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# Photocatalytic Oxidation of Orth-nitrophenol by $SO_4^{2-}/TiO_2$-$WO_3$

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**Abstract**: The photocatalysts of $SO_4^{2-}/TiO_2$-$WO_3$ with different loading of $SO_4^{2-}$ anion from different concentration of $H_2SO_4$ were prepared. The photocatalytic effect of the photocatalysts on orth- nitrophenol was investigated. It was found that the photocatalytic activity of $SO_4^{2-}/TiO_2$-$WO_3$ was higher than that of $TiO_2$-$WO_3$. The catalytic activity of $SO_4^{2-}/TiO_2$-$WO_3$ depends on the sulfuric acid concentration and the best sulfuric acid concentration, calcination temperature and doping of tungsten oxide were 0.2 mol. $L^{-1}$, 550 ℃ and w($WO_3$) = 3%, respectively. The experimental results showed that the degradation rate of orth-nitrophenol approximately follows the first order kinetics.

**Key words**: $SO_4^{2-}/TiO_2$-$WO_3$; Superacid; Photocatalytic oxidation; orth- nitrophenol;
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Recently, photo catalytic oxidation of pollutant in water with semiconductor photocatalyst such as titanium-dioxide has become very hot in environmental science. But the common titanium-dioxide semiconductor photocatalyst has lower quantum yield (approximately at the rate of 4%). The present research measures to overcome the shortcoming of $TiO_2$ are mainly transitional metal-ion doping, noble metal superficial deposition, diminishing grain size, semiconductor recombination, surface photosensitization, etc. It has been reported that semiconductor photocatalyst can be compounded with $WO_3$ and $TiO_2$, which can improve the photocatalytic performance of $TiO_2$. In the study mentioned in this paper, $TiO_2$-$WO_3$ is modified by $SO_4^{2-}$ and the solid ultra-acid $SO_4^{2-}/TiO_2$-$WO_3$ was compounded. Orth-nitrophenol, which is a representative substance in pollutant, is selected as the target pollutant, and high voltage mercury lamp of 125 w is selected as the light source. Photochemical catalytic degradation of orth-nitrophenol through $SO_4^{2-}/TiO_2$-$WO_3$ compounded by acidifying with ultra-acid of various acid concentrations was studied in home-made photochemical catalytic reactor. And the results have proved that this method is very effective [1].

## 1 Experimental

### 1.1 Preparation of photocatalyst

$Ti(OC_4H_9)_4$ of 17 mL was dissolved in absolute alcohol of 22 mL. The mixed liquor consisting of 5 mL glacial acetic acid, 2 mL deionized water and 22 mL absolute alcohol was slowly dropped in while agitating. Natrium wolframate water-solution of 0.058, 0.176 and 0.300 g was slowly dropped in separately with continuous agitating during the forming of uniform and hyaloid $TiO_2$-sol without forming of gel. Then the mixture was agitated continuously for 3 h until the gel was formed, then it was left standing for 48 h, dried at the temperature of 100 ℃ and grinded into powder. So the $TiO_2$-$WO_3$ powder with $WO_3$ doped amount of 1%, 3% and 5% was produced respectively.

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With the matching of 5 mL $H_2SO_4$ solution per gram of $TiO_2$-$WO_3$, $TiO_2$-$WO_3$ was impregnated respectively in sulphuric acid solution with concentrations of 0.1 mol. $L^{-1}$, 0.2 mol. $L^{-1}$ and 0.3 mol. $L^{-1}$ for 6 h, dried at the temperature of 80 ℃, calcinated in muffle furnace at the temperature of 450 ℃、550 ℃、650 ℃ for 3 h respectively. Accordingly $SO_4^{2-}$/ $TiO_2$-$WO_3$ photocatalyst was produced.

### 1.2 Photochemical catalytic reaction procedure

Photochemical catalytic reaction was performed in the home-made photochemical catalytic reactor of 500 mL (with glass jacket). 0.2 g photocatalyst was mixed uniformly with 400 mL water solution of 20 mg/L orth-nitrophenol, then the mixture was put into the reactor. The solution was illuminated directly with 125 W high voltage mercury lamp and the solution surface was 12 $cm^2$ above from the light source. At the same time, air was ventilated to the solution from the bottom at the rate of 120 mL/min. The sample of 5 mL reactive liquid was taken every 15 minutes with pipet. The photocatalyst was centrifugally separated. The absorption spectrum of the reactive liquid was determined by 752UVL grating spectrophotometer. The change of orth-nitrophenol concentration in water solution can be measured according to the absorbance at 278nm and the experimental temperature was controlled in range of 22 ± 1 ℃.

## 2 Results and discussion

### 2.1 Effect of sulphuric acid concentration on photochemical catalytic activity

Table. 1 shows the degradation rate of orth-nitrophenol respectively treated with $SO_4^{2-}$/ $TiO_2$-$WO_3$ photocatalyst impregnated in different sulphuric acid concentration at different reaction time of 15 min, 30 min, and 45 min, respectively. All photocatalysts have been calcinated at the temperature of 550 ℃. It can be seen that the photochemical catalytic activity reaches its maximum when the sulphuric acid concentration is 0.2 mol. $L^{-1}$.

**Table 1 Effect of degradation rate of orth-nitrophenol on photocatalysts with the different $SO_4^{2-}$ quantity**

| Catalyst mol. $L^{-1}$ reaction time min | non acidified $TiO_2$-$WO_3$ | | | 0.1 mol. $L^{-1}$ $SO_4^{2-}$/$TiO_2$-$WO_3$ | | | 0.2 mol. $L^{-1}$ $SO_4^{2-}$/$TiO_2$-$WO_3$ | | | 0.3 mol. $L^{-1}$ $SO_4^{2-}$/$TiO_2$-$WO_3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 15 | 30 | 45 | 15 | 30 | 45 | 15 | 30 | 45 |
| Degradation ratio of orth-nitrophenol (%) | 41 | 63 | 76 | 53 | 75 | 85 | 77 | 97 | – | 59 | 81 | 92 |
| Rate constant $min^{-1}$ | 0.0333 | | | 0.0462 | | | 0.1074 | | | 0.0570 | | |

Figure. 1 shows the relationship of $lnC_0/C_t$ and reaction time t. It is clear that the change of orth-nitrophenol's concentration with reaction time is a linear relationship, which proves that the photochemical catalytic degradation-reaction of orth-nitrophenol is first-order reaction. Its rate equation is expressed as $lnC_0/C_t = kt$ (where k is reaction rate constant, $C_0$ and $C_t$ respectively represent the concentration of orth-nitrophenol at the incipient and reacting time). The calculated rate constant according to kinetic equation of first order reaction is listed in Table. 1. From Fig. 1, it can be seen that the rate constant is in line with degradation rate of orth-nitrophenol, and the photochemical catalytic activity of 0.2 mol. $L^{-1}$ is the highest.

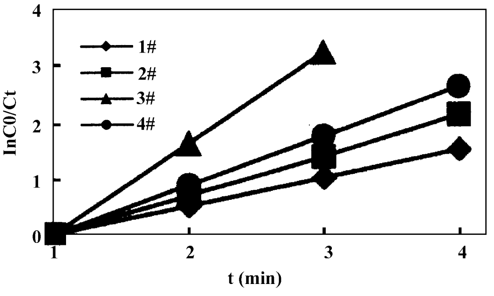

Fig. 1 The relationship of $lnC_0/C_t$ and reaction time t
1#: $TiO_2$-$WO_3$; 2#: 0.1 mol. $L^{-1}$;
3#: 0.2 mol. $L^{-1}$; 4#: 0.3 mol. $L^{-1}$

Through XRD analysis (Figure 2), it can be found that both acidified and non acidified $TiO_2$-$WO_3$ photocatalyst exist in two crystal forms of anatase and rutile. The activity of these $TiO_2$ catalysts with mixed crystal forms is relatively high. It can be seen from the infrared spectrum of $SO_4^{2-}$/ $TiO_2$-$WO_3$ (Figure. 3) that the sample of $SO_4^{2-}$/$TiO_2$-$WO_3$ which has been calcinated at the temperature of 550 ℃ has absorption peaks at 1384, 1131and 1 042cm$^{-1}$, which indicates that there is sulphur-containing substance on the surface of catalyst where a strong acid center is formed. This is consistent with the result that some $SO_4^{2-}$/ MxOy solid ultra-acids have absorption peaks, which has been reported. There are two strong and wide absorption peaks at 1636 and 3 415cm$^{-1}$, respectively, which can be presumed bending vibration of adsorbed water and stretching-vibrating absorption of -OH. There is a sharp-pointed absorption peak at 1 383 cm$^{-1}$ in the infrared spectrum, which indicates that the sample surface of catalyst at 1 383 cm$^{-1}$ has chelate dipolar bonds with $SO_4^{2-}$. It can be inferred according to the foregoing construction that electrons on the metal titanium will migrate to oxygen atom by the influence of S = O strong attracting electronic inductive effect. So the electropositivity of the surface titanium ion is potentized significantly, which is beneficial to surface migration of the photogenic electron on the $TiO_2$ conduction band and thus improves the photochemical catalytic quantum efficiency and makes photochemical catalytic activity of the $TiO_2$-$WO_3$ catalyst potentized[2~3]

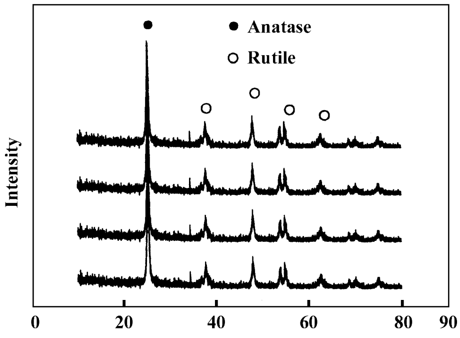

Fig. 2 XRD partterns of different catalyst

1. $TiO_2$-$WO_3$; 2. 0.1 mol. L$^{-1}$(550 ℃); 3. 0.2 mol. L$^{-1}$(550 ℃); 4. 0.3 mol. L$^{-1}$(550 ℃)

## 2.2 Effect of calcination temperature on catalyst activity

The catalyst activity of $SO_4^{2-}$/ $TiO_2$-$WO_3$ produced at different calcination temperature is different. Table 2 shows the degradation rate of orth-nitrophenol treated with different $SO_4^{2-}$/ $TiO_2$-$WO_3$ photocatalyst calcinated at different calcinations temperatures. For different temperatures, catalyst activity calcinated at the temperature of 550 ℃ is the highest. It is because of sulphur-containing amount and specific surface area of the catalyst decreased when the calcination temperature is too high, which leads to activity descent. But ultra-acid can't be produced if the calcination temperature is too low. Thus the calcination temperature is usually set at the range of 450 ℃ ~ 650 ℃, namely calcination is performed near the decomposed temperature of ultra-acid center on the catalyst's surface.

**Table 2 Degradation rate of orth-nitrophenol on 0.2 mol · L$^{-1}$ $SO_4^{2-}$/ $TiO_2$-$WO_3$ photocatalysts with the different calcination temperatures**

| Temperature (℃) | Degradation rate of orth-nitrophenol (%) 15 min | 30 min | 45 min |
|---|---|---|---|
| 450 | 66 | 87 | 93 |
| 550 | 77 | 97 | - |
| 650 | 68 | 89 | 94 |

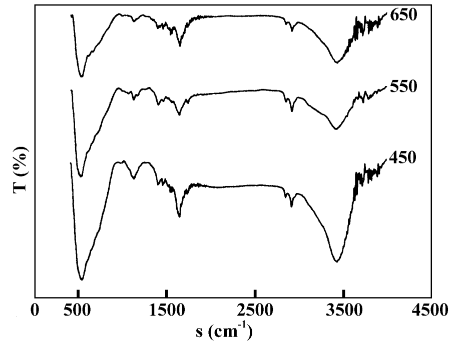

Fig. 3 IR spectra of 0.2 mol. L$^{-1}$ $SO_4^{2-}$/ $TiO_2$-$WO_3$ calcinated at different temperatures

## 2.3 Effect of wolfram doping amount on catalyst activity

The catalyst activity of $SO_4^{2-}$/ $TiO_2$-$WO_3$ is the highest when w ($WO_3$) = 3% and the degradation rate of 30 min is up to 97%. The rate is 54% higher than that of $TiO_2$-$WO_3$. Some related findings show that photogenic electrons on the $TiO_2$ conduction band can be efficiently transferred to the $WO_3$ conduction band when doping $WO_3$, so the oxygen is deoxidized and W(Ⅴ) shape is formed. In addition, since the 62 pm radius of $W^{6+}$ ion is close to the radius of $Ti^{4+}$ ion (60pm), $W^{6+}$ can replace $Ti^{4+}$ in the lattice position so that it is more easy to absorb the photogenic electron produced near $TiO_2$. However, the formed electron transferring center may be changed into electron recombinating center once the doping amount of wolfram is too much, thus the efficiency of separating the photogenic electron from the hole will decrease, which will make photochemical catalytic activity of the catalyst degraded[4].

## 3 Conclusions

The photochemical catalytic activity of $TiO_2$-$WO_3$ is improved significantly when it is acidified by ultra-acid. the best processing condition for $TiO_2$-$WO_3$ is impregnated by 0. 2 mol. $L^{-1}$ $H_2SO_4$ solution for 6h, doped 3% $WO_3$, and calcinated at the temperature of 550 ℃ for 3 h. 97% Orth-nitrophenol can be degraded in 30 min. Dynamics study indicates that the photochemical catalytic degrading rate of orth-nitrophenol follows the kinetic rule of first order.

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# $SO_4^{2-}/TiO_2$-$WO_3$光催化氧化邻硝基苯酚

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**摘 要:** 采用不同浓度的硫酸溶液浸渍处理 $TiO_2$-$WO_3$, 制得不同 $SO_4^{2-}/TiO_2$-$WO_3$光催化剂. 考察了光催化剂对邻硝基苯酚溶液的光催化行为. 发现 $SO_4^{2-}/TiO_2$-$WO_3$的光催化活性高于 $TiO_2$-$WO_3$的光催化活性, 浸渍液中 $H_2SO_4$的浓度对 $SO_4^{2-}/TiO_2$的催化活性有一定的影响, $H_2SO_4$溶液的最佳浓度为0.2 mol/L, 最佳焙烧温度为550 ℃. 最佳 $WO_3$的掺杂量 w($WO_3$)为3%. 催化降解过程符合一级动力学规律.

**关键词:** $SO_4^{2-}/TiO_2-WO_3$; 超强酸; 光催化氧化; 邻硝基苯酚