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The research on the deactivation mechanism of TiO_2 nanotube

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ABSTRACT

To explore the deactivation mechanism of TiO_2 nanotube, freshly prepared and deactivated TiO_2 nanotubes were characterized by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The morphologies, the element speciation, and content of the two TiO_2 nanotubes were comparatively studied. The results indicated that the two TiO_2 nanotubes were different in morphologies. For the deactivated TiO_2, the upper end of the nanotubes turned thinner and porous. There was also great difference in element speciation, content and some functional groups on the surface of the two types of TiO_2 nanotubes. In the deactivated TiO_2 nanotubes, the lattice oxygen (Ti–O) was consumed heavily, which could provide oxygen and let down hole-electron recombination during the catalysis reaction, and the titanium was lost partially, whereas the contents of some carbon/nitrogen functional groups (C–O, C=O, COOR, O–Ti–N) and oxygen species (O^-, O_2^{2-}) increased. It showed that the effective constituent of TiO_2 decreased, and some intermediate products adsorbed or deposited on the surface of the TiO_2, which not only reduced the ·OH producing rate, but also hindered the adsorption of reactants. That could explain the reasons for the deactivation mechanism of TiO_2 nanotube.

Keywords: TiO_2 nanotube; Deactivation; Mechanism

1. Introduction

TiO_2 catalyst had been widely studied by many researchers and the related literature reports that after being used for a certain period of time, the catalytic activity of TiO_2 declines gradually and even becomes lost completely [1,2]. In the reutilization research of TiO_2, a clear deactivation of the catalytic activity was also shown [3–5]. As photocatalytic materials, the sustainment of catalytic activity and service life are the key factors that restrict the practical application of TiO_2 catalyst. Thus, it is of great significance from practical standpoint to enhance the catalytic activity, prolong the service life and increase the reutilization rate of TiO_2 catalyst. To address the first problem related to the catalytic activity, the deactivation mechanism of TiO_2 catalyst needs to be investigated. The reports on the deactivation mechanism of TiO_2 are quite a few until now. In Yu study [6], the V_2O_5-WO_3/TiO_2 catalyst deactivation could be interpreted by the valence change of the V atoms, thermal sintering and aluminum sulfate formation on the catalyst surface. Wu [7] thought that depletion of PtO_2 by electrons could lead to deactivation of Pt/TiO_2

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catalyst. A large number of oxygen vacancies formed on the surface of the used TiO_2, which were thought to be responsible for the loss in photoactivity of TiO_2 [2]. Doping with alkali metal might also cause deactivation of vanadium-based catalyst, because the surface coverage by the alkali metals can lead to decrease in the surface area and total pore volume [8]. Zheng [9] summarized that chemical poisoning of active sites and physical blocking of the surface area were the primary deactivation mechanisms for the V_2O_5-WO_3/TiO_2 catalyst.

In this study, TiO_2 nanotube was used as catalyst and comparative studies between freshly prepared and deactivated TiO_2 nanotubes were performed. The morphology of the TiO_2 nanotubes, element speciation, content and functional groups on the surface of the two TiO_2 nanotubes were studied by SEM and XPS. Moreover, the deactivation mechanism was also investigated. These observations may provide the theoretical basis for improving the stability of catalytic activity of TiO_2 and prolonging its service life.

2. Experimental

2.1. Chemicals and materials

The titanium sheets (0.3 mm thick, 99.6% purity) and nickel sheets (99.5% purity) were purchased from Tianjin Gerui Co., China. The tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC) were obtained from the Jiangsu Institute for Food and Drug Control, China. All other chemical reagents were purchased from Country Medicine Reagent Co., China, and they were analytic reagent grade, except methanol and acetonitrile, which were chromatographic grade. Double-distilled water was used in the experiments.

2.2. Preparation and application of TiO_2 nanotube

The titanium sheets were cut into samples of size 120 × 100 mm, and then they were bent to arc shape. TiO_2 nanotube arrays were fabricated by anodizing titanium sheets in a two-electrode electrochemical cell, with a nickel sheet as a cathode, at a constant potential at room temperature [10–12]. First, titanium sheets were etched in a mixture of acids (HF and HNO_3) and water for 30 s (volume ratio of HF:HNO_3:H_2O, 1:3:6). After it was rinsed with double-distilled water, the clean titanium sheet was anodized in electrolyte (glycol containing 0.5% NH_4F, m m^{-1}) for 3 h at a potential of 50 V to form TiO_2 nanotube arrays on titanium substrates. Finally, the TiO_2 nanotube arrays were crystallized by annealing in an air atmosphere for 1 h at 450℃ with heating and cooling rates of 2℃ min^{-1}.

The experiments of catalytic degradation were carried out in a cylindrical photo reactor (XPA, Nanjing Xujiang Electromechanical Plant, China) with a 15 W medium pressure mercury lamp ($\lambda \geq 365$ nm) with an illumination intensity of 21.2 μW $(cm^2)^{-1}$ (Fig. 1). The reactor was put in a box to prevent interference with natural daylight. The objective degradation was the mixtures of TC, OTC, and CTC (TCs solution), and its initial total concentration was 30 mg L^{-1} (10 mg L^{-1} each of TC, OTC and CTC) mixed into 500 mL of aqueous solution. The TCs solution (adjusting pH value with dilute H_2SO_4 and NaOH solution) was degraded in the reactor for 3 h, and the TiO_2 nanotube acted as catalyst in the experiments. During the reaction, the TCs solution was sampled periodically, and the concentrations of TC, OTC, and CTC were measured by high-performance liquid chromatography (HPLC; L6, Beijing Purkinje General Instrument Co., China).

2.3. Characterization of TiO_2 nanotube

The morphologies of the newly prepared and deactivated TiO_2 nanotubes were studied using a field-emission scanning electron microscope (Hitachi S-4800, Japan). X-ray photoelectron spectroscopy (PHI 5000 VersaProbe, Japan) analysis was used to determine the element speciation and element content of the two TiO_2 nanotubes.

3. Results and discussions

3.1. The catalytic activity stability of the TiO_2 nanotubes

After participating in catalysis reaction many times, the catalytic activity of freshly prepared TiO_2 nanotubes declined gradually and then lost completely [1,4]. This catalyst with lost activity will be referred to as the deactivated TiO_2 nanotubes. In this study, the TiO_2 nanotube was reutilized in the degradation experiments. After being used 9–10 times, the degradation efficiency of TCs was decreased (Fig. 2).

3.2. Morphology of the TiO_2 nanotubes

Fig. 3(a) and (b) present the field-emission scanning electron microscopy images of the two TiO_2 nanotubes. The freshly prepared TiO_2 nanotubes were clearly visible, and there was less coverage on the nanotubes. On the other hand, for the deactivated TiO_2 nanotubes, some filaments were found to cover the catalyst surface, and some holes were found. The thickness of the walls of the two TiO_2 nanotubes was 91 and 61 nm respectively, and the walls of the

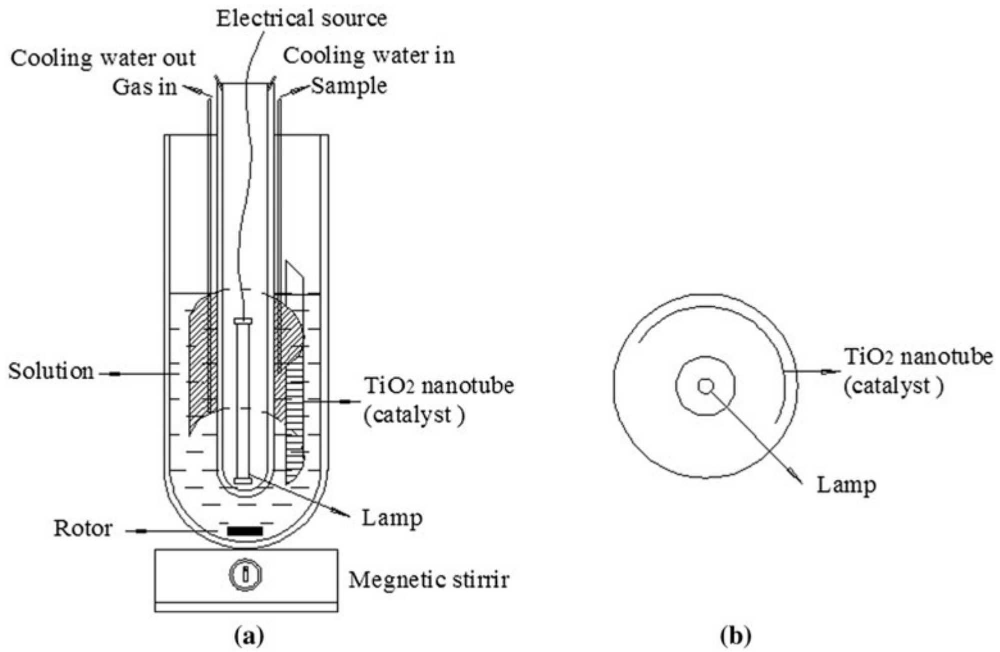

Fig. 1. Schematic diagram of catalytic reaction device: (a) cross-sectional view and (b) top view.

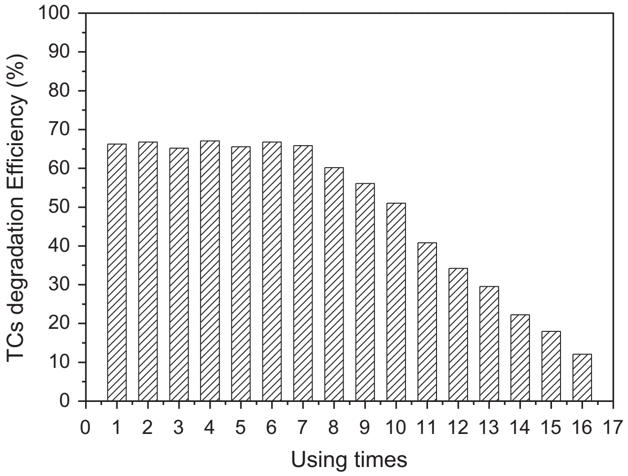

Fig. 2. The recycling of TiO_2 nanotube for the degradation of TCs.

deactivated TiO_2 nanotubes were thinner. However, the tubular structure of the nanotubes showed no change.

3.3. XPS analysis

The freshly prepared and deactivated TiO_2 nanotubes were characterized by XPS, and the spectra are shown in Fig. 4. Table 1 presents some atomic content on the surface of the two types of TiO_2 nanotubes.

As shown in Fig. 4. and Table 1, the types of elements and the amount of C1s, N1s, and Cl2p increased on the surface of the deactivated TiO_2 nanotubes. These elements came from the surface deposition and adsorption during the catalyzed reaction. After using the catalyst many times, other substances would be adsorbed or deposited on the surface of the TiO_2 nanotubes, and its surface properties or structure would change [13–15]. The content of O1s and Ti2p of the deactivated TiO_2 nanotubes reduced evidently. It was probably because of the catalyst's participation in the reaction several times, which led to the loss of titanium.

The changes in the element content and speciation on the surface of TiO_2 nanotubes are discussed in detail below, and it had great significance in studying the catalytic activity decrease of TiO_2 nanotubes.

The C1s XPS spectrum is shown in Fig. 5. The peaks at 284.6, 286.5, 287.9, and 288.4 eV were assigned to C–C, C–O, C=O, and COOR, respectively [16–19]. The peak strengths of C–O, C=O, and COOR in the deactivated TiO_2 nanotubes were higher than those in the freshly prepared TiO_2 nanotubes. It could be inferred that after the catalysis reaction organic residues were adsorbed or deposited on the surface of TiO_2 nanotubes, which resulted in an increasing amount of carbon functional groups.

Fig. 6 presents the XPS O1s spectra of TiO_2 nanotubes surface. Two peaks of interest can be deconvoluted from the broad O1s band: one near 529.9 eV was

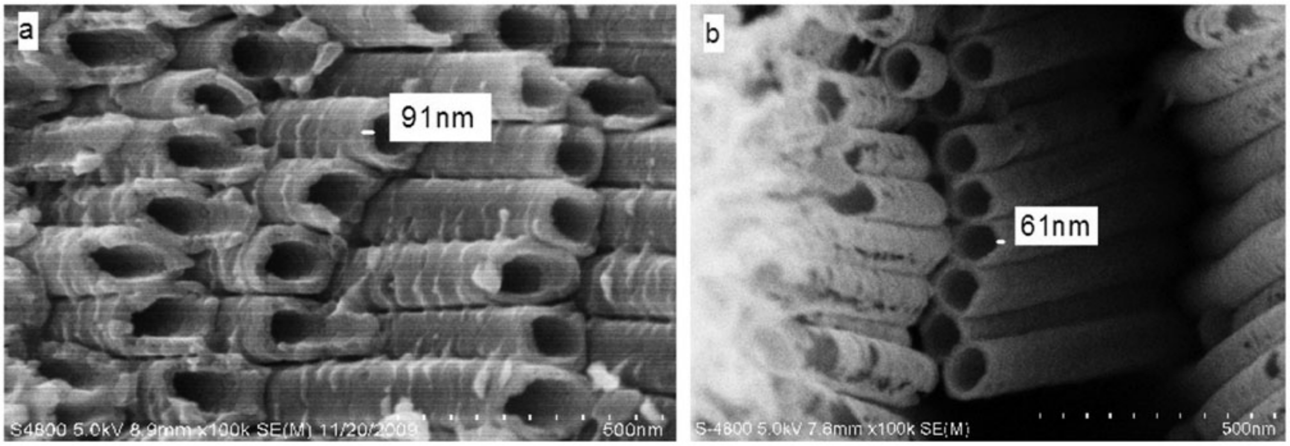

Fig. 3. The morphology of TiO_2 nanotubes: (a) freshly prepared and (b) deactivated.

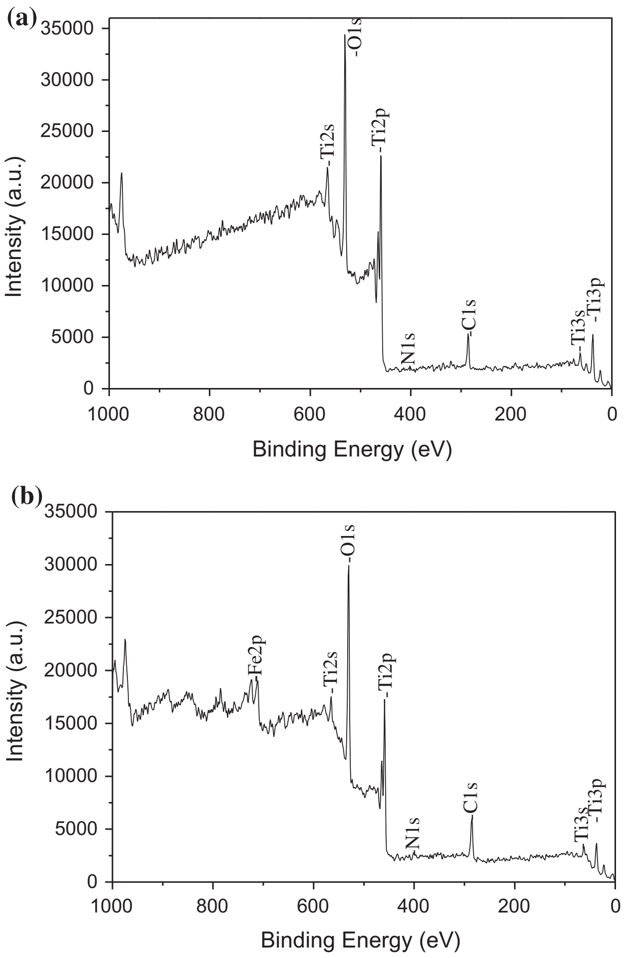

Fig. 4. XPS spectra of TiO_2 nanotubes: (a) freshly prepared and (b) deactivated.

Table 1
The elemental content on the surface of TiO_2 nanotubes

	Relative content[a]/%				
TiO_2 nanotubes	C1s	O1s	Ti2p	N1s	Cl2p
Freshly prepared	20.86	54.37	23.18	1.59	0
Deactivated	26.21	50.00	13.32	2.01	0.29

[a]The result from XPS analysis.

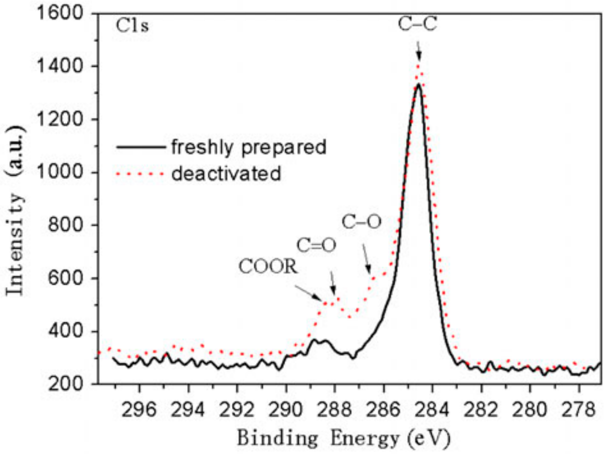

Fig. 5. The C1s XPS spectra of the two TiO_2 nanotubes.

attributed to the lattice oxygen (Ti–O) and the other at 531.5 eV was assigned to hydroxyl oxygen (–OH) or the adsorbed oxygen species (O^-, O_2^{2-}) [20–23]. Comparing Fig. 6(a) and (b), the peak strength of lattice oxygen (Ti–O) obviously reduced while that of

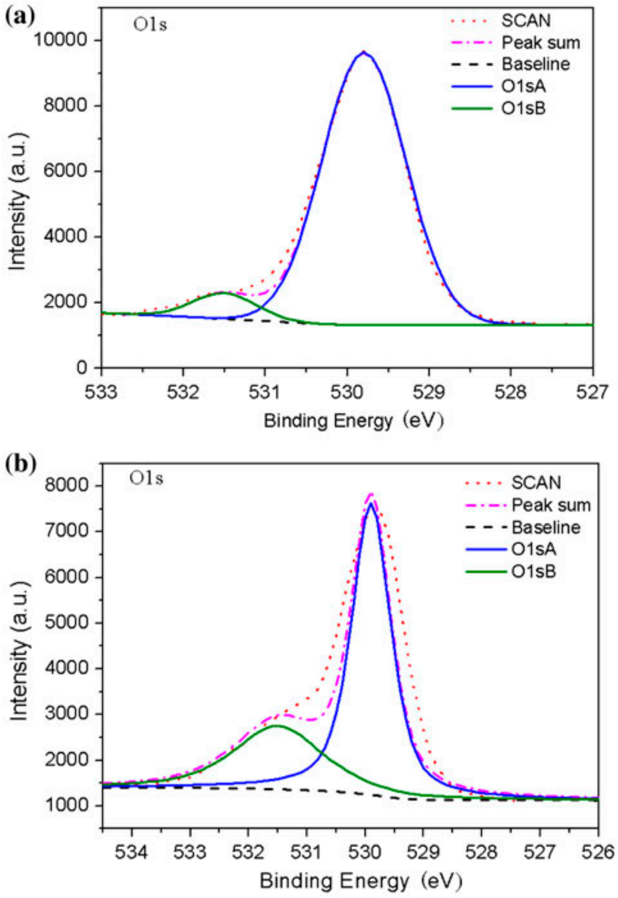

Fig. 6. The O1s XPS spectra and its peak deconvolution in TiO_2 nanotubes: (a) freshly prepared and (b) deactivated.

adsorbed oxygen species (O^-, O_2^{2-}) increased for the deactivated TiO_2 nanotubes. The lattice oxygen and adsorbed oxygen species could provide oxygen during the catalysis reaction and reduce hole-electron recombination [24]. After repeated participation in the reaction, lattice oxygen (Ti–O) of the deactivated TiO_2 nanotubes was largely consumed, and probably that was one of the main reasons for the deactivation of TiO_2 nanotubes.

In Fig. 7, The N1s XPS spectrum is showed. Lei et al. and Yang et al. [25,26] discussed the N XPS spectrum of N-doped TiO_2, and the peak at 400.1 eV were attributed to O–Ti–N. In the study of Nakamura and Mrowetz [27,28], the peaks near 399.6 eV were attributed to the adsorbed nitrogen compounds such as NOx or NHx. Yang [17] assigned the peak near 399 eV to NOx and NH_3. According to these reports, the peaks at 399.3, 399.8 eV could be the assigned to adsorbed nitrogen compounds (such as NOx or NHx), and the peak at 400.1 eV could be the assigned to O–Ti–N in this experiment. However, the strength of these peaks enhanced in the deactivated TiO_2 nanotubes. This is possibly due to the adsorption of nitrogen or nitrogen-containing product, which replaced some of the oxygen atoms from TiO_2 to form O–Ti–N [29].

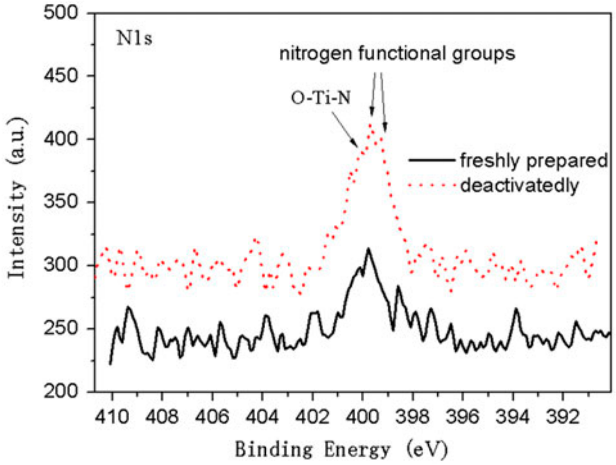

Fig. 7. The N1s XPS spectra of the two TiO_2 nanotubes.

It can be seen from Fig. 8 that the two bands assigned to Ti2p$_{1/2}$ and Ti2p$_{3/2}$, can be attributed to Ti^{4+}. It was established that titanium mainly existed in the state of O–Ti–O in TiO_2 nanotubes [17,30]. For the deactivated TiO_2 nanotubes, the strength of the two bands decreased, and accordingly, the Ti2p amount displayed a sharp decline (Table 1). In this experiment, the titanium loss from the TiO_2 nanotubes could be due to its repeated participation in the reaction. The titanium loss resulted in a decrease in the effective component, due to which the catalytic activity of the nanotubes declined.

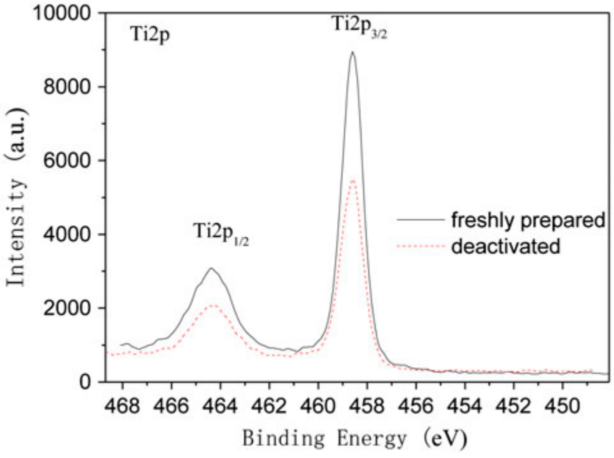

Fig. 8. The Ti2p XPS spectra of the two TiO_2 nanotubes.

3.4. The deactivation mechanism of TiO_2 nanotube

According to the analysis above, the deactivation mechanism of TiO_2 nanotube can be summarized as follows:

1. From the morphology of the TiO_2 nanotubes, the surface of the deactivated TiO_2 nanotubes was covered by some filaments, and the upper end of the nanotubes turned thinner and porous.
2. The lattice oxygen (Ti–O) in deactivated TiO_2 catalyst had been consumed heavily in the process of providing oxygen to the catalysis reaction and the hole-electron recombination decreased.
3. After participating in catalysis reactions for several times, the amount of Ti2p exhibited a sharp decline and there was a partial loss of titanium. Thus the effective constituent of TiO_2 decreased.
4. Based on the XPS analysis, compared to the freshly prepared TiO_2 nanotubes, the amount of C1s, N1s, and Cl2p increased. The contents of some carbon/nitrogen functional groups (C–O, C=O, COOR, O–Ti–N, etc.) and oxygen species (O^-, O_2^{2-}, etc.) increased in the deactivated TiO_2 nanotubes. It showed that some intermediate products were adsorbed or deposited on the surface of the TiO_2, which not only reduced the ·OH formation rate, but also hindered the adsorption of reactants.

According to the reasons listed above, the catalytic activity of TiO_2 had declined after being used for a lot of times.

4. Conclusions

By means of SEM and XPS, the morphologies, the element speciation and element content of the freshly prepared TiO_2 and deactivated TiO_2 nanotubes were comparatively studied. Great differences between the two types of TiO_2 nanotubes were found with respect to surface morphologies, element speciation and organic functional groups. For the deactivated nanotubes, some filaments were found to cover the catalysts surface, while the upper end of the nanotubes turned thinner and porous. In the deactivated TiO_2 nanotubes, the amount of C1s, N1s and Cl2p increased, while that of O1s and Ti2p decreased. It was also found that the lattice oxygen was consumed heavily, whereas the contents of some carbon/nitrogen functional groups and oxygen species increased. It showed that the effective constituent of TiO_2 decreased, and some intermediate products were adsorbed or deposited on the surface of the TiO_2, which not only reduced the ·OH formation rate, but also hindered the adsorption of reactants. That might be the deactivation mechanism of TiO_2 nanotube after being used many times.

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