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## Monomeric peroxo titanate coordinated with cyclohexanediaminetetraacetate: Towards the active oxygen species of the Ti(IV) site hosted in the titanium silicalite catalyst TS-1

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## ABSTRACT

Hexadentate chelated *trans*-1,2-cyclohexanediaminetetraacetato titanate(IV) was used as a model of the Ti(IV) species in the constrained environment of TS-1 (H<sub>4</sub>cdta = *trans*-1,2-cyclohexanediaminetetraacetic acid,  $C_{14}H_{22}O_8N_2$ ; TS, titanium silicalite). Several complexes were isolated and well characterized, including [Ti(cdta)(H<sub>2</sub>O)]·2H<sub>2</sub>O (**1**), Na<sub>2</sub>[Ti(O<sub>2</sub>)(cdta)]·2H<sub>2</sub>O (**2**) and (NH<sub>4</sub>)<sub>2</sub>[TiO(cdta)]·1.5H<sub>2</sub>O (**3**). Octadentate cdta peroxo titanate(IV) (**2**) is obtained quantitatively from the reaction of the hydrated titanium cdta complex **1** with hydrogen peroxide. The bond distances between O–O and Ti–(O<sub>2</sub>) are 1.464(3) and 1.908(2) Å, respectively. Transformation of the peroxo titanate in H<sub>2</sub>O–H<sub>2</sub>O<sub>2</sub> solution. The catalytic activity of **2** was studied for phenol hydroxylation using 30% H<sub>2</sub>O<sub>2</sub>, and this was monitored by <sup>1</sup>H and <sup>13</sup>C NMR techniques. The main product of the reaction is catechol.

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## 1. Introduction

It is widely recognized that titanium-containing molecular sieves (TS-1) are among the best catalysts for selective oxidation reactions, for example, alkane and alkene oxidation to alcohol or epoxide, and phenol oxidation into hydroquinone and catechol using hydrogen peroxides as the oxidant [1-4]. The later is an industrially important process because the products are widely used as starting materials for medicine, perfume and many fine chemicals. In the past decade, considerable research effort was dedicated to the development of mesoporous titanium-containing materials capable of oxidizing large amounts of organic substrates. The mechanism for the activation is considered to involve the addition of a peroxo group and its transfer to the substrate [5]. However, not much evidence for the active species was obtained. In this report, catalytic reactions by the restricted peroxo titanate  $Na_2[Ti(O_2)(cdta)] \cdot 2H_2O(2)$  are studied for phenol hydroxylation, in which the titanium atom is coordinated by the hexadentate cdta ligand, and exists in an octa-coordinated environment. The conversion of peroxo titanium complexes are studied, which might provide structural information on titanium complexes that is relevant to key intermediates in selective oxidation.

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## 2. Experimental

## 2.1. Preparations

## 2.1.1. Preparation of [Ti(cdta)(H<sub>2</sub>O)]·2H<sub>2</sub>O (**1**)

*Trans*-cyclohexanediaminetetraacetic acid (1.09 g, 3.0 mmol) was dissolved in 10 mL deionized water at pH 6.0 with ammonium hydroxide (5.0 M). The solution was added to TiCl<sub>4</sub> (0.57 g, 3.0 mmol) to give plenty of white powder, which was collected and washed with cold water and 95% ethanol to give 1.26 g [Ti (cdta)(H<sub>2</sub>O)]·2H<sub>2</sub>O (**1**) in 95% yield. C, H and N elemental analyses for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>11</sub>Ti, Calc.: C, 37.9; H, 5.5; N, 6.3. Found: C, 38.0; H, 5.4; N, 6.2%. IR (KBr, cm<sup>-1</sup>):  $v_{as}(CO_2)$  1690<sub>vs</sub>, 1634<sub>w</sub>;  $v_s(CO_2)$  1403<sub>m</sub>, 1354<sub>s</sub>, 1291<sub>m</sub>. <sup>13</sup>C NMR  $\delta_C$  (D<sub>2</sub>O) ppm: 181.2, 179.9 (-CO<sub>2</sub>), 70.6, 66.8 (-CH<sub>2</sub>CO<sub>2</sub>), 60.2 (=NCH), 28.0 (=NCHCH<sub>2</sub>), 26.1 (=NCHCH<sub>2</sub>CH<sub>2</sub>).

## 2.1.2. Preparation of $Na_2[Ti(O_2)(cdta)] \cdot 2H_2O(2)$

 $H_4$ cdta (5.47 g, 15.0 mmol) was dissolved in 10 mL deionized water at pH 6.0 with sodium hydroxide (5.0 M). The solution was added to TiCl<sub>4</sub> (2.85 g, 15.0 mmol) and a 30% solution of  $H_2O_2$  (5.0 mL). The pH value of the solution was adjusted to 5.5 with sodium hydroxide (5.0 M) to give a clear orange solution. The mixture was stirred continuously for 5 h and kept in a refrigerator for 5 days to deposit red crystals of **2** (7.20 g, 95%). C, H and N elemental analyses for  $C_{14}H_{22}N_2Na_2O_{12}Ti$ , Calc.: C, 33.4;



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H, 4.4; N, 5.6. Found: C, 33.2; H, 4.5; N, 5.7%. IR (KBr, cm<sup>-1</sup>):  $v_{as}(-CO_2)$  1661<sub>s</sub>, 1630<sub>vs</sub>;  $v_{s}(CO_2)$  1412<sub>s</sub>, 1367<sub>s</sub>, 1316<sub>m</sub>; v(O-O) 861<sub>m</sub>;  $v[Ti-(O_2)]$  576<sub>m</sub>, 542<sub>m</sub>. <sup>13</sup>C NMR  $\delta_C$  (D<sub>2</sub>O) ppm: 181.2 (-CO<sub>2</sub>), 69.9, 66.5 (-CH<sub>2</sub>CO<sub>2</sub>), 59.3 (=NCH), 28.2 (=NCHCH<sub>2</sub>), 26.4 (=NCHCH<sub>2</sub>CH<sub>2</sub>).

#### 2.1.3. Preparation of $(NH_4)_2$ [TiO(cdta)]·1.5H<sub>2</sub>O (**3**)

H<sub>4</sub>cdta (10.93 g, 30.0 mmol) was dissolved in 10 mL deionized water with ammonium hydroxide (5.0 M). The solution was added to TiCl<sub>4</sub> (1.91 g, 10.0 mmol) and 30% hydrogen peroxide (5.0 mL). The pH value of the solution was adjusted to 6.0 with ammonium hydroxide to give a clear orange solution. The mixture was stirred at room temperature for 5 h and heated at 70 °C for 2 days to deposit colorless crystals of **3** (2.45 g, 52%). C, H and N elemental analyses for C<sub>14</sub>H<sub>29</sub>N<sub>4</sub>O<sub>10.50</sub>Ti, Calc.: C, 35.8; H, 6.2; N, 12.0. Found: C, 35.9; H, 6.4; N, 12.3%. IR (KBr, cm<sup>-1</sup>):  $v_{as}(CO_2)$  1686<sub>m</sub>, 1626<sub>vs</sub>;  $v_s(CO_2)$  1448<sub>m</sub>, 1403<sub>s</sub>, 1353<sub>s</sub>; v(Ti=O) 941<sub>m</sub>. <sup>13</sup>C NMR  $\delta_C$  (D<sub>2</sub>O) ppm: 182.3, 182.2 (-CO<sub>2</sub>), 67.0, 64.1 (-CH<sub>2</sub>CO<sub>2</sub>), 57.5 (=NCH), 27.2 (=NCH<sub>2</sub>), 26.6 (=NCH<sub>2</sub>CH<sub>2</sub>).

#### 2.2. Physical methods and analyses

Data collections for **1–3** were performed on an Oxford Gemini S Ultra system with graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Adsorption corrections were applied by using the CRYSALIS program. Empirical absorption corrections were applied using the SADABS program. Structures were solved by the WingGX package, and refined by full-matrix least-squares procedures with anisotropic thermal parameters for non-hydrogen atoms using SHELXL-97 [6,7]. Hydrogen atoms were located from a difference Fourier map and refined anisotropically. Crystallographic data are summarized in Table S1. Selected bond distances and bond angles of the complexes are listed in Tables S2–S4.

All chemicals used were analytical grade reagents. The pH values were measured using a potentiometric method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed with an EA 1110 elemental analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in D<sub>2</sub>O on a Bruker AV 400 NMR spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal reference. Confocal Raman microspectroscopy was conducted at room temperature with a Renishaw Inva Raman System equipped with a CCD detector and a Leica DMLM microscope. The line at 532.5 nm of an Ar<sup>+</sup> laser was used for excitation. The laser power was reduced to ~1.5 mW to ensuring that no sample damage was caused by the laser irradiation.

#### 2.3. Hydroxylation of phenol

Reactions were performed in a two-necked round-bottom flask, which was equipped with a magnetic stirrer, a reflux condenser and a dropping funnel in a temperature controllable water-bath. In a typical run, 1.89 g of phenol, 10 mL deionized water and 10 mL 30% hydrogen peroxide were charged into the flask. After the mixture was heated to 90 °C under continuously stirring, a solution of the catalyst  $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O$  (2) (0.23 g, 0.46 mmol) was added drop-wise to the reactor. The pH value of the solution was adjusted to 6.0, and the reaction proceeded for a certain period of time. After the reaction was finished, the mixture was cooled and analyzed. The conversion of phenol to catechol in the presence of **2** with elapsed time was monitored by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies.

### 3. Results and discussion

## 3.1. Synthesis and characterization

The syntheses of cdta titanates were carried out in weakly acidic aqueous solutions. The synthetic conditions are similar, except for the molar ratios and reaction temperatures. Direct reaction of  $TiCl_4/H_4$ cdta in an equimolar ratio results in the formation of an aquo complex **1** quantitatively. When an excess of hydrogen peroxide is added to the solution of  $[Ti(cdta)(H_2O)]\cdot 2H_2O$  (**1**), the peroxo complex **2** is obtained in 95% yield, which could be transformed to the oxotitanate **3** in warm solution with excess cdta ligand, as shown in Scheme 1. Previously, an oxotitanate was a suspected species in the reaction of edta titanate [8].

Figs. 1–3 show the neutral and anion structures of 1–3, respectively. The cdta ligands in 1-3 coordinate hexadentately to the central titanium cations through two nitrogen atoms and four oxygen atoms of monodentate  $\beta$ -carboxy groups. In **1**, the titanium(IV) cation is surrounded by the cdta ligand and a water molecule (O1W) heptadentately, in a distorted pentagonal bipyramid environment. This resembles to the coordinations in [Ti(edta)(H<sub>2</sub>O)] [9] and  $Na[VL(H_2O)] \cdot nH_2O$  (L = edta, n = 3; L = cdta, n = 5) [10,11]. The coordinated water molecule is easily substituted with the addition of hydrogen peroxide, forming a peroxo species 2 quantitatively. In the distorted octa-coordinated geometry of 2, the peroxo group  $O_2^{2-}$  binds to the Ti(IV) cation with a strong Ti–O bond [1.908(2) Å] in a side-on  $\eta^2$ -fasion, occupying two coordination sites in the equational plane. This is different from the hepta-coordinated edta peroxo titanium complex reported previously, which could be degraded to edta titanate selectively [8,12]. It is interesting to note that an oxotitanate is isolated in the  $H_2O_2/H_2O$  system. A terminal oxygen atom occupies the seventh coordination site instead of coordinated water molecule and peroxo group, with a strong short Ti–O bond [1.671 (2) Å].

As shown in Tables S2–S4, the Ti– $O_{carboxy}$  bond distances in the cdta titanium complexes **1–3** vary systematically. The Ti– $O_W$  bond distance [2.046(3) Å] in **1** is longer than those of the Ti–O bonds to the coordinated carboxy groups; this is an expected result ascribable to the ionic contribution from the charged glycinate oxygen atom. The Ti– $O_{peroxo}$  bond distance of **2** is 1.908(2) Å, which is longer than those found in the other seven-coordinated peroxo titanium complexes, such as (NH<sub>4</sub>)<sub>2</sub>[Ti(O<sub>2</sub>)(edta)]·2H<sub>2</sub>O [1.845(3), 1.858(3) Å] [8], (NH<sub>4</sub>)<sub>4</sub>[Ti(O<sub>2</sub>)(cit)]<sub>2</sub>·2H<sub>2</sub>O [1.852(2), 1.890(2) Å] [13] and Ba<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>[Ti<sub>4</sub>(O<sub>2</sub>)<sub>4</sub>(Hcit)<sub>2</sub>(cit)<sub>2</sub>]·10H<sub>2</sub>O [1.873(3), 1.884(3), 1.841(4), 1.855(4) Å] [14]. This should be related to the steric hindrance of the octa-coordination. It is interesting to note



Scheme 1. Synthesis and transformation of the titanium(IV) cdta complexes.



Fig. 1.  $_{\rm ORTEP}$  plot of the anion structure in  $[Ti(cdta)(H_2O)]\cdot 2H_2O$  (1) with 30% probability levels.



Fig. 2.  $_{ORTEP}$  plot of the anion structure in  $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O~(2)$  with 30% probability levels.

that the Ti=O bond distance [1.671(2) Å] in  $(\text{NH}_4)_2[\text{TiO}(\text{cdta})]$ ·1.5H<sub>2</sub>O (**3**) is significantly shorter than any other Ti–O bond distances, which are comparable to related Ti(IV) complexes, such as  $[C(\text{NH}_2)_3]_4[\text{TiO}(\text{CO}_3)_3]\cdot2\text{H}_2\text{O}$  [1.680(2) Å] [15], TiO (OEPMe<sub>2</sub>) (OEPMe<sub>2</sub> =  $\alpha, \gamma$ -dimethyl- $\alpha, \gamma$ -dihydro octaethylporphinate) [1.619(4) Å] [16] and [LTiO(NCS)<sub>2</sub>] (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) [1.638(3) Å] [17]. While the Ti–N bond



Fig. 3.  $_{\rm ORTEP}$  plot of the anion structure in  $(NH_4)_2[TiO(cdta)]\cdot 1.5H_2O$  (3) with 30% probability levels.

distances [2.504(2) and 2.447(2) Å] in **3** are the longest bond distances found in Ti-cdta species. The Ti-N bonds in **3** are weaker than those of the other two titanium-cdta complexes. It is reasonable that shorter Ti=O bonds cause longer Ti-N bonds, showing a strong structural *trans* effect in the TiO complex.

FT-IR spectra of 1-3 exhibit strong vibrations for the carboxy groups of cdta, as shown in Fig. S1. Different types of Ti-O vibrations are illustrated in Table S5. The sharp peaks near 1690 and  $1350 \text{ cm}^{-1}$  (1690 and  $1354 \text{ cm}^{-1}$  for **1**, 1661 and  $1412 \text{ cm}^{-1}$  for **2**, 1686 and 1448  $\text{cm}^{-1}$  for **3**) are assigned to the asymmetric and symmetric stretching frequencies of the carboxy groups in the equatorial glycinate ring, respectively, while the vibrations between 1634 and 1291 cm<sup>-1</sup> (1634 and 1291 cm<sup>-1</sup> for **1**, 1630 and 1367 cm<sup>-1</sup> for **2**, 1626 and 1403 cm<sup>-1</sup> for **3**) are assigned to the asymmetric and symmetric stretching frequencies of carboxy groups that lie in the axial glycinate ring, respectively. They shift to lower values with respect to the carboxy groups of the free cdta ligand. This is in harmony with coordinated structures. The vibration of the peroxo group in **2** is found at 861 cm<sup>-1</sup>. There is also a sharp peak at 576 cm<sup>-1</sup>, which is attributed to the  $v_{as}$ [Ti–(O<sub>2</sub>)] vibration. The corresponding frequency for  $v_s$ [Ti–(O<sub>2</sub>)] is observed around 542 cm<sup>-1</sup>, which is in agreement with the corresponding assignments in the other peroxo titanium complexes [13,18]. The obvious band at 941 cm<sup>-1</sup>, below the usual region of 972-890 cm<sup>-1</sup> [8], which is absent in **1** and **2**, corresponds to the titanyl moiety in **3**. The lack of absorptions in the 1700–1750 cm<sup>-1</sup> region suggests that the carboxy groups in 1-3 are protonated.

The peroxo vibrations in **2** are also in harmony with the corresponding Raman spectrum. Fig. S2 demonstrates characteristic features of the coordinated peroxo  $(O_2^{2^-})$  species [14]. A sharp peak near 550 cm<sup>-1</sup> is assigned to the  $v(Ti-O_2)$  symmetric stretching vibration, while 856 cm<sup>-1</sup> corresponds to the v(O-O) mode of the peroxo group. The observed positions of v(O-O) and  $v(Ti-O_2)$  are in accordance with a side-on  $\eta^2$ -peroxo coordination.

The solution <sup>13</sup>C NMR spectra of 1-3 were measured in D<sub>2</sub>O as shown in Figs. S3–S5. The titanium-cdta complexes 1-3 gave only



Fig. 4.  $^{13}$ C NMR spectra of the reaction mixture after 2 and 5.5 h; phenol (o), 1,2-catechol (\*).

one set of resonances. The signals show obvious downfield shifts compared with free ligand, which were attributed to the carboxy and methylene groups of the cdta ligand. Due to the low solubility of **1**, its signals are weaker than those of the peroxo and oxotitanates. No additional species of titanium-cdta complexes are observed in the <sup>13</sup>C NMR spectra, showing no decomposition of the cdta complexes in solution.

Due to the similarity of the <sup>13</sup>C NMR spectra for **1–3**, only complex **2** is discussed. Its two resonances of 66.5 and 181.2 ppm are assigned to the methylene and carboxy groups of the cdta ligand from the equatorial glycinate ring, while the other two peaks (69.9 and 181.2 ppm) are assigned to the methylene and carboxy groups of the cdta ligand from the axial glycinate ring. The remaining three peaks, appearing at 59.3, 28.2 and 26.4 ppm, were assigned to the methylene and methine groups of the cdta ligand.

Compared with the free cdta ligand [170.9 (CO<sub>2</sub>), 61.8 (–CH<sub>2</sub> CO<sub>2</sub>), 52.0 (=NCH), 24.9 (=NCH<sub>2</sub>), 24.1(=NCH<sub>2</sub>CH<sub>2</sub>)], complex **2** shows large downfield shifts for the carboxy and  $\alpha$ -methylene carbon resonances ( $\Delta\delta$  10.3 and 8.1 ppm) due to coordination. This indicates that the carboxylic acid groups in cdta are fully deprotonated and coordinate to the titanium cation simultaneously.

### 3.2. Catalytic activity

In order to find suitable conditions for the catalytic oxidation of phenol, various parameters, such as solvent, amount of catalyst **2**, reaction time and temperature have been taken into consideration.

Water is used as a reaction medium. This is due to the solubility of the reactant and catalyst.  $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O(2)$  disperses more easily in water than in organic solvents. The other reason is the active species produced in organic solvents may give other side-reactions. Moreover, water is safe, cheap and an environmentally friendly solvent.

No product was detected when the reaction was carried out without the catalyst  $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O$  (2). Complex 2 showed an obvious catalytic activity for hydroxylation of phenol and resulted in a catechol selectivity of 99%.

Figs. 4 and 5 show the <sup>13</sup>C NMR spectra of a reaction mixture refluxed in a 90 °C water bath for 2, 5.5 and 7.5 h, respectively, which demonstrate the influence of reaction time on the hydroxylation of phenol at pH 6.0. As shown in Fig. 4, only four peaks at 155.0, 129.8, 121.1 and 115.5 ppm, assigned to the signals of phenol, were observed after 2 h, revealing no hydroxylation of phenol in solu-



Fig. 5.  $^{13}$ C NMR spectrum of the reaction mixture after 7.5 h; phenol (o); catechol (\*); benzoquinone (#).



Fig. 6.  $^{13}$ C NMR spectrum of the reaction mixture after 7.5 h. Na<sub>2</sub>[Ti(O<sub>2</sub>)(cd-ta)]·2H<sub>2</sub>O (x).

tion. After reacting for 5.5 h, the spectrum showed another two peaks at 123.8 and 119.1 ppm, as illustrated in Fig. 5, which were attributed to the <sup>13</sup>C NMR signals of catechol. This indicated that phenol was oxidized to catechol gradually.

It is noteworthy that the intensities of the catechol resonances increase with time. When the solution reacted for 7.5 h, an obvious peak at 146.7 ppm, assigned to the signal of catechol, was observed in solution, which demonstrates that catechol is a main product after a long period of time. Only a small amount of product was further oxidized to benzoquinone, observed at 137.0 ppm, as shown in Fig. 5. The peaks at 180.1, 179.9, 69.9, 65.0, 58.8, 28.2 and 26.3 ppm in Fig. 6 were attributed to the signals of Na<sub>2</sub>[-Ti(O<sub>2</sub>)(cdta)]·2H<sub>2</sub>O (**2**), which indicated that the peroxo titanium complex **2** was used as a catalyst without change. The <sup>1</sup>H NMR spectrum of reaction solution in Fig. S6 is similar to the spectrum of catechol, which confirms the oxidation of phenol to catechol.

Table T									
Catalytic	conversion	and	selectivity	in	phenol	hydroxylation	by	$H_2O_2$	over
Na <sub>2</sub> [Ti( $\Omega_2$ )(cdta)].2H <sub>2</sub> O ( <b>2</b> ) with various reaction times <sup>a</sup>									

Time (h)	Phenol conv. (mol%)	Product sele	Product selectivity (%)		
		Catechol	Benzoquinone		
5.5	2	99.0	1.0		
7.5	5	80.0	20.0		

<sup>a</sup> Reaction conditions: water as a solvent, reaction temperature 90 °C,  $H_2O_2/$  phenol = 5 (molar ratio), catalyst/phenol = 1:50 (molar ratio).

It is clear that the yield of catechol and the conversion of phenol increases with reaction time, as shown in Table 1. The phenol conversion and selectivity to benzoquinone increased with reaction time, while the selectivity of catechol increased to a maximum value, and then decreased with reaction time. A relatively short time resulted in no conversion of phenol. In the region from 0 to 7.5 h, a change in the reaction is notable. When the reaction time was 2 h, no phenol hydroxylation reaction occurs. At 5.5 h, the catechol selectivity is 99%, which is the maximal selectivity of the hydroxylation products. When the reaction time was further prolonged, the phenol conversion increased continuously, while catechol selectivity decreased a little. A possible reason is that hydroquinone is consumed in the formation of the benzoquinone products, whereas catechol, a thermodynamically favored isomer, is not easily oxidized [19].

The influence of the reaction temperature was also investigated. When the reaction proceeded at 70 °C, no conversion of phenol was observed. After the temperature was increased to 90 °C, signals for catechol were found, which indicates that the hydroxylation of phenol in the presence of catalyst  $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O(2)$  could only occur at a relative high reaction temperature.

## 3.3. Catalytically active species and suggested mechanism

As outlined in Scheme 1,  $[Ti(cdta)(H_2O)]\cdot 2H_2O$  (1) in aqueous solution could be transformed to the peroxo and oxotitanium(IV) cdta complexes, respectively. The water soluble peroxo titanate Na<sub>2</sub>[Ti(O<sub>2</sub>)(cdta)]\cdot 2H<sub>2</sub>O (2) and the oxotitanate (NH<sub>4</sub>)<sub>2</sub>[TiO(cd-ta)]\cdot 1.5H<sub>2</sub>O (3) are accessible by the hydrolysis of TiCl<sub>4</sub> in the presence of H<sub>2</sub>O<sub>2</sub> and the cdta ligand, and are isolated as the sodium and ammonium salts, respectively.

Compared with the data for the other cdta complexes, 2 is the best catalyst for the transformation of phenol. The following factors may be responsible for this. First of all, peroxo Ti(IV) has a relatively high affinity for oxygen ligation compared to the other transition metals, it prefers a seven or eight coordination number rather than six [9], and the coordination ring size of cdta is large enough to allow the flexible hexadentate cdta ligand to be wrapped around the Ti(IV) ion, which leads to the formation of the octa-coordinated complex 2 with a stable configuration, as shown by structural analysis. Secondly, in the titanium silicalite catalyst, Notari [20] and Huybrechts et al. [21] have suggested that a titanium peroxo species is an active intermediate in Scheme 2. Compared with the active oxidative species in TS-1,  $[Ti(O_2)]^{2+}$  as the possible catalytically active species is supported, which may be related to the electric and geometric arrangement of the octadentate coordinated structure. This intermediate transfers the coordinated oxygen atoms to the substrate for the product. Finally, the oxo group persists during the oxidative cleavage reaction, indicating its participation in the process, presumably an oxo anion facilitates oxidative electron removal.

Here a catalytic mechanism for the hydroxylation of phenol is proposed in Scheme 3, which involves the transformation of the oxotitanate species **3** in the process, on interaction with hydrogen peroxide in a pre-equilibrium step. The intermediate species rap-



Scheme 2. Titanium peroxo species as a suggested intermediate for TS-1.



**Scheme 3.** Catalytic cycle proposed for hydroxylation of phenol to catechol by the peroxotitanium complex  $Na_2[Ti(O_2)(cdta)]$ - $2H_2O$  (**2**).

idly transforms into a relatively more stable peroxotitanium species **2** on loss of a water molecule. The peroxotitanium complex **2** interacts with the substrate phenol in another pre-equilibrium step to give a metallo-peroxy-arene intermediate species. Transfer of oxygen by C–H bond activation takes place as a rate determining step to give a titanium phenoxy intermediate species. Hemolytic cleavage results in rapid dissociation to give catechol and regenerating the oxotitanate species **3** in the catalytic cycle.

#### 4. Conclusion

In conclusion, we have isolated and characterized three new titanium-cdta complexes in aqueous solution, in which the peroxo titanate(IV) **2** exists in an octadentate environment and an interesting short Ti=O bond distance [1.671(2)Å] was found in the oxo titanium complex **3**. In this work, the catalytic reaction of phenol conversion is tested, which shows obvious hydroxylation of phenol to catechol in the presence of the peroxo titanium complex **2** at 90 °C after 5.5 h. The oxidative reaction is unique and is believed to share some mechanistic commonality with the TS-1 catalyst. As a detailed mechanistic interpretation for each step involves many possibilities, this shows direct evidence of  $\eta^2$ -O<sub>2</sub> and an oxo titanium species in the catalytic reaction.

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## Appendix A. Supplementary data

IR, Raman and <sup>13</sup>C NMR spectra of compounds **1–3**, crystal data and selected bond distances and angles for **1–3** can be found in the online version. CCDC 851721–851723 contain the supplementary crystallographic data for **1–3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.12.037.

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