Phenol oxidation over titanosilicalite-1: experimental and DFT study of solvent

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Abstract

Water addition to a reaction solvent accelerates the catalytic oxidation of phenol with hydrogen peroxide over titanosilicalite-1 (TS-1). The amount of produced dihydroxybenzene (hydroquinone and catechol) increases from 4.33 to 6.58 mmol with increasing the water concentration in methanol solvent from 14.4 up to 57.2% by weight. Density functional theory (DFT) study shows that the coordination of a hydrogen peroxide to a $Ti(OSiH_3)_4$ cluster, which is a model of the reaction center of TS-1, is stabilized by the coordination of a water or a methanol. The coordination stabilization energy of $Ti(OSiH_3)_4–H_2O_2–H_2O$, -48.1 kJ/mol, is greater than that of both $Ti(OSiH_3)_4–H_2O_2$, -15.8 kJ/mol, and $Ti(OSiH_3)_4–H_2O_2–CH_3OH$, -44.1 kJ/mol. These results suggest that the addition of water into the solvent increases the amount of coordinated hydrogen peroxide to the Ti center, which is considered to be an active species, or its precursor, of oxidation, and consequently accelerates the reaction rate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Titanosilicalite-1 (TS-1) is a superior catalyst for the oxidation reactions, for example alkane and alkene oxidation into alcohol or epoxide, and phenol oxidation into hydroquinone (HQ) and catechol (CL), using hydrogen peroxide (H_2O_2) as oxidant [1–3]. Among these oxidation reactions, interestingly, the reaction rate and production ratio of hydroquinone/catechol of the phenol oxidation over TS-1 is very sensitive to the nature of solvent [4]. These phenomena invoked many works concerning the solvent effect on the oxidation reaction over TS-1 by means of both experimental [5,6] and theoretical methods [7–9].

The solvent having the structure of ROH (R = H or CH_3) has been considered to coordinate to the Ti center and to affect the reactivity of the hydroperoxo titanium species, Ti–OOH [7–9]. The hydroperoxo titanium species has been generally accepted to be the active species of the oxidation reactions over TS-1. However, the mechanism of the activation of hydrogen peroxide and the oxidation of substrates over TS-1 has remained to be clear.

Some authors have studied the mechanisms of the oxidation by theoretical study using quantum chemical method. Tantanak et al. examined ethene epoxidation over TS-1 by using 3-21G* basis sets and B3LYP functional [8]. Their calculations were conducted by using a $Ti(OSiH_3)_3–O(1)–O(2)H–CH_3OH$ cluster and

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an ethene molecule. They examined the energetics and structure of the transition states, and the reaction barriers were calculated as 49.8 kJ/mol (11.9 kcal/mol) for the O(1) attack, and 133.9 kJ/mol (32.0 kcal/mol) for the O(2) attack, respectively. Therefore, they concluded that the O(1) oxygen of the Ti–O(1)–O(2)–H structure attacks the double bond of ethene. The CH_3OH molecule coordinated to the Ti center assisted both the attacks by O(1) and O(2). They also applied a continuum model of water solvent and calculated the reaction barrier of the oxidation reaction. They found that the reaction barrier was unaltered by the bulk of water surrounding the transition state complex.

Vayssilov and van Santen [10] have proposed another possible reaction mechanism for the ethene epoxidation with hydrogen peroxide over TS-1 according to their results of density functional theory (DFT) study. They calculated by using Slater-type double-zeta basis sets and a functional of the generalized gradient approximation level [10]. Their examination was done with a non-dissociated form of hydrogen peroxide and a $Ti(OSiH_3)_4$ cluster. They found that the interaction of the hydrogen peroxide molecule with the $Ti(OSiH_3)_4$ cluster is very weak. They also estimated the reaction barrier of direct ethene epoxidation by hydrogen peroxide as 221 kJ/mol, and the reaction barrier was drastically decreased to 83 kJ/mol if the $Ti(OSiH_3)_4$ cluster was included to the calculation. They also calculated the coordination stabilization energy of $Ti(OSiH_3)_3$–OOH–ligand cluster (ligand = H_2O, CH_3OH, and SiOH, which is formed by a protonation of the Ti–O–Si bond). These ligand molecules are coordinated to the Ti center by its oxygen atom. The stabilization energies of these clusters were all endothermic, +129 kJ/mol ($Ti(OSiH_3)_3$–OOH–H_2O cluster), +91 kJ/mol ($Ti(OSiH_3)_3$–OOH–CH_3OH cluster), and 104 kJ/mol ($Ti(OSiH_3)_3$–OOH–SiOH cluster), respectively. They concluded from these results that in order to activate hydrogen peroxide molecule, the dissociation of a O–H bond in the coordinated hydrogen peroxide is not necessary for the catalytic oxidation over TS-1. Unfortunately, both Tantanak et al. [8] and Vayssilov and van Santen [10] have not examined the effect of a solvent molecule on the nature of hydrogen peroxide molecule coordinating to the Ti center, so that the effect of solvent

on the oxidation rate and selectivity has remained to debate.

The aim of this work is to examine the effect of solvent, especially that having ROH (R = H, CH_3) structure, on the oxidation of phenol over TS-1. We represented in this report the experimental results of the phenol oxidation in the mixture of H_2O and methanol, and also DFT calculation results for the cluster models made of the Ti center model having a structure as $Ti(OSiH_3)_4$, a hydrogen peroxide, and a solvent molecule. Finally, we tentatively proposed the role of water in the oxidation reaction.

2. Method

2.1. Experimental

TS-1 (NE Chemcat, Si/Ti = 68, powder form) was used as purchased. TS-1 was calcined at 823 K for at least 2 h before use as catalyst. Reagent grade phenols, methanol, acetonitrile, 30% hydrogen peroxide aqueous solution (Wako) were used without further purification. Deionized water was treated with Millipore equipment and used as solvent. The oxidation reactions were done in a 300 ml round bottomed flask equipped with a water-cooled condenser and a magnetic stirrer. Under an atmosphere of dry nitrogen the mixture of 1.00 g of phenol, 0.20 g of catalyst, and 5.00 g of solvent in the flask were heated up to 349 K using a oil bath. At that temperature, 1.20 g of 30% hydrogen peroxide aqueous solution was added dropwisely into the mixture for about 5 min. In this procedure 30% hydrogen peroxide aqueous solution was used so that at least 0.84 g of solvent water, which is included in a 1.20 g of 30% hydrogen peroxide aqueous solution, was existed in the reaction mixture. Therefore, water addition effect was examined in the higher concentration than 14.4% in solvent mixture (methanol + water) by weight. The reaction was maintained for 3 h after the first dropping of hydrogen peroxide aqueous solution. The reaction mixture was cooled to room temperature and the catalyst was removed by filtration. The products were analyzed by means of Hitachi 263-70 gas chromatograph equipped with both a 2 m glass column of 3% OV-17 supported gaschrom Q (80/100 mesh) and an FID detector. Biphenyl was

used as internal standard for the gas chromatograph analysis.

2.2. Calculation

DFT calculations were done with DMol3 program (MSI) [11,12]. The numerical basis of DNP level, which is comparable to 6-31G** analytical basis, and non-local by Parr and Yang functional [13] were used for both the geometry optimization and energy estimation. Delley [11], the original author of DMol3, reported the superiorities of the numerical exact LDF spherical atomic basis set used in DMol3 method. According to the author, by using the numerical–spherical atomic orbital, basis set superposition error (BSSE), which often occurs in the case with low quality analytical Gauss-type basis set, is expected to be small. Therefore, we supposed the BSSE to be small in the calculation by DMol3 program, and showed the calculated values without correction of BSSE in this report.

Prior to the DFT calculations, for the sake of economy of CPU time, the structures of clusters were optimized by molecular mechanics method using Discover 3 program with esff force field (MSI). In order to obtain fully optimized structure by molecular mechanics method, molecular dynamics simulation using the same force field was carried out (at 300–400 K, 1000–3000 step, NVE) several times until the lowest energy structure was obtained. After MM/MD calculation, the structures of cluster were fully re-optimized by means of DFT method using DNP basis and BLYP functional.

3. Results and discussion

3.1. Solvent effect on the phenol oxidation over TS-1

Table 1 shows the results of the phenol oxidation at 349 K for 3 h in water–methanol mixed solvents. Very small amount of hydroquinone (HQ) and catechol (CL) were produced if the reaction was carried out without TS-1 at this temperature. The HQ production was about a twice that of CL and the ratio of HQ/CL was gradually decreased by the further water addition. The selectivity of HQ and CL slightly decreased with the addition of water. This would be due to successive oxidation of accumulated HQ and/or CL. The result without water addition is very similar to that reported by Tuel et al. [4].

The production of HQ and CL and the conversion of phenol clearly increased by the water addition as shown in Table 1. The solvent effects on the oxidation over TS-1 have been studied experimentally by some authors [4–6]. Tuel et al. [4] also reported that the oxidation rate of phenol by hydrogen peroxide over TS-1 in acetone was higher than in methanol. They also observed that the tar adhered on a used catalyst surface was effectively removed by a washing with acetone. They concluded that the superiority of acetone as a solvent for the phenol oxidation over TS-1 was due to its ability to keep the catalyst surface from adhering of tar. This is not the case of the present work, because its high polarity, water is expected to be worse washing solvent than methanol for the tar.

Table 1
Phenol oxidation over TS-1 in H_2O and methanol mixture solvent[a]

	HQ (mmol)	CL (mmol)	HQ + CL (mmol)	HQ/CL	PhOH conversion (%)	Sel. (%)[b]
$CH_3OH:H_2O$[c]						
85.6:14.4	2.86	1.44	4.33	1.99	43.64	91.97
77.0:23.0	3.27	1.79	5.06	1.82	51.67	91.76
42.8:57.2	3.89	2.69	6.58	1.44	70.16	87.24
$CH_3CN:H_2O$						
85.6:14.4	0.68	2.21	2.89	0.31	32.00	83.27

[a] Reaction conditions: reaction time, 3 h; reaction temperature, 349 K (oil bath temperature); Cat, 0.20 g; phenol, 1.00 g; 30% H_2O_2 aq, 1.20 g; solvent, 5.0 g.
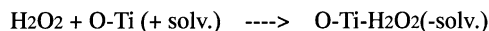
[b] Sel. (%) = {(produced HQ + CL)/(consumed PhOH)} × 100 (mol/mol).
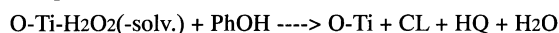
[c] Solvent mixed ratio in weight.

Although the polarizability of a reaction mixture is increased by the addition of water, the effect of the bulk properties such as polarizability of the solvent for the oxidation remained to debate in following work. Table 1 also shows the result of the phenol oxidation in acetonitrile. The dielectric constant of acetonitrile, 36 at 298 K, is slightly higher than that of methane, 32.6 at 298 K. The oxidation rate in acetonitrile was slower than that in methanol so that the polarizability of solvent would not be the main reason of the acceleration of the oxidation. On the other hand, it is clearly shown in Table 1 that the production ratio of HQ/CL is strongly depends on the solvent used. These results suggest that the solvent molecule affect the structure of transition states.

Bellussi et al. [5], and Clerici et al. [6] studied hydrolysis of *cis*- and *trans*-2,3-epoxybutane in the presence of TS-1 and hydrogen peroxide in methanol, ethanol, and water. According to Scheme 1, hydrogen peroxide interacts with Ti–O–Si in framework affording Ti–OOH and SiOH, and solvent molecules coordinated to Ti center improves the acidity of Ti–OOH moiety. They found the order of methanol > ethanol > water for the hydrolysis of

<Step 1>

$H_2O_2 + \text{O-Ti} \, (+ \text{solv.}) \quad ----> \quad \text{O-Ti-}H_2O_2(\text{-solv.})$

<Step 2>

$\text{O-Ti-}H_2O_2(\text{-solv.}) + PhOH ----> \text{O-Ti} + CL + HQ + H_2O$

Scheme 1.

cis-2,3-epoxybutane. In their case, the water addition rather inhibited the hydrolysis reaction.

3.2. Density functional study of solvent effect

The cluster models are shown in Fig. 1. The structural parameters are shown in Tables 2 and 3 Ti–O bond length, 183.2 pm, is slightly longer than that estimated by EXAFS technique, 181 pm [14]. In the Ti–H_2O_2 cluster, the bond length of Ti–O(H)OH was calculated as 253 pm, which is slightly longer than that has been reported by Vayssilov and van Santen [10], 247 pm, using non-local Becke and Perdew exchange and correlation functionals. It is also shown in the Fig. 1 and Table 1 that the structure of the TiO₄
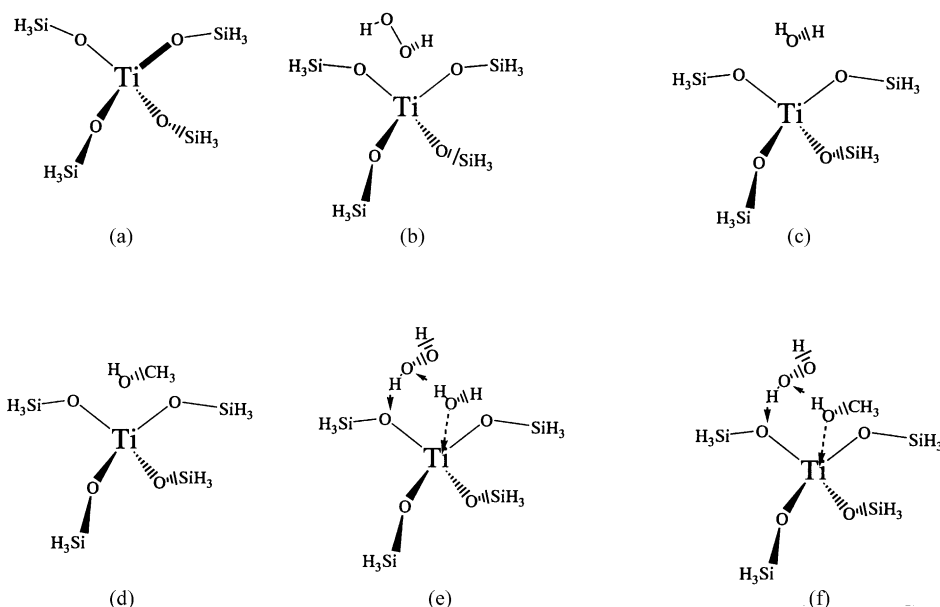

Fig. 1. Ti cluster-models. (a) Ti cluster; (b) Ti–H_2O_2 cluster; (c) Ti–H_2O cluster; (d) Ti–MeOH cluster; (e) Ti–H_2O_2–H_2O cluster; (f) Ti–H_2O_2–MeOH cluster. Basis of DNP level and BLYP functional were used for the DFF calculations.

Table 2
Bond lengths (pm) and angles (°) of optimized clusters

Length (pm)					Bond angle (°)[a]	
Ti–O	Ti–O(H)OH	Ti–O(H)R	ROH–O(H)OH	Ti(Si)O–HOOH	O–Ti–O (upper)	O–Ti–O (lower)
Ti cluster						
183.2	–	–	–	–	109.1	109.1
Ti–H_2O_2 cluster						
189.3[b]	253.0	–	–	–	116.5	103.2
182.7–186.5						
Ti–H_2O cluster						
183.3–187.7	–	250.3	–	–	114.8	101.9
Ti–CH_3OH cluster						
184.1–186.7	245.6	–	–	114.9	101.1	
Ti–H_2O_2–H_2O cluster						
191.8	238.3	181.2	175.7	120.8	100.4	183.2–186.0
Ti–H_2O_2–CH_3OH cluster						
193.9[b]	–	234.6	172.7	172.7	117.0	99.2
186.5–186.0						

[a] Angles of the upper and lower O–Ti–O bond of the cluster models shown in the Fig. 1.

[b] Ti–O bond length in which O atom interacts with an H atom of H_2O_2.

moiety is deformed by the interaction with hydrogen peroxide and solvent molecule. For example, the bond angle of upper, facing to the hydrogen peroxide and solvent molecules, O–Ti–O increased from 109.1° in the Ti cluster to about 114.8° in the Ti–H_2O cluster. Zicovich-Wilson et al. [15] studied water coordination to Ti in zeolite framework by periodic density functional calculation and reported about the same value, 113–116°, as that of our results for O–Ti–O angle. These results suggest that the interacting molecules pull out the Ti atom from its original zeolite wall position during the oxidation reactions.

Table 3 shows O–O bond length of hydrogen peroxide before and after coordination to Ti cluster. The O–O bond length of hydrogen peroxide molecule and clusters are in the narrow range of around 150 pm. The value of 149.4 pm in Ti–H_2O_2 cluster is about the same as reported by Vayssilov and van Santen [10]. It is also shown in the Table 3 that coordinated solvent molecule alters the mode of coordination of hydrogen peroxide but not affects the O–O bond length, and the calculated values are different only 2 pm.

The total energies of cluster models and coordination stabilization energies are shown in Tables 4 and 5, respectively. The coordination stabilization energies

Table 3
O–O bond lengths of hydrogen peroxide (pm)

Cluster	O–O bond length
H_2O_2	150.0[a]
Ti–H_2O_2 cluster	149.4
Ti–H_2O_2–H_2O cluster	149.8
Ti–H_2O_2–CH_3OH cluster	151.5

[a] Dihedral angle of HO–OH = 113.3°.

Table 4
Total energies of the clusters

	Energy (Hartree)[a]
H_2O	−76.4518880
H_2O_2	−151.6088720
CH_3OH	−115.7391260
Ti cluster	−2316.1443440
Ti–H_2O	−2392.6010920
Ti–CH_3OH	−2431.8868320
Ti–H_2O_2	−2467.7592199
Ti–H_2O_2–H_2O	−2544.2234290
Ti–H_2O_2–CH_3OH	−2583.5092050

[a] 1 Hartree = 627.51 kcal/mol; 1 calorie = 4.184 J.

Table 5
Coordination energies of the clusters

Ti–H_2O_2	−15.8
Ti–H_2O_2[a]	−33.1
Ti–H_2O	−12.8
Ti–CH_3OH	−8.8
Ti–H_2O_2–H_2O	−48.1
Ti–H_2O_2–CH_3OH	−44.4

[a] Vayssilov and van Santen [10].

were estimated by following equation:

the coordination stabilization energy

$\quad$ = (total energy of a cluster)

$\quad\quad$ −(sum of total energies of Ti cluster and

$\quad\quad$ coordinated molecules).

For example, the coordination stabilization energy of Ti–H_2O_2–H_2O cluster was estimated as

the coordination stabilization energy of Ti–H_2O_2–H_2O

$\quad$ = (total energy of Ti–H_2O_2–H_2O)

$\quad\quad$ −{(total energy of Ti cluster)

$\quad\quad$ +(total energy of H_2O_2) + (total energy of H_2O)}

The coordination energy of H_2O_2 was calculated as −15.8 kJ/mol, which is lower than that has been reported by Vayssilov and van Santen [10]. The difference is reflected in the longer bond length of Ti–$O(H)OH$, 253 pm, than that by Vayssilov and van Santen [10], 247 pm.

4. Conclusion

The water addition accelerated the oxidation of phenol by hydrogen peroxide over TS-1. The coordinated solvent molecule stabilized the coordination of hydrogen peroxide and the coordination stabilization energy of Ti–H_2O_2–H_2O cluster is larger than that of Ti–H_2O_2–MeOH cluster. These results suggested that the water increases the coordinated, activated, hydrogen peroxide over TS-1 and consequently accelerates the oxidation of phenol. Diffusion dynamics of the solvent and reactant molecules in zeolitic pore is frequently subjected [16–18], and that would affects the overall oxidation rate. The authors are now discussing this problem with the effect of solvent structure on the oxidation rate [19,20], and further work is now undergoing [21].

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