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Preparation, characterization and photo-catalytic behavior of WO₃-TiO₂ catalysts with oxygen vacancies

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Abstract: TiO₂ photocatalysts compounded with WO₃ were prepared via a modified hydrolysis process and the 2% WO₃-TiO₂ catalysts with different oxygen vacancies were obtained by calcination at 873 K in H₂ atmosphere. The catalysts were identified using X-ray diffractometry (XRD), specific surface measurement (BET), electron paramagnetic resonance spectroscopy (EPR), UV-Vis diffusion refraction spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of 2% WO₃-TiO₂ with different oxygen vacancies was investigated employing splitting of water for O₂ evolution. The results indicate that appropriate oxygen vacancies can obviously improve the photocatalytic activity of 2% WO₃-TiO₂ catalysts, and using Fe³⁺ as an electron acceptor under UV irradiation in 12 h, the maximum rate for O₂ evolution is 667 μ mol/(L·h). **Key words:** TiO₂; oxygen vacancies; photocatalyst; calcination

1 Introduction

Pure titania has low photo-activity and slow photolysis speed for photo-catalysis of water, and it is very difficult to be used practically[1]. So, it is necessary to improve its photo-activity and enhance the photolysis speed for water splitting. Generally, the photo-catalytic activity of semiconductors can be improved through doping, loading and compositing the semiconductor.

Most of these doped semiconductors were used to photo-decompose organic pollutants[2–4], and some of them were used to split water with low photo-catalytic efficiency[1] because the generated electron-hole pairs on the photocatalyst surface were easy to recombine. ZHANG et al[5] reported that WO₃ thin films sputtered on TiO₂ can improve the speed of the photo-catalytic degradation of methylene blue. However, there is no further report about its application in water splitting. In our previous work[6], WO₃ compounding can improve the photo-catalytic activity of TiO₂ and the optimum concentration of compounded WO₃ is 2%. GAO et al[7]

presented that calcination can change the band gap of WO₃ using H₂ as the reducing atmosphere. HARRIS and SCHUMACHER[8], and HELLER et al[9] found that calcination using H₂ as the reducing atmosphere can prolong the life of the generated electron-hole pairs on the photocatalyst surface. CHEN et al[10], HOWE and GRATZEL[11], QIN et al[12], REKOSKE and BARTEAU[13] and LIU et al[14] reported that the oxygen vacancies(OV) and the Ti³⁺ generated after calcination using H₂ as the reducing atmosphere are major factors for the improvement of the photo-catalytic activity of TiO₂. However, most of the researchers only calcined the anatase TiO2 or WO3 in H2 atmosphere, and there is less further report about rutile TiO_2 and compounding conductors calcined in H₂ atmosphere. So, in the work, compounding conductor $(2\% \text{ WO}_3\text{-TiO}_2)$ was calcined at 873 K in the H₂ atmosphere to evaluate the effects of oxygen vacancies on the photo-catalytic activity. The reaction of photo-catalytic splitting water is carried out via two semi-reactions, of which one is the photo-reduction with H₂ evolution, and the other is the photo-oxidation with O₂ evolution with the latter being

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more difficult to achieve. Because of the low separation efficiency of photo-electrons and holes, the evolution rate of oxygen is low and it is difficult to match the rate of hydrogen evolution in the "Double-Bed" splitting water system. In the present work, in order to improve the photocatalytic activity of rutile TiO_2 , the catalyst, 2% WO_3 - TiO_2 , with oxygen vacancies is employed for the photocatalytic oxidation of water with O_2 evolution.

2 Experimental

2.1 Synthesis of 2% WO₃-TiO₂ powder with oxygen vacancies

The compounded 2% WO₃-TiO₂ was synthesized according to our previous work[6]. The powder of 2% WO₃-TiO₂ was loaded in a navicular quartz vessel to be calcined at 873 K for 2, 3, 5, 7 and 9 h, respectively, in H₂ atmosphere and the series of catalysts were titled as k1, k2, k3, k4 and k5 in turn. Especially, the catalyst 2% WO₃-TiO₂ which was calcined in air was titled as k0.

2.2 Characterization of catalysts

X-ray diffraction analysis (XRD) was used to check the coexistence of different crystal phases of the catalyst by a HATCHI D/max2250 powder X-ray diffractometer. The diffraction profiles were recorded with Cu K_{α 1} radiation (0.154 056 nm) over a 2 θ range of 10°–90° operating at 40 kV and 300 mA. A plumbaginous counter with monochromator was used.

The pore size of 2% WO₃-TiO₂ with oxygen vacancies was obtained with a Quantachrome surface area and pore size analyzer (Quantachrome Corporation, Model NOVA-1000) using N₂ as the exposed gas. Typically, 0.5–1.0 g of the catalysts was used for the measurement. The catalysts were outgassed at 300 $^{\circ}$ C before the nitrogen physical adsorption at 70 K.

Diffusing reflectance UV-Vis spectra (UV-DRS) measurements were carried out on a Purkinje TU–1901 UV/Vis spectrophotometer (Beijing, China) equipped with a diffusion reflectance accessory with an IS19–1 integrating sphere, and $BaSO_4$ powder was used as reference.

The X-ray photoelectron spectra were examined to identify the surface state of the samples by a Kratos XSAM800 spectrometer with Mg K_{α} as a radiation source. The charging effect of XPS spectra was calibrated with a carbon peak at 284.7 eV as a standard.

The in situ electron paramagnetic resonance (EPR) measurement was performed using an Endor spectrometer (JEOL JES-F1XG) at the liquid nitrogen temperature of 77 K. A microwave with the frequency of 9.44 GHz was used and its power was set at 1 mW. The g factor was obtained by taking the signal of manganese as

an internal standard. A specially designed cell in the in situ EPR measurement under H_2 environment was used. After being thermally treated, the TiO₂ samples were cooled to room temperature gradually, and then transferred together with the reactor into the resonance cavity of the EPR spectrometer still under the H_2 environment.

The results were examined by HATCHI SP-2305 gas chromatography which was equipped with a thermal conductivity detector. The argon was used as the carrier gas and the fixed phase was molecule sieve (0.5 nm).

2.3 Photo-activity tests

Photo-oxidation experiments were conducted in a cylindrical photo reactor surrounded with a circulating water jacket as described in our previous work[6]. A light source (250 W high-pressure Hg lamp or 250 W Xe, Changsha Kexing, China) was covered with a glass jacket made of quartz (cutting off < 200 nm). The reactor temperature was kept constant at 293 K using cooling water. A mixture of catalyst (2 g), distilled water (640 mL) and a required amount of $Fe_2(SO_4)_3$ as electron acceptor were put into the reactor and then argon gas was introduced into the system to degas completely. The catalyst powder was suspended by using a magnetic stirrer. The product gas oppressed the liquid in the reactor into the graduated cylinder through the outlet, so the volume of product gas could be read through the graduated cylinder indirectly. The evolution of O2 was detected by gas chromatography.

3 Results and discussion

3.1 Characterization of catalyst

Fig.1 shows the XRD patterns for 2% WO₃-TiO₂ catalysts with oxygen vacancies. From the patterns, the TiO₂ was rutile crystal, and it did not show the change of the structure of the TiO₂ after being thermally treated in reducing atmosphere. From its peak shape, it could be seen that the crystal structure was already quite complete, and the characteristic peaks of rutile TiO₂ were located at $2\theta = 27.56^{\circ}$, 36.21° , 41.38° , 54.44° , 56.74° , 69.09° corresponding to the (110), (101), (111), (211), (220) and (311) crystal faces, respectively, which were consistent characteristic peaks of TiO₂ rutile with the completely[15]. At the same time, some distinct peaks for WO₂ could be observed after being thermally treated for 2-7 h (k1, k2, k3, k4), and peaks for WO₃ disappeared after being thermally treated for 9 h (k5).

Fig.2 shows the EPR patterns for the 2% WO₃-TiO₂ catalysts with oxygen vacancies. Considering the fact that there are unpaired electrons in the structure of either Ti^{3+} or OV, the TiO₂ samples treated with different calcination time were measured by the in situ EPR to

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Fig.1 XRD patterns of 2% WO_3 -Ti O_2 catalysts with oxygen vacancies



Fig.2 EPR patterns of 2% WO₃-TiO₂ catalysts with oxygen vacancies

determine their presence and alteration during the H₂ reduction. The analytical results as shown in Fig.2 indicated that the peak with a *g* factor of 1.94 could be assigned to Ti^{3+} , since it was very close to 1.946[16] and 1.989[11]. The peak with a *g* factor of 2.00 might be assigned to OV[15]. The very weak signals of Ti^{3+} and OV were presented for the sample k1(thermally treated for 2 h), and strong signals of Ti^{3+} and OV were presented for the sample k5 (thermally treated for 9 h).

Fg.3 shows the diffusion reflectance UV-Vis spectra of the catalysts k0, k1, k3, k4 and k5, and the pattern of k2 is deleted for its very little difference with k1. All patterns show obvious absorbing band-edge, which means that the samples have semiconductor characteristic. The absorbing band-edge near 413 nm means that the samples are rutile $TiO_2[17]$, which has a good agreement with the XRD results. The UV-Vis spectra of the catalysts show that the samples have the same absorbing ability for UV-light and the different absorbing ability for visible light. Just as XU[18] reported, when the metal oxide was thermally treated in reducing atmosphere, the following reactions occurred frequently:

$$O_0^x - \frac{1}{2}O_2(g) + V_0 + e$$
 (1)
V 0 - V 0 - + e (2)

where O_0^x is the initial status of the oxygen element in TiO₂; Vo·, Vo·· are the oxygen vacancies in the metal oxide. The oxygen vacancies in the metal oxide are the centers of the positive charges, which bound electrons easily. The electrons around OV are easily excited to the conduction band and thus they took the role of the donors. The band energy of the oxygen vacancies, E_D , is near the base of the conduction band E_C [19]. Longer time calcination makes more OV for the catalysts WO₃-TiO₂, which can band more electrons. So, in the range of 420–700 nm, the optical absorption properties of the catalysts become more strong with increasing the amount of oxygen vacancies (OV). Thus, longer time calcination means better absorption for visible light.



Fig.3 Diffusion reflectance UV-Vis spectra of 2% WO₃-TiO₂ catalysts with oxygen vacancies

The particle size distribution of the compounded 2% WO₃-TiO₂ with oxygen vacancies is shown in Fig.4. It can be seen that the particle size distribution of k1 is narrower compared with samples k1–k5, and with prolonging the calcination time, the distributions become wider. The average particle size of samples k1–k5 is shown in Fig.5. With prolonging the calcination time, the average particle size becomes large fast.

XPS spectra of element W on the surface of samples k0, k3 and k5 are shown in Fig.6. For sample k0, there is only one kind of valence for W element and it is in the valence of +6. The band energies of W $4f_{7/2}$ and $4f_{5/2}$ are 35.900 eV and 37.590 eV, respectively. But the third peak "t" is for Ti 3p in TiO₂, and the band energy is 37.00 eV. All these present that W element on the surface of WO₃/TiO₂ which is not thermally treated in H₂ atmosphere is only in valence of +6. However, for



Fig.4 Size distribution of 2% WO₃-TiO₂ catalysts with oxygen vacancies



Fig.5 Dependence of average particle diameter on heating time of 2% WO₃-TiO₂ with oxygen vacancies

sample k3, there are two kinds of valences for W element on the surface of WO₃/TiO₂, +6 and +4. The band energies of W⁴⁺ 4f_{7/2}, W⁴⁺ 4f_{5/2} are 33.483 eV and 35.653 eV, respectively. For sample k5, there is only one kind of valence for W element and it is in the valence of +4, which shows that after 9 h calcination WO₃ has changed to WO₂ entirely. This is in agreement with the result of XRD.

XPS spectra of element Ti on the surface of samples k1 and k5 are shown in Fig.7. The band energies of Ti⁴⁺ $2p_{1/2}$, Ti⁴⁺ $2p_{3/2}$, Ti³⁺ $2p_{1/2}$ and Ti³⁺ $2p_{3/2}$ are 465.40, 459.500, 464.51 and 458.940 eV, respectively. For sample k1 the peak areas of Ti⁴⁺ $2p_{1/2}$ and Ti⁴⁺ $2p_{3/2}$ are 1 702.863 and 5 083.813, and those of Ti³⁺ $2p_{1/2}$ and Ti³⁺ $2p_{3/2}$ are 1 329.947 and 2 447.097, respectively. According to the peak areas, the contents, of Ti⁴⁺ and Ti³⁺ are 64.25% and 35.75%, respectively. Compared with the XPS spectra of the sample k1, the position of each peak in sample k5 is unchanged, but the peak areas are changed: 1 271.861, 4 203.676, 1 781.036 and



Fig.6 XPS patterns of W element in 2% WO₃-TiO₂ catalysts with oxygen vacancies: (a) k0; (b) k3; (c) k5

2 600.000 for $Ti^{4+} 2p_{1/2}$, $Ti^{4+} 2p_{3/2}$, $Ti^{3+} 2p_{1/2}$ and $Ti^{3+} 2p_{3/2}$, respectively. Thus, the contents of Ti^{4+} and Ti^{3+} change to 55.55% and 44.45%, respectively. So, with prolonging the calcination time, the Ti^{3+} content increases, which means that the amount of oxygen vacancies increases with increasing the Ti^{3+} content.

3.2 Photocatalytic activity of catalyst

The photocatalytic activities of the 2% WO₃-TiO₂ catalysts with oxygen vacancies were studied through the splitting of water for O₂ evolution under UV-light

irradiation. The results are presented in Fig.8. The results show that the subsequence for O₂ evolution of the catalysts are as follows: $k_3 > k_2 > k_4 > k_5 > k_1 > k_0$, under 12 h irradiation. The maximum rate for O₂ evolution is 667 µmol/(L·h) (k3). For k1 and k2, the subsequence of O₂ evolution has a good agreement with their oxygen vacancy concentration and the absorption ability within 420–700 nm. For k4 and k5, with the increase of the concentration of the oxygen vacancies, the



Fig.7 XPS patterns of Ti element in 2% WO₃-TiO₂ catalysts with oxygen vacancies: (a) k1; (b) k5



Fig.8 Photocatalytic activity for O₂ evolution of splitting water of 2% WO₃-TiO₂ catalysts with oxygen vacancies

absorbing ability becomes stronger, and the O₂ evolution rates become slower.

When the surface of the semiconductor is irradiated by the light whose energy is larger than the band gap of the semiconductor, electrons will obtain enough energy to jump onto the conduction band and become free electrons named photoelectrons. Thus, holes are left in the valence band[20]. Generally, The photocatalytic activity of photocatalyst is determined by its ability of light absorbing, the efficiency of separation between photoelectrons and holes, and the transfer rate of charge carriers[21]. With prolonging the calcination time, the particle size is enlarged, and the BET is decreased. The decrease of BET leads to the weakness of the absorbing ability and the photocatalytic reaction for H_2 or O_2 evolution in this triphase reactor of solid-liquid-gas. The photo-redox reaction proceeds on the surface of the catalysts. So, on one hand the decrease of the BET of catalysts leads to its lower O2 evolution rate. On the other hand, when the calcination time is prolonged, the oxygen vacancy concentration increases. Appropriate oxygen vacancies can obviously improve the efficiency of the separation of electrons and holes and the absorbing ability for Vis-light, so as to improve the photocatalytic activity of the photo-catalysts[19]. However, too much oxygen vacancies could bond too much charge, leading to the decrease of the efficiency of electron-hole separation and photocatalytic activity.

4 Conclusions

1) The 2% WO₃-TiO₂ catalysts with oxygen vacancies were prepared using H_2 atmosphere calcined at 873 K. The XRD patterns show that some distinct peaks for WO₂ can be observed after being thermally treated for 2 h (k1), and peaks for WO₃ disappear after being thermally treated for 9 h (k5).

2) When the calcination time is prolonged, the particle size is enlarged. The EPR results show that very weak signals of Ti^{3+} and OV are present after being thermally treated for 2 h, and strong signals of Ti^{3+} and OV are present after being thermally treated for 5 h. The UV-Vis spectra of the catalysts show that the samples have the same absorption ability of UV-light and different absorption ability of visible light. Longer time calcination means better absorption of visible light.

3) From the XPS spectra, the content of Ti^{3+} increases with the calcination time.

4) Using Fe³⁺ as the electron acceptor, the maximum rate for O_2 evolution is 667 μ mol/(L·h) under UV irradiation in 12 h.

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