

# 半导体氧化物超细粉末对 Cr(VI) 的光催化还原作用研究\*

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**摘要** 对不同反应条件下 ZnO/TiO<sub>2</sub> 超细粉末对水溶液中六价铬的还原作用影响进行了研究与对比。结果表明, 半导体氧化物 ZnO/TiO<sub>2</sub> 对水溶液中六价铬有明显的光催化还原作用, ZnO 比 TiO<sub>2</sub> 的效果更显著, 经 90min 处理后, Cr(VI) 含量从初始的 100 mg/L 降为 0.47 mg/L 以下; 可降解有机物的存在能促进反应的进行, 提高六价铬的转化率; 随着 pH 值的升高, 光催化效果减弱。本文还对反应机制和反应速度与反应物浓度的关系, 以及废水处理过程中移植(替代)现有 Cr(VI) 处理工艺(还原法)的可能性进行了探讨。

**关键词** 光催化, 六价铬, TiO<sub>2</sub>, ZnO。

半导体氧化物作为光催化材料, 可催化降解多种有机污染物<sup>[1-4, 6-11]</sup>。Cr(VI) 是工业废水中一种常见的有毒污染源, 目前, 工业上对其主要采取添加还原剂进行处理, 此法存在一些明显的缺点。为此, 笔者等开展了利用光催化材料的还原作用处理 Cr(VI) 的研究工作。一般来讲, 光催化反应均采用半导体粉末做为催化剂, 粉末粒度越细, 则催化效果越佳。研究中采用自制的 TiO<sub>2</sub>、ZnO 超细粉<sup>[12]</sup>作为催化剂, 其粒度在 0.1 μm 以下, 效果比较理想。

## 1 实验部分

### 1.1 实验工艺过程

用结晶铬酸钠(NaCrO<sub>4</sub> · 4H<sub>2</sub>O, A. R.)和稀硫酸配制 pH=2.5, 六价铬浓度一定的铬酸钠溶液。

在 100 ml 烧杯中加入一定量的 TiO<sub>2</sub>/ZnO 粉末, 然后加入上述铬酸钠溶液 80 ml, 在磁力搅拌的同时, 进行光照(400 W 高压汞灯或太阳光), 一定时间后, 取出试样, 进行过滤。

用 NaOH 调节过滤后溶液的 pH 值, 使 pH 达到 8, 沉淀完成后, 过滤, 取滤液进行分析。整个实验过程如图 1 所示。

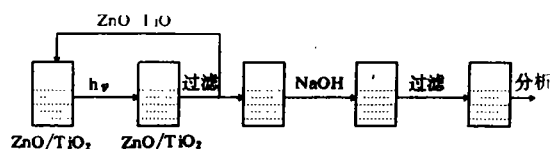


图 1 光催化还原六价铬的工艺流程示意图

### 1.2 样品分析

初始铬酸钠溶液与处理后溶液的铬浓度均采用火焰原子吸收光谱进行定量分析。

## 2 实验结果与讨论

### 2.1 TiO<sub>2</sub>/ZnO 光催化还原作用的对比

从图 2 可以看出, 半导体氧化物在 400 W 紫外灯照射, 初始浓度 100 mg/L, 氧化物加入量 4 g/L 条件下, 对 Cr(VI) 有明显的还原作用。ZnO 的催化效果要优于 TiO<sub>2</sub>, 经 90 min 照射后, Cr(VI) 含量从初始的 100 mg/L 迅速降为 0.47 mg/L 以下(处理后溶液的铬总含量为 0.47 mg/L, 其中包括未沉淀完全的 Cr(III)), 达到了国家废水排放标准。

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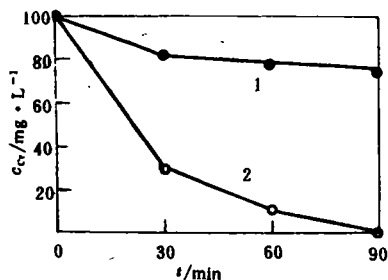


图2 Cr含量随时间变化关系

1. TiO<sub>2</sub> 2. ZnO

## 2.2 不同光照条件对Cr(VI)转化效率的影响

为研究 ZnO 超细粉在废水处理方面的实际应用,用太阳光做光源,ZnO 粉加入量 4 g/L,Cr(VI)初始浓度 100 mg/L,与紫外灯照射效果进行了对比,如图 3 所示。结果表明,2 种光源的效率接近,太阳光完全可以用于工业中含 Cr(VI)的废水处理。

由于光催化过程与目前常用的 Cr(VI)还原法处理过程极其相似,即酸化、还原、碱化、过滤,又不需要特殊的附加光源,所以在不进行大的设备、流程改动的基础上,即可将光催化还原应用于现有的工业 Cr(VI)处理工艺中。目前工艺中,由于在还原过程中需添加硫酸亚铁、亚硫酸盐等还原剂,而产生大量沉渣,若处理不当,还会产生二次污染。而在这种新型处理工艺中,引入的半导体氧化物只作催化剂,并不直接参加反应,可循环使用,而且所得到的纯 Cr(OH)<sub>3</sub> 沉淀,容易作为副产品回收。

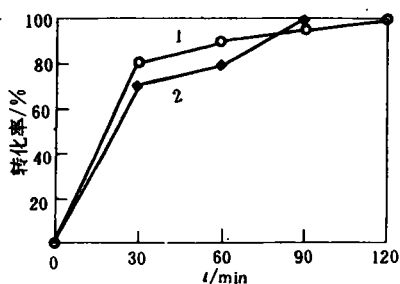


图3 不同光照条件下,六价铬转化率随时间变化曲线

1. 太阳光照射 2. 紫外照射

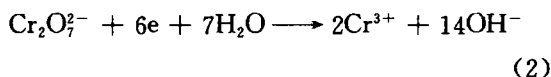
## 2.3 有机添加剂对还原作用的影响

从图 4 中可以看出,溶液中加入酒精,对 TiO<sub>2</sub> 的光催化作用有明显的促进作用(400 W

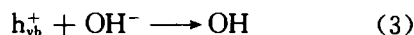
紫外灯照射,Cr(VI)初始浓度 200 mg/L,TiO<sub>2</sub> 加入量 4 g/L)。前面提到,光化学效应是形成一个具有强氧化-还原作用体系,则 Cr(VI)的还原与有机物的氧化就成为共轭反应。反应式如下:

$$\text{ZnO/TiO}_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+ \quad (1)$$

$e_{cb}^-$  与  $\text{Cr}_2\text{O}_7^{2-}$  (酸性条件下,Cr(VI)以  $\text{Cr}_2\text{O}_7^{2-}$  形式存在)反应:



$h_{vb}^+$  与 OH 反应形成活泼的 OH 基<sup>[8]</sup>



OH 具有极强氧化性,使有机物降解氧化<sup>[1-4]</sup>。

可以看出,正是由于共轭反应的存在,降低了空穴-电子对的复合机会,促进了反应的进行,因此,对既含 Cr(VI)又含有机污染物的废水,光催化处理效果将更加显著。

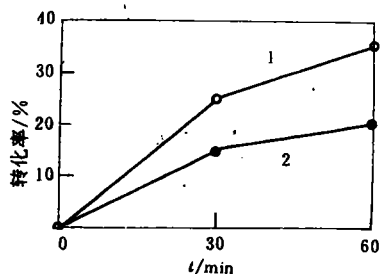


图4 有机添加剂对光催化还原作用的影响:

1. 纯 TiO<sub>2</sub> 2. 加酒精

## 2.4 pH 值对 Cr(VI)还原作用的影响

实验中发现,随着 pH 的降低,反应速度加快,Cr(VI)的转化率提高,当溶液为中性或碱性时,Cr(VI)的还原则十分微弱。对 pH 值为 2.5 的酸性溶液,经 60 min 照射后,pH 值大约要提高 2 左右。这可以从反应(2)中得到合理解释。因为反应产生的 OH<sup>-</sup> 会引起 pH 值升高,并阻碍反应的进一步进行。

## 2.5 反应速度与反应物浓度的关系

根据质量作用定律,如果反应(2)为基元反应,其反应速度可表达为:

$$v = k \cdot c_{\text{Cr}} \cdot c_e^2$$

其中, $v$  为反应速度, $c_{\text{Cr}}$  为 Cr(VI)浓度, $c_e$  为自由电子浓度。

当光照强度一定, 氧化物粉末浓度一定时,  $c_0$  基本保持常数, 则反应呈一级反应. 图 5 为太阳光照射下, 铬初始浓度为 100 mg/L, ZnO 加入量为 4 g/L 时的  $-\ln c/c_0-t$  关系图. 其中  $c$  为反应进行到  $t$  时间的 Cr(VI) 浓度,  $c_0$  为初始 Cr(VI) 浓度. 从图 5 可以看出, 其基本呈线性关系, 其它反应条件下也有类似关系, 说明反应确为一级反应, 即反应速度与反应物浓度成正比. 这与文献[9]在研究  $\text{TiO}_2$  降解有机物动力学时所得结果是一致的.

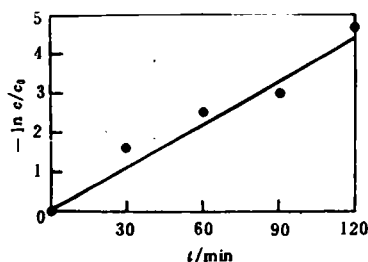


图 5  $-\ln c/c_0-t$  关系图

### 3 结论

(1) 半导体氧化物 ZnO/ $\text{TiO}_2$  对水溶液中 Cr(VI) 有明显的光催化还原作用. ZnO 比  $\text{TiO}_2$  的效果更显著, 经 90 min 处理后, 铬含量可达

到国家废水排放标准.

(2) 可降解有机物的存在能促进反应的进行, 提高 Cr(VI) 的转化率.

(3) 随着 pH 值的升高, 光催化效果减弱.

(4) 反应速度与反应物浓度成正比, 为一级反应.

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中会产生氯仿, 在相同的 pH 和温度下, 当氯浓度恒定时, 氯仿的生成速度主要取决于 HA 的浓度. 浓度愈高、速度愈快. 因此设法降低原水中 HA 含量是降低氯仿含量的有效方法.

pH 与温度对氯仿的生成速度也产生很大的影响. 研究表明, pH 在 7.3—9.0 范围内氯仿生成速度较高, 而温度愈高则氯仿的生成速度愈快.

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In order to apply plasma technology in environmental protection, and find a new way to treat air pollutants, the experiment selected  $\text{CF}_2\text{ClBr}$ , a kind of chemical stable extinguisher as the research material, and the influence of  $\text{He}$ ,  $\text{N}_2$ ,  $\text{O}_2$  and air in degradation of  $\text{CF}_2\text{ClBr}$  by plasma was studied, and  $\text{CF}_2\text{ClBr}$  was successfully degraded at normal pressure. The main products of degradation were similarly to only degrading  $\text{CF}_2\text{ClBr}$  when  $\text{He}$  or  $\text{N}_2$  was added to the degradation system. The degradation products was mainly  $\text{CF}_2\text{O}$ ,  $\text{Br}_2$ ,  $\text{Cl}_2$  in the presence of  $\text{O}_2$  and air. The order of extra gases influencing degradation of  $\text{CF}_2\text{ClBr}$  was following:  $\text{He} < \text{N}_2 < \text{O}_2$ , air.

**Key words:**  $\text{CF}_2\text{ClBr}$ , plasma, degradation.

**Photodissociation of  $\text{CF}_2\text{ClBr}$  at 185 nm of Ultraviolet Radiation.** Duan yang et al. (Institute of Environmental Science, Fudan University, Shanghai 200433), Zhu Shaolong et al. (Institute of Electric Light Sources, Fudan University, Shanghai 200433); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 24—26

The photodissociation of  $\text{CF}_2\text{ClBr}$  and its photooxidation at the existence of  $\text{O}_2$  at 185 nm of ultraviolet radiation were studied using low pressure mercury lamp. The results showed that the dissociation of pure  $\text{CF}_2\text{ClBr}$  at 185 nm of ultraviolet radiation is a balance reaction, and the ultimate dissociation rate is about 26%. The dissociation of  $\text{CF}_2\text{ClBr}$  is a first order reaction and the rate constant is  $1.70 \times 10^{-3} \text{ s}^{-1}$  at the existence of  $\text{O}_2$ . The dissociation procedure of  $\text{CF}_2\text{ClBr}$  at 185 nm of ultraviolet radiation and the mechanism of its photoreaction with  $\text{O}_2$  was discussed.

**Key words:**  $\text{CF}_2\text{ClBr}$ , photodissociation, photooxidation.

**Computation of the A-Weighted Insertion Loss for Sound Barriers Used in Traffic Noise Control of Elevated Complex Road.** Chen Ziming and Wang Shuquan (Dept. of Physics, Ocean University of Qingdao, Qingdao 266003); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 27—30

In order to solve the problem of computing the insertion loss of sound barriers used on elevated complex roads, this paper presented the computation method of the A-weighted insertion loss of sound barriers installed at different positions for different types of vehicles, different speeds, and different vehicle flows. It was found that the computational results are generally in agreement with measurements, the error is less than 1.5 dB(A). This model is of practical significance for the estimation of traffic noise of elevated complex roads with sound barriers, especially at night when traffic flow is relatively low.

**Key words:** traffic noise, elevated complex road, sound barrier, insertion loss computation.

**Basic Study for the Formation of Trihalomethanes (THMs) in Chlorination Process of Humic Acid.** Pan

Jinfang and Zhang Danian (East China University of Science & Technology, Shanghai 200237), Maeda Yasuaki and Kitano Masaru (Osaka Prefecture University, Sakai, Osaka, Japan); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 31—33

In order to study carcinogenic by-products for example chloroform in disinfection of drinking water with chlorine, the research on reaction between low molecular weight humic acid and sodium hypochlorite which produced chloroform was carried out. The experimental results indicated that under certain temperature, certain concentration of sodium hypochlorite and pH, the amount of chloroform produced increased with the increase of the concentration of humic acid. When pH was in the range of 7.3—9.0, the chloroform-producing rate was the fastest. When pH was higher than 9.0, the chloroform-producing rate decrease with the increase of pH. The amount of chloroform produced was in direct proportion to temperature. The activated energy that chlorinated humic acid to chloroform was 51.8 kJ. So the effective way to decrease the concentration of chloroform was to decrease the concentration of humic acid in the water.

**Key words:** humic acid, chlorination, chloroform.

**A Study on Photocatalytic Reduction of  $\text{Cr(VI)}$  in Aqueous Solutions Using Ultrafine Powders of Oxide Semiconductors.** Dai Xiaming, Chen Yonghua et al (Beijing Fine Ceramic Laboratory, Tsinghua University, 102201, Beijing); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 34—36

The photocatalytic reductions of  $\text{Cr(VI)}$  in aqueous suspensions of  $\text{ZnO/TiO}_2$  under UV illumination were investigated. The study had been performed by determination of the amount of  $\text{Cr(VI)}$  photoreduced at different kinds of irradiations, different reaction times, pH and organic additives. The results obtained showed that the concentration of  $\text{Cr(VI)}$  decreases apparently by the new kind of treatment. The efficiency of  $\text{ZnO}$  is higher than  $\text{TiO}_2$  in same reaction condition. The concentration of  $\text{Cr(VI)}$  is reduced from 100 mg/L to below 0.47 mg/L after 90 min treatment by using  $\text{ZnO}$  powder as catalyst at optimum condition. It was found that the presence of organic additive and the lower pH can increase the reduction ratio of  $\text{Cr(VI)}$ . The reaction mechanism and the relation between reaction rate and  $\text{Cr(VI)}$  concentration were also discussed. The technique is convenient for existing industrial processing of reduction of  $\text{Cr(VI)}$ .

**Key words:** photocatalytic reduction,  $\text{Cr(VI)}$ ,  $\text{ZnO/TiO}_2$ .

**Pressurized Thermogravimetric Study on the Reaction of Desulfurization by Limestones and Dolomites.** Qiu Kuanrong et al. (Dept. of Coal Utilization, China, Univ. of Min. & Tech., Xuzhou 221008); *Chin. J. Environ. Sci.*, 17(6), 1996, pp. 37—39

The desulfurization reaction of limestones and dolomites was studied by pressurized thermogravimetric analysis method. Results showed that the rate of converting  $\text{CaCO}_3$  to  $\text{CaSO}_4$  of four limestones and two dolomites is in-