## RESEARCH PAPER

# Destructive adsorption of carbon tetrachloride on nanometer titanium dioxide

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The reaction between nanometer  $TiO_2$  and  $CCl_4$  in the presence of oxygen has been studied in order to investigate the potential of nanometer  $TiO_2$  as a destructive reagent for chlorinated hydrocarbons. Two kinds of nanometer  $TiO_2$  of different size were synthesized. The properties of the destructive adsorption of  $CCl_4$  over nanometer  $TiO_2$  of about 40 nm in size were compared with that over nanometer  $TiO_2$  of about 80 nm in size. The reactivity toward  $CCl_4$  of nanometer  $TiO_2$  of about 40 nm in size was remarkably higher than that of nanometer  $TiO_2$  of about 80 nm in size. The products produced included  $CO_2$ ,  $COCl_2$ ,  $Cl_2$ , titanium oxychloride,  $TiCl_4$ , carbon, CO and HCl. HCl was a major gaseous product. Hydrogen of HCl came from traces of water in the carrier gas and surface OH groups of  $TiO_2$ . The formation of  $TiCl_4$  made the interaction surface renew so that  $CCl_4$  could further interact with the bulk of the particles.  $TiO_2$  was regenerated through the exchange of chlorine with oxygen at 550 °C in the carrier gas so that larger quantities of  $CCl_4$  are decomposed over nanometer  $TiO_2$  in the presence of oxygen. A mechanism has been proposed for the destructive adsorption and desorption of  $CCl_4$  over nanometer  $TiO_2$  in the presence of oxygen.

## Introduction

Carbon tetrachloride (CCl<sub>4</sub>) is a volatile organic compound,<sup>1</sup> and has been widely used as a chemical intermediate for producing chlorofluorocarbons (CFCs) such as  $CCl_2F_2$  and  $CCl_3F$ , which can continuously destroy the stratospheric ozone.<sup>2</sup>  $CCl_4$  is also extensively applied as an industrial solvent.<sup>3</sup> The increasing amounts of  $CCl_4$  released in the environment, together with its suspected toxicity and carcinogenic, hepatotoxic, and nephrotoxic properties,<sup>4,5</sup> have prompted researchers worldwide to find clean and effective methods for its destruction.

Methods for the disposal of CCl<sub>4</sub> include incineration<sup>6</sup> and photodecomposition.<sup>7</sup> Incineration is presently the most widely used method. Unfortunately, high temperatures are required, and toxic byproducts, such as dioxins and furans are frequently formed.<sup>8</sup> Therefore, there appears to be a need for the development of simpler and cleaner methods for safely destroying CCl<sub>4</sub>.

During the past decade, nanoparticle research has become quite popular in various fields of chemistry, physics and materials.9 Nanomaterials are clusters of atoms or molecules of materials, ranging in size from <1 nm to almost 100 nm, falling between single atoms or molecules and bulk materials.<sup>10</sup> Since the grain sizes are so small, a significant volume of the microstructure in nanometer materials is composed of interfaces, mainly grain boundaries, i.e., a large volume fraction of the atoms resides in grain boundaries. Consequently, nanometer materials display novel and often-enhanced properties compared to traditional materials.<sup>11</sup> There has been a continued increase in the number of research investigations in recent years on the potential chemical applications of these novel materials. Nanometer metal oxides, an example of important nanomaterials, possess very high lattice energies and melting points due to their high ionicity. Furthermore, these solids can exist with numerous surface sites with enhanced surface reactivity, such as crystal corners, edges, or ion vacancies.<sup>12</sup>

An alternative and cleaner destruction method than incineration is oxidative catalysis over metal oxides as proposed in the literature.  $^{13-17}$ 

Recently, Klabunde and co-workers have shown that CaO and MgO are able to destroy chlorinated hydrocarbons, yielding CO<sub>2</sub> traces of COCl<sub>2</sub>, and the corresponding metal chlorides.<sup>18</sup> They also showed that complete transformation of the oxide into the chloride was possible by depositing transition-metal oxides (*e.g.*, Fe<sub>2</sub>O<sub>3</sub>) onto the oxide.<sup>19</sup>

Weckhuysen et al.<sup>20</sup> indicated that the activities of the alkaline earth metal oxides for decomposing CCl<sub>4</sub> paralleled their basicity; CO<sub>2</sub> was the only gas-product formed when CCl<sub>4</sub> was reacted with BaO and SrO at 200-300 °C. At 450-600 °C, CaO and MgO were very active, and COCl<sub>2</sub> was found in the destruction of CCl<sub>4</sub>. Weckhuysen et al.<sup>21</sup> also studied the destructive adsorption of  $CCl_4$  on  $La_2O_3$  and  $CeO_2$  in the absence of oxygen by X-ray photoelectron spectroscopy and in-situ Raman spectroscopy; La2O3 was much more reactive than CeO<sub>2</sub>. Recently, the Weckhuysen group has developed novel and stable catalyst systems based on supported lanthanide oxides for the hydrolysis of CHCs into CO<sub>2</sub> and HCl at relatively low temperatures in the presence of steam. The active phase consists of a lanthanide oxide chloride, and COCl<sub>2</sub> is a reaction intermediate involved in this catalytic hydrolysis process.22,23

According to the literature, the destructive adsorption of CCl<sub>4</sub> on metal oxides such as La<sub>2</sub>O<sub>3</sub>,<sup>21</sup> CeO<sub>2</sub>,<sup>21</sup> alkaline earth metal oxides,<sup>18,20,24–29</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>19,27–29</sup> CuO<sup>30,31</sup> and NiO<sup>31</sup> was performed in the absence of any oxidant, and therefore only N<sub>2</sub>, He or Ar were used as carrier gases. However, the amount of carbon tetrachloride removed in the presence of oxygen was increased slightly<sup>32</sup> although the influence of oxygen on lanthanide oxide materials brought a detrimental effect on the catalytic properties of the materials.<sup>22,23</sup> Moreover, for atmospheric samples, CCl<sub>4</sub> always coexists with oxygen (O<sub>2</sub>). Hence, the destructive adsorption of CCl<sub>4</sub> in the presence of O<sub>2</sub> is more relevent than in the absence of O<sub>2</sub>.

Another disadvantage in the current reports is that the lifetime of the reactor used for the destructive adsorption of CCl<sub>4</sub> is very limited, because of the formation of metal chlorides and metal oxychlorides, *e.g.*, BaCl<sub>2</sub>, *etc.* To regenerate the reactor, a series of processes including dissolution, precipitation, filtration, and calcination was needed, which limits the application of the reactor to real environmental treatment of pollution by CCl<sub>4</sub> in air.<sup>20</sup>

The aim of this work was to investigate the potential of nanometer  $\text{TiO}_2$  for the destructive adsorption of  $\text{CCl}_4$  in the presence of oxygen. The formation of  $\text{TiCl}_4$  during the destructive adsorption of  $\text{CCl}_4$  makes the interaction surface renew so that  $\text{CCl}_4$  can further interact with the bulk of the particles.  $\text{TiO}_2$ was regenerated through the exchange of chlorine with oxygen in the carrier gas at 550 °C so that larger quantities of  $\text{CCl}_4$ can be decomposed over nanometer  $\text{TiO}_2$  in the presence of oxygen.

# Experimental

### Reagents

The procedure for synthesis of TiO<sub>2</sub> nanoparticles was as follows: 25 mL of tetrabutyl titanate was slowly added to 50 mL ethanol solution at room temperature and 0.1 mL water was added to this mixture. Then, 3 mL NH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was added dropwise to the mixed solution under stir. A light yellow solution was obtained and allowed to stand for 3 days. Then 95% ethanol solution was added into the solution. A transparent primrose sol-gel was obtained after the mixed solution was hermetically sealed for 1 day. After being allowed to dry, it was divided into two portions and calcined in air. The temperature was raised to either 650 and 800 °C at 6-8 °C min<sup>-</sup> and maintained for 2 h. Then, the TiO<sub>2</sub> powder was cooled to room temperature in air. Two TiO<sub>2</sub> powders were obtained (Ti-650 (650 °C) and Ti-800 (800 °C)). Carbon tetrachloride was of analytical reagent grade purchased from Beijing Chemical Factory.

#### Characterization of materials

Materials were characterized by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Brunauer-Emmet-Teller (BET) surface area analysis. The topography and particle size of the materials were measured using a Hitachi H-800 transmission electron microscope. The accelerating voltage of the electron beam was 200 kV. The samples for TEM experiments were dispersed in water with ultrasonic treatment for approximately 10 min and then transferred to a copper grid with a polymer membrane in order to disperse the nanoparticles. XRD measurements were obtained using a Bruker D8 Advance diffractometer with Cu-K $\alpha$  radiation. BET surface areas were measured on a Micromeritics ASAP 2010 instrument using nitrogen gas adsorption at liquid-nitrogen temperature.

#### Studies of destruction of CCl<sub>4</sub>

The adsorption and chemical desorption of carbon tetrachloride were performed with a TiO<sub>2</sub> packed quartz column. 100 mg of nanometer TiO<sub>2</sub> was introduced into a quartz microcolumn (50 mm × 4 mm i.d.) plugged with a small portion of glass wool at both ends. One end of this column was connected to the sample inlet. Before use, the quartz column was conditioned by programming temperature from room temperature to 600 °C at a rate of 20 °C min<sup>-1</sup> to eliminate the influence of previous absorbates. The temperature of the reactor was monitored and controlled by a temperature controller. The carrier gas was composed of 78% N<sub>2</sub>, 21% O<sub>2</sub> and 1% Ar (by volume). The carrier gas was allowed to flow through the reactor at a rate of 12 mL min<sup>-1</sup>. Measured amounts of  $CCl_4$  were injected through a septum inlet positioned at the beginning of the reactor so that the  $CCl_4$  in the flow stream evaporated immediately in the reactor.  $CCl_4$  was introduced in the reactor as a pulse of 2  $\mu$ L, and the time period between the pulses was about 5 min. The contact time was 15 s.

The gaseous products, eluted by the carrier gas, were collected in an airtight syringe. The volume of the gaseous products collected was 40 mL, and then injected into an IR cell equipped with two KBr windows. FTIR spectra were recorded on a Perkin-Elmer FTIR spectrometer (1760X) for the gaseous products after each injection of 2  $\mu$ L CCl<sub>4</sub> by comparing a background under the same conditions. The gaseous products after chemical desorption were also monitored in the same manner.

The solid products were monitored using X-ray photoelectron spectroscopy (XPS). The XPS spectra were acquired using a Perkin-Elmer (PHI) model 5300 ESCA spectrometer. XPS spectra were typically recorded using a pass energy of 89.45 eV, a step increment of 0.8 eV, and an Al anode power of 250 W at a base pressure of  $10^{-10}$  Torr.

Quantitative analysis of Ti was carried out using an inductively coupled plasma-mass spectrometer (ICP-MS) (Elan 6000 (PE Sciex, Toronto, Canada)). This system consists of a cross flow nebuliser and a Scott double pass Ryton spray chamber. A Ti standard was purchased from the National Research Center of Certified Reference Materials (China).

Analysis of  $Cl_2$  was performed by bubbling the effluent stream through a 0.1 mol L<sup>-1</sup> NaOH solution. The  $Cl_2$  concentration was determined by titration with sodium thiosulfate using starch as an indicator after the collected solution was reacted with about 1 g KI.<sup>33</sup>

## **Results and discussion**

In order to compare the destructive adsorption of different sizes of nanometer  $TiO_2$ , two nanometer  $TiO_2$  samples were synthesized as described above. Ti-650 and Ti-800 were about 40 and 80 nm in size, respectively, as seen from Fig. 1. As shown in Fig. 2, both anatase and rutile crystals were present in Ti-650 and Ti-800, most of the crystals were anatase in Ti-650 while most of crystals were rutile in Ti-800.

The results obtained from BET measurements showed that the surface area and average pore diameter of Ti-650 were 9.76 m<sup>2</sup> g<sup>-1</sup> and 6.74 nm, respectively, while the surface area and average pore diameter of Ti-800 were 8.60 m<sup>2</sup> g<sup>-1</sup> and 13.3 nm, respectively.

The gaseous products evolving from the titanium dioxide surface during the destructive adsorption process were mainly monitored by FTIR spectroscopy. Results obtained for Ti-650



Fig. 1 TEM images (a) Ti-650 and (b) Ti-800.



Fig. 2 XRD patterns of (a) Ti-650 and (b) Ti-800.

was compared with those for Ti-800 at 450 °C as shown in Table 1 and in Fig. 3(a)–(e). The observed main products from the decomposition of carbon tetrachloride over Ti-650 and Ti800 at 450 °C included carbon dioxide as indicated by the  $\nu_{C=O}$  vibration at 2340 cm<sup>-1</sup>, phosgene as shown by the  $\nu_{C=O}$  vibrations at 1827 and 1812 cm<sup>-1</sup> and by the  $\nu_{C-CI}$  vibrations at 863 and 849 cm<sup>-1</sup>, hydrogen chloride as revealed by the  $\nu_{H-CI}$  vibration at 3100–2640 cm<sup>-1</sup> and a small amount of carbon monoxide as shown by the  $\nu_{CO}$  vibrations at 2170 and 2110 cm<sup>-1</sup>. However, the two different titania samples exhibited significant quantitative and qualitative differences in their behavior toward carbon tetrachloride.

In the case of Ti-650, carbon tetrachloride was completely removed in each injection until a total of 80  $\mu$ L was injected. After that, a very small portion of CCl<sub>4</sub> as indicated by the  $\nu_{C-Cl}$  vibration at 794 cm<sup>-1</sup> was undecomposed and released from the reactor with the produced products. The amount of phosgene increased with increasing the amount of CCl<sub>4</sub> undecomposed, but before that the amount of phosgene almost did not change, which suggested that phosgene was an intermediate product in the decomposition of CCl<sub>4</sub>. The sample weighed 0.1050 g before reaction and 0.1010 g after reaction, indicating a weight loss of 3.8% because a portion of titania was converted to titanium tetrachloride as illustrated later by ICP-MS in this paper.

Table 1 Destructive adsorption of CCl<sub>4</sub> on nanometer TiO<sub>2</sub>

Sample	Temp./ °C	Initial weight <sup>a</sup> /g	Final weight <sup>a</sup> /g	Weight loss <sup>a</sup> (%)	$\mathrm{BT}^{b}/\mathrm{\mu L}$
Ti-650	250	0.1072	0.1017	5.1	2
	350	0.1040	0.9360	10.0	4
	450	0.1050	0.1010	3.8	80
	550	0.1050	0.1050	0.0	>180
Ti-800	450	0.1047	0.0877	16.2	50

<sup>*a*</sup> Data refer to the weight of the sample before adsorption and after adsorption of 180  $\mu$ L of CCl<sub>4</sub>. <sup>*b*</sup> BT, break through volume, the amount of CCl<sub>4</sub> completely removed before any undecomposed CCl<sub>4</sub> is observed in the effluent.

In the case of Ti-800, carbon tetrachloride was completely removed in each injection until a total of 50  $\mu$ L was injected. After that, a very small portion of CCl<sub>4</sub> was undecomposed and released from the reactor with the reacted products. The undecomposed CCl<sub>4</sub> increased as more carbon tetrachloride was introduced. The amount of phosgene also increased with increasing the amount of CCl<sub>4</sub> undecomposed, but the amount of phosgene almost did not change until a total of 100  $\mu$ L possibly because active oxygen atoms over the surface of titania were replaced by a certain number of chlorine atoms, and led to homeostasis. The sample weighed 0.1047 g before reaction and 0.0877 g after reaction, indicating a weight loss of 16.2%.

To investigate the effect of the temperature on the decomposition efficiency the destruction of CCl<sub>4</sub> over Ti-650 was studied at different temperatures (250, 350, 450 and 550 °C) by FTIR. The results obtained are shown in Table 1 and in Fig. 3(a)-(e). At 250 °C traces of undecomposed CCl<sub>4</sub> were observed in the releases from the reactor even during the initial injections, suggesting that a portion of CCl<sub>4</sub> was decomposed at 250 °C. The overall ability of Ti-650 to decompose carbon tetrachloride increased with increasing the temperature from 250 to 550 °C. At 550 °C no carbon tetrachloride was observed with release from the reactor during the destructive adsorption until a total of 180 µL was injected. Carbon monoxide was apparently observed in the gaseous products at 550°C, but no carbon monoxide was observed at 250 °C. However, when the reactor was heated to 550 °C after a total of 120 µL CCl<sub>4</sub> was injected at 250 °C, the releases from the reactor contained carbon monoxide, indicating that carbon was produced during the destructive adsorption at lower temperature, which was further proved by the XPS experiments, and carbon reacted with oxygen in the carrier gas to produce carbon monoxide at higher temperature. Tetrachloroethylene was not detected at temperatures in the range from 250 to 550 °C, because the  $\nu_{\rm C-Cl}$  vibration at 920 cm<sup>-1</sup> was not observed, although some literature reported that tetrachloroethylene was formed during the destructive adsorption of CCl<sub>4</sub>.<sup>19,32</sup> At 350 °C the change of the amount of phosgene formed was apparently observed. First, the amount of phosgene increased with increasing the total amount of CCl<sub>4</sub> injected until a total of 32 µL, but after that, the amount of phosgene decreased with continuing to increase the total amount of CCl<sub>4</sub> injected, because at the initial reaction stage the chlorination of the surface of titanium dioxide was relatively complete, then the ability of chlorination of the surface of titanium dioxide decreased as a result of the replacement of oxygen on the surface of titanium dioxide by the chlorine atoms. Therefore, the amount of phosgene produced increased. However, when the capacity of titanium dioxide to decompose carbon tetrachloride started to decline, the amount of phosgene produced decreased as the amount of carbon tetrachloride eluted from the reactor further increased. At 550  $^{\circ}\mathrm{C}$  no phosgene was observed, which showed that the phosgene produced further reacted with the surface. The results above proved that phosgene was an intermediate product in the decomposition of CCl<sub>4</sub>. The weight losses at 250, 350, 450, 550 °C were 5.1, 10.0, 3.8 and 0.0%, respectively. The weight loss mainly resulted from formation of titanium tetrachloride as illustrated by ICP-MS. The reason why the weight loss increased and then decreased with the increase of temperature was that at lower temperature the chlorine in the oxychloride produced during the chlorination was not easy to be replace by oxygen atoms in the carrier gas, and oxychloride was further chlorinated to form titanium tetrachloride; however, at higher temperature the chlorine in the oxychloride produced during the chlorination readily reacted with oxygen atoms in the carrier gas to form titanium dioxide, and titanium tetrachloride was no longer formed. The weight loss was less at 250 °C than at 350 °C because less of carbon tetrachloride was decomposed at 250 °C. At 550 °C the weight loss was 0.0%

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Fig. 3 FTIR spectra of the gaseous products of CCl<sub>4</sub> over Ti-650 at 250 (a), 350 (b), 450 (c) and 550 °C (d) and over Ti-800 at 450 °C (e): t = total amount of CCl<sub>4</sub> (in  $\mu$ L) introduced.

during the destructive adsorption of a total of 180  $\mu$ L injected, indicating that Ti-650 had remarkable potential to decompose CCl<sub>4</sub>.

An experiment was carried out to examine the possibility of reusing the catalyst. The column packed with Ti-650 was conditioned to the adsorption temperatures (250, 350, 450 and 550 °C). 2 μL CCl<sub>4</sub> was injected as a pulse into the carrier gas flow for CCl<sub>4</sub> adsorption on the catalyst. The temperature was held for 5 min until all CCl<sub>4</sub> molecules adsorbed on the catalyst were decomposed. This procedure was repeated 90 times at the same working conditions. The peak height of the  $\nu_{C-Cl}$  vibration at 794 cm<sup>-1</sup> was used as a quantitative standard for CCl<sub>4</sub>. Fig. 4 shows the run number vs. decomposition efficiency at different temperatures. At 250 °C, the maximum decomposition efficiency of CCl4 over Ti-650 was 74.77% of the first run. Then, the decomposition efficiency of CCl<sub>4</sub> over Ti-650 decreased rapidly with an increase of the run number. At 350 °C, the maximum decomposition efficiency of CCl<sub>4</sub> over Ti-650 was 99.96% for the first run. Then, the decomposition efficiency of CCl<sub>4</sub> over Ti-650 decreased with the increase of the run number with a value of 87.45% for the ninetieth run. At 450 °C, the decomposition efficiency of  $CCl_4$  over Ti-650 was 100% from the first run to the fortieth run. Then, the decomposition efficiency of  $CCl_4$  over Ti-650 decreased slightly with an increase of the run number. Even so, the decomposition efficiency was 99.00% for the ninetieth run.



Fig. 4 Run number dependence of decomposition efficiency of  $CCl_4$  over Ti-650 at different temperatures (250, 350, 450 and 550 °C).

At 550 °C, the decomposition efficiency of CCl<sub>4</sub> over Ti-650 was 100% from the first run to the ninetieth run. The results indicated a satisfactory efficiency of decomposition of CCl<sub>4</sub> over TiO<sub>2</sub> for reuse at temperatures higher than 450 °C.

In the literature it was reported that the thermal decomposition of CCl<sub>4</sub> over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at temperatures of 400–600 °C in a fixed-bed pulse reactor resulted in the formation of Cl<sub>2</sub>.<sup>19</sup> Therefore we investigated whether Cl<sub>2</sub> was formed during the destructive adsorption and during the desorption over Ti-650 using an iodometric method. 10 mL of 0.1 mol  $L^{-1}$ NaOH solution was used as the absorption solution. The collection times during the destructive adsorption at different temperatures (250, 350, 450 and 550 °C) and during the desorption at 550 °C were 1 and 10 min, respectively. The concentration of  $Cl_2$  in the absorption solution during the chlorination were 0 mol  $L^{-1}$  at 250 °C,  $0.8\times10^{-4}$  mol  $L^{-1}$  at 350 °C,  $1.2\times10^{-4}$ mol  $L^{-1}$  at 450 °C, and  $1.5 \times 10^{-4}$  mol  $L^{-1}$  at 550 °C, respectively, indicating that Cl<sub>2</sub> was produced during the destructive absorption except at temperatures lower than 250 °C and the amount of Cl<sub>2</sub> increased with an increase of the temperature in the range from 250 to 550  $^\circ\text{C}.$  The concentration of  $\text{Cl}_2$  in the absorption solution during the desorption at 550 °C after the adsorption at different temperatures (250, 350, 450 and 550 °C) were 3.4 mol  $L^{-1}$  at 250 °C,  $4.6\times10^{-4}$  mol  $L^{-1}$  at  $350 \,^{\circ}\text{C}$ ,  $6.4 \times 10^{-4} \text{ mol } \text{L}^{-1}$  at  $450 \,^{\circ}\text{C}$ , and  $6.5 \times 10^{-4} \text{ mol}$  $L^{-1}$  at 550  $^{\circ}\text{C},$  respectively, indicating that  $Cl_2$  was produced during the destructive absorption and the amount of Cl<sub>2</sub> increased with the increase of the temperature. Cl<sub>2</sub> produced during the destructive adsorption in the presence of oxygen, also, resulted not from decomposition of phosgene but from decomposition of oxychloride produced during the chlorination, because no chlorine gas formed although phosgene was produced at 250 °C.

Our preliminary experiment has shown that when 50 µL CCl<sub>4</sub> was injected as a pulse into the reactor, a yellow liquid which produced a white fog when exposed to air was effluent from the reactor, suggesting that the yellow liquid produced may be TiCl<sub>4</sub> (boiling point *ca*.  $136 \,^{\circ}$ C)<sup>34</sup> evaporated over the quartz column at 250 °C and liquefied in the vessel behind the reactor. To investigate whether TiCl<sub>4</sub> was formed and evaporated during destructive adsorption at 250 °C, the absorption solutions of gas-phase products after decomposition of CCl<sub>4</sub> on nanometer TiO<sub>2</sub> were detected using ICP-MS, a very sensitive technique for the detection of Ti species. CCl<sub>4</sub> was added in one batch of 600 mL instead of pulses. The results are shown in Fig. 5. The titanium species was not detected by ICP-MS when a portion of CCl<sub>4</sub> below 10000 ppm was injected. For higher concentrations of CCl<sub>4</sub>, however, the evaporated Ti species was detected by ICP-MS. It seems that TiCl<sub>4</sub> could only be produced from the reaction of TiO<sub>2</sub> and  $CCl_4$  above 10000 ppm  $CCl_4$ , which suggested that the solid product obtained from the chlorination was titanium oxychloride as a result of partial chlorination of nanometer TiO<sub>2</sub>.

According to the literature, metal oxides were transformed to  $M_xCl_y$  (such as BaCl<sub>2</sub>) by the injection of CCl<sub>4</sub> into the column during the destructive adsorption of  $\text{CCl}_4.^{18-20,24-29}$  In order to monitor the chlorination process of destructive adsorption in the present study, XPS was employed for the characterization of the solid products on nanometer titanium dioxide particles when 50 µL CCl<sub>4</sub> was injected as a pulse. The sample was heated to 550 °C and held for 15 min after destructive adsorption. Fig. 6 shows the acquired Ti 2p, O 1s, Cl 2p and C 1s spectra.<sup>35</sup> The Ti 2p spectra included two lines: Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ . The Ti  $2p_{3/2}$  line was identified by a single peak at a binding energy of 458.67 eV. The separation between the Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  peaks was 5.7 eV. The measured binding energy of the  $Ti 2p_{3/2}$  and  $Ti 2p_{1/2}$  peaks indicated that titanium mainly existed as TiO2. The O1s spectra showed a main peak at a binding energy of 529.27 eV with a shoulder at a binding energy of 530.97 eV. This shoulder



Fig. 5 ICP-MS analysis of  $TiCl_4$  evaporation corresponding to the concentration of the  $CCl_4$  injection.

corresponded to hydroxyl species on the surface because the surface of  $TiO_2$  exposed in air before the measurement absorbed some water.<sup>36</sup> No apparent differences in the Ti 2p and the O Is spectra were observed for samples before destructive adsorption, after destructive adsorption and after regeneration, indicating that the solid sample was mainly presented in the form of TiO<sub>2</sub> whether before or after reaction.

Two carbon C ls peaks at a binding energy of 284.57 and 288.37 eV were observed on all the samples. The lowbinding-energy region was associated with surface pollution which corresponded to the fact that the samples are exposed to air before the XPS experiments while the high-bindingenergy region was due to carbonate species on the surface formed during synthesis of  $TiO_2$ .<sup>36</sup> The intensity of the C ls peak at the binding energy of 284.57 eV after destructive adsorption was higher than before destructive adsorption, which indicated that deposited coke was formed during destructive adsorption. No differences of the C ls spectra were observed between samples before destructive adsorption and after regeneration, indicating that deposited coke was decomposed at relatively high temperature.

The Cl 2p spectrum at a binding energy of 197.97 eV was observed after destructive adsorption, but no chlorine atoms could be detected before destructive adsorption, which proved that the chlorinated product was produced after destructive adsorption. The chlorinated product was a partially chlorinated product, not TiCl<sub>4</sub>, since the concentration of the Cl species was extremely low in comparison with the Ti and O species, and since the boiling point of TiCl<sub>4</sub> was 136.4 °C. No chlorine was detected after heating to 550 °C, which indicated that the partially chlorinated product was regenerated due to the exchange of oxygen with chlorine.

#### Discussion

The thermal decomposition of CCl<sub>4</sub> over nanometer TiO<sub>2</sub> at a temperature of 250-550 °C in the quartz column resulted in HCl, CO<sub>2</sub>, COCl<sub>2</sub>, Cl<sub>2</sub>, titanium oxychloride, TiCl<sub>4</sub>, CO, and carbonaceous deposits. HCl was shown as a major gaseous product in all IR spectra. Hydrogen of HCl came from traces of water in the carrier gas and surface OH groups of  $TiO_2$ . The above results obtained suggest a possible reaction pathway for the destructive adsorption of CCl<sub>4</sub> over nanometer TiO<sub>2</sub> as shown in Scheme 1. The first step involves the physisorption of CCl<sub>4</sub> on the nanometer TiO<sub>2</sub> surface. The relatively positive carbon atom interacts with a negative oxygen site and the relatively negative chlorine atoms interact with positive metal ion sites to form an intermediate. The covalent C-Cl is then polarized and broken by the TiO lattice. The overall result of this process leads to a dissociative adsorption of CCl<sub>4</sub> to form COCl<sub>2</sub> as a result of oxygen abstraction



Fig. 6 XPS spectra: (a) Ti 2p, (b) O 1s, (c) Cl 2p, (d) C 1s.

from the TiO<sub>2</sub> surface and a partially chlorinated TiO surface as a result of chlorine abstraction from the CCl<sub>4</sub> molecules.

COCl<sub>2</sub> is an intermediate product in the decomposition of CCl<sub>4</sub> as proved above, which is consistent with the



Scheme 1 Scheme of the destructive adsorption of CCl4 over nanometer  $TiO_2$  in the presence of oxygen.

literature.<sup>19,20,32</sup> COCl<sub>2</sub> is readsorbed, and further reacts with the surface to form CO<sub>2</sub> after abstraction of another oxygen from the surface. Further chlorination results in the formation of a fully chlorinated material.

The formation of hydrogen chloride during the destructive adsorption of CCl<sub>4</sub> could result from COCl<sub>2</sub> reaction with traces of water in the carrier gas, because the amount of hydrogen chloride scarcely changed with the increase of the total amount of CCl<sub>4</sub> at the same temperature, such as at 250 °C, and the fact that traces of water existed in the carrier gas was proved by measurement of the carrier gas using FTIR which showed the  $\nu_{O-H}$  vibration as a broad band from 3650 to 3000  $cm^{-1}$ 

The formation of carbon in the destructive adsorption of CCl<sub>4</sub> at 350 °C is proved by XPS. When CCl<sub>4</sub> was adsorbed on the partially chlorinated TiO<sub>2</sub> surface, the relatively negative chlorine atoms interact with positive metal ion sites, but the relatively positive carbon atom can not interact with a negative oxygen site, thus leading to an unstable intermediate. The interaction of chlorine with the metal weakens the covalent C-Cl in this intermediate. The overall result of this process leads to a dissociative adsorption of CCl4 to form carbon and a further chlorinated TiO surface as a result of chlorine abstraction from the CCl<sub>4</sub> molecules. Carbon formed could react with oxygen gas at relatively high temperature in the carrier gas to produce CO and CO2.

The partially chlorinated TiO<sub>2</sub> could still exchange chlorine atoms with oxygen atoms of oxygen in the carrier gas. When oxygen was adsorbed on the partially chlorinated TiO2 heated to certain temperature, such as 550 °C, the interaction of the relatively negative oxygen with the relatively positive Ti led to disconnection of chlorine with the Ti center. As a result, TiO<sub>2</sub> was regenerated, and Cl<sub>2</sub> was formed due to the recombination of chlorine cleaved from the partially chlorinated TiO<sub>2</sub>, in agreement with our previous work.<sup>3</sup> ′ The regeneration of TiO<sub>2</sub> makes us believe that nanometer TiO<sub>2</sub> could be potentially applied to deal with chlorinated hydrocarbons.

The further chlorinated TiO surface could be fully chlorinated with CCl<sub>4</sub> to form TiCl<sub>4</sub>. Since the boiling point of TiCl<sub>4</sub> was lower than the temperature the reactor was heated to, the formation of TiCl<sub>4</sub> resulted in the weight loss of the reactor, and oxide surface regeneration for further adsorption. The smaller sized nanometer TiO<sub>2</sub> sample was more reactive than the larger sized sample, possibly because first, the anatase/ rutile ratio was different for those two samples that can account for variation in activities; second, the difference in apparent densities of powders resulted in variation of contact times and should influence of the degree of CCl<sub>4</sub> conversion; further, the concentration of surface OH groups should be different for Ti-650 and Ti-800. The partially chlorinated TiO<sub>2</sub> derived from 40 nm TiO<sub>2</sub> also could be more reactive so that the exchange of chlorine atoms with oxygen atoms of oxygen gas in the carrier gas was faster. Therefore, the 40 nm TiO<sub>2</sub> was regenerated more rapidly than the 80 nm TiO<sub>2</sub>. Hence, the weight loss of the 40 nm TiO<sub>2</sub> was lower than the 80 nm TiO<sub>2</sub>. Similarly, the partially chlorinated TiO<sub>2</sub> derived from the 40 nm TiO<sub>2</sub> at higher temperature could be more reactive so that the exchange of chlorine atoms with oxygen atoms of oxygen gas in the carrier gas was faster. TiO<sub>2</sub> was regenerated more rapidly at higher temperature. Therefore, the weight loss of nanometer TiO<sub>2</sub> was less at higher temperature than at lower temperature.

In conclusion, nanometer TiO<sub>2</sub> synthesized by the sol-gel method could have a remarkable potential to remove chlorinated hydrocarbons in the environment. The smaller 40 nm TiO<sub>2</sub> sample adsorbed and decomposed more carbon tetrachloride than the larger 80 nm TiO<sub>2</sub> sample. The formation of TiCl<sub>4</sub> made the interaction surface renew so that CCl<sub>4</sub> could further interact with the bulk of the particles. TiO<sub>2</sub> was regenerated through the exchange of chlorine with oxygen in the carrier gas so that large quantities of CCl<sub>4</sub> would be decomposed over nanometer  $\hat{\text{TiO}}_2$  in the presence of oxygen. A mechanism has been proposed for the destructive adsorption and desorption of CCl<sub>4</sub> over nanometer TiO<sub>2</sub>.

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