sub> -O <sub>b</sub>	--	1.477	1.463	1.484	1.470
O <sub>a</sub> -H <sub>a</sub>	--	0.986	0.987	2.030	2.500
O <sub>b</sub> -H <sub>b</sub>	--	0.986	1.008	0.986	1.032
O <sub>1</sub> -H <sub>a</sub>	--	2.619	2.543	0.986	0.986
O <sub>3</sub> -H <sub>a</sub>	--	2.186	1.959	2.377	2.424
O <sub>2</sub> -H <sub>b</sub>	--	2.608	--	2.590	--
O <sub>4</sub> -H <sub>b</sub>	--	2.113	--	2.271	--
O <sub>c</sub> -H <sub>b</sub>	--	--	1.649	--	1.547
O <sub>4</sub> -H <sub>c</sub>	--	--	2.454	--	1.938
O <sub>5</sub> -H <sub>c</sub>	--	--	2.193	--	2.651
O <sub>6</sub> -H <sub>d</sub>	--	--	2.737	--	--

Note: For the numbering system, see Figure 2.

with the EXAFS data of  $1.80\text{-}1.81 \pm 0.01$  Å [35]. This validates our theoretical models and method. In the physisorbed H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O complexes, one oxygen atom of H<sub>2</sub>O<sub>2</sub> bonds to the Ti center in short distances (2.351, 2.245 Å, respectively), while the other is in rather longer distances (3.228, 3.174 Å,

respectively). In addition, there is multiple hydrogen bonding between the zeolite lattice oxygen atoms and the hydrogen atoms of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O with the O $\cdots$ H distances from 1.959 to 2.737 Å. In the co-adsorbed H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O complex, there is a strong interaction between H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O, as indicated by the rather short O<sub>c</sub> $\cdots$ H<sub>b</sub> distance

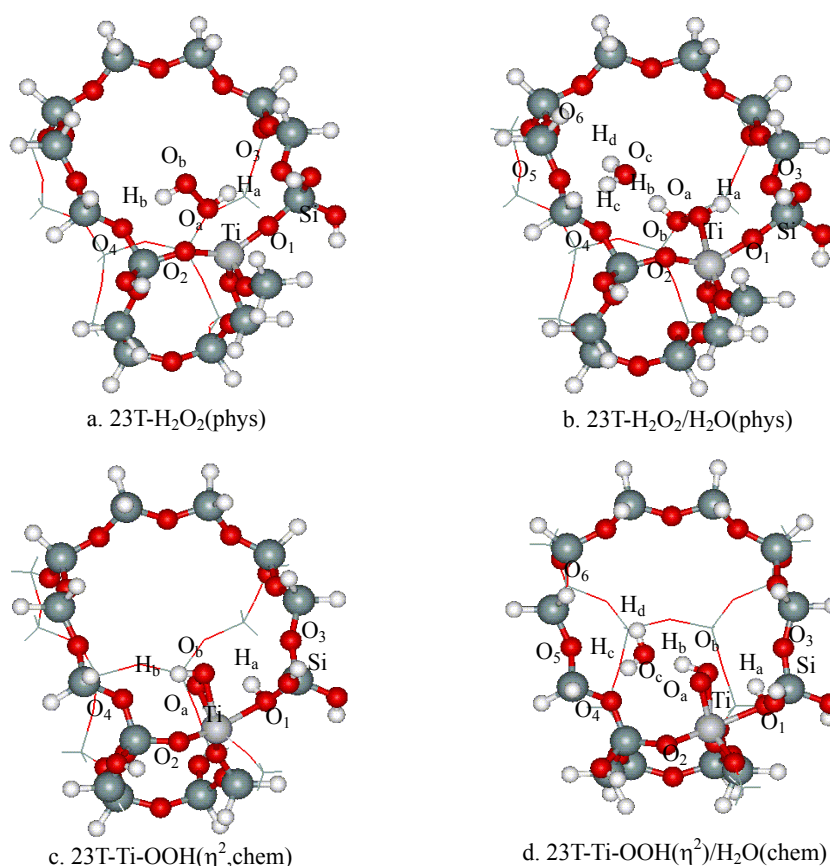


Figure 2 Structure of the physically and chemically adsorbed complexes for H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O on 23T cluster

(1.649 Å). The co-adsorbed H<sub>2</sub>O strengthens the interaction between H<sub>2</sub>O<sub>2</sub> and the TS-1 framework, as reflected by multiple hydrogen bonding and the shorter Ti-O(H<sub>2</sub>O<sub>2</sub>) distances (Ti-O<sub>a</sub> and Ti-O<sub>b</sub> in Table 1). After adsorption, the average Ti-O (Si) distance in TS-1 is elongated because of the augment of the coordination sphere of the Ti site.

In our work only the bidentate Ti-OOH( $\eta^2$ ) species is found in the chemisorbed H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O complexes (Figure 2c and d). The two Ti-O (H<sub>2</sub>O<sub>2</sub>) distances are 1.961, 2.256 Å and 1.925, 2.274 Å, respectively. It is to note that the local structure of Ti-OOH ( $\eta^2$ ) in the co-adsorbed H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O complex is in good agreement with the available experimental data [36], i.e. 1.925 vs. 1.91 Å for Ti-O<sub>a</sub>, 2.274 vs. 2.21 Å for Ti-O<sub>b</sub>, and 1.470 vs. 1.47 Å for O<sub>a</sub>-O<sub>b</sub>. H<sub>a</sub> migrates to O<sub>1</sub> with a distance of 0.986 Å and forms a Si-OH, and the Ti-O<sub>1</sub> bonds are therefore

elongated to 2.193 and 2.237 Å in the two complexes, indicating very weak Ti-O bonds as compared to the normal Ti-O distance of about 1.8 Å. Similar to the physisorbed complexes, there is multiple hydrogen bonding in the chemisorbed H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O than in the chemisorbed H<sub>2</sub>O<sub>2</sub>.

### 3.2 The energy change of the adsorption

The total energy of the zeolite model and the adsorption complexes as well as the energy changes for the formation of these species are presented in Table 2. It is shown that the formation of the physisorbed 23T-H<sub>2</sub>O<sub>2</sub> (Figure 1a) is more favored than that of 23T-H<sub>2</sub>O by 4.5 kcal/mol, and the formation of the co-adsorbed 23T-H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (Figure 1b) is more favored than that of 23T-H<sub>2</sub>O<sub>2</sub> by 5.8 kcal/mol. The adsorption energy of co-adsorbed 23T-H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (-22.6 kcal/mol) is lower than the sum of both physisorbed 23T-H<sub>2</sub>O<sub>2</sub> and 23T-H<sub>2</sub>O (-16.8

and  $-12.3$  kcal/mol, respectively), but higher than their individual values. This indicates that when TS-1 catalyst is in contact with  $\text{H}_2\text{O}_2$  aqueous solution, further adsorption with one  $\text{H}_2\text{O}$  is energetically possible, and the most likely formed physisorbed species is the co-adsorbed  $23\text{T-H}_2\text{O}_2/\text{H}_2\text{O}$  rather than the singly physisorbed  $23\text{T-H}_2\text{O}$  and  $23\text{T-H}_2\text{O}_2$ . For the chemisorbed complexes, further coordination of one  $\text{H}_2\text{O}$  to  $23\text{T-Ti-OOH}(\eta^2)$  (Figure 1c) to form the co-adsorbed  $23\text{T-Ti-OOH}(\eta^2)/\text{H}_2\text{O}$  (Figure 1d) is also favored energetically by  $6.8$  kcal/mol. This agrees well with the cooperative role of  $\text{H}_2\text{O}$  in the stabilization of the Ti-OO intermediate as found experimentally [29]. It is also interesting to note that the energetic effect of one additional  $\text{H}_2\text{O}$  is nearly the same in the physisorbed and chemisorbed species ( $5.8$  vs.  $6.8$  kcal/mol, respectively).

**Table 2** The total energy of the physisorbed and chemisorbed  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$

complexes and the energy changes for the formation of these species

	$E_{\text{tot}}$ (au)	$\Delta E^a$ (kcal/mol)
23T	-9501.13707	--
23T- $\text{H}_2\text{O}$ (phys) <sup>b</sup>	-9577.59784	-12.3
23T- $\text{H}_2\text{O}_2$ (phys)	-9652.74699	-16.8
23T- $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (phys)	-9729.21078	-22.6
23T- $\text{H}_2\text{O}_2$ (chem)	-9652.72185	-1.0
23T- $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (chem)	-9729.18722	-7.8

a.  $\Delta E = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}})$

b. The total energy of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  is  $-76.44120$ ,  $-151.58317$ , and  $-228.03767$  au, respectively

### 3.3 The electronic properties of the adsorption complexes

**Table 3** Mulliken atomic charges on selected atoms in the adsorbed complexes<sup>a</sup>

	23T	23T- $\text{H}_2\text{O}_2$ (physisorbed)	23T- $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (physisorbed)	23T- $\text{H}_2\text{O}_2$ (chemisorbed)	23T- $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (chemisorbed)
Ti	1.623	1.554	1.561	1.442	1.433
O <sub>1</sub>	-0.909	-0.899	-0.897	-0.729	-0.734
O <sub>2</sub>	-0.867	-0.868	-0.856	-0.864	-0.856
O <sub>a</sub> <sup>b</sup>	--	-0.318	-0.354	-0.410	-0.396
O <sub>b</sub>	--	-0.277	-0.292	-0.287	-0.370
H <sub>a</sub>	--	0.374	0.385	0.372	0.379
H <sub>b</sub>	--	0.355	0.354	0.350	0.387
$\text{H}_2\text{O}_2$ ( $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) <sup>c</sup>	--	0.134	(0.136)	0.025	(0.090)

a. For the numbering system, see Figure 2.

b. The Mulliken atomic charge on oxygen and hydrogen atom of  $\text{H}_2\text{O}_2$  is  $-0.285$  and  $0.285$ , respectively.

c. Total charge on  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  in the adsorbed complexes.

The Mulliken atomic charges on selected atoms in the adsorbed complexes are given in Table 3. It can be seen that upon the absorption of H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O, the positive charge on the Ti center is decreased, and the adsorbed molecule is positively charged, indicating charge transfer between the adsorbates to the zeolite adsorbent. For O<sub>a</sub> which is in shorter distance to the electrophilic center of Ti than O<sub>b</sub>, it is more negatively charged, indicating stronger bonding. It is also found that in the co-adsorbed H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O complex, the charge transfer is stronger than that of H<sub>2</sub>O<sub>2</sub> complexes, which is in agreement with the stronger interaction in the former, and confirms the role of water molecule in the stabilization of the Ti-OO reactive intermediates in partial oxidation reactions.

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