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Photocatalytic Reduction of Wo-3-Tio-2 Composite Catalyst in Cr (Ⅵ) Ion

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ABSTRACT. *In the presence of strong acidity and salicylic acid, the photoreduction process of Cr (Ⅵ) ion with different concentrations was in accordance with the zero order kinetic model, The kinetic model of photocatalytic reduction of Cr (Ⅵ) on TiO2-WO3 composite catalyst still accords with the zero order reaction of surface catalysis*

KEYWORDS: *Photocatalysis, Hexavalent chromium ion, Titanium dioxide, Tungsten trioxide, Composite semiconductor*

1. Introduction

The research on Photocatalytic Properties of semiconductors with solar chemical conversion and storage as the main background began in 1917, but the research on photocatalytic degradation of pollutants in water by semiconductor materials began in the 1980s. In 1976, S.N. Frank et al. Used TiO2 powder to catalyze the photodegradation of pollutants in water with satisfactory results. Based on the pioneering work of S.N. frank, The research work of photocatalytic oxidation has been extended to metal ions. The research of photocatalytic reduction has guiding significance for the treatment and purification of industrial sewage and waste water by making full use of sunlight. Cr (Ⅵ) ion has strong carcinogenicity, and its toxicity is more than 100 times higher than Cr (Ⅲ), The maximum allowable amount of Cr (Ⅵ) ion in the discharged industrial wastewater is less than 0.5mg/l[1]. In this paper, the photocatalytic reduction of Cr (Ⅵ) ion in the presence of strong acidity and salicylic acid is discussed with the mixed catalyst of TiO2 and WO3.

2. Experimental Part

2.1 Mechanism of Photocatalytic Reduction

The results show that TiO2, WO3, SrTiO3, ZnO, CDs and other semiconductor catalysts have good catalytic performance. In this paper, the mixture of TiO2 and WO3 powder is used as catalyst. When there is no other electron donor, Cr (Ⅵ) ion can be reduced to trivalent from the photoexcited semiconductor catalyst. The reaction can be generally expressed as TiO2 + HV TiO2 (E - + H +, WO3)+ Hvwo3 (E - + H +), 16h + + 2cro2-4 + 6e - 2C R3 + + 8H2O or 2cr2o2-7 + 28h + + 12e - 4cr3 + + 14h2o are used to excite the electron absorption light energy on the semiconductor valence band to the conduction band, so that a highly active electron (E -) with negative charge is generated on the conduction band, and a hole (H -) with positive charge is generated on the valence band, forming an oxidation-reduction system, The absorption (E -) of Cr (Ⅵ) is reduced to Cr (Ⅲ).

2.2 Instruments, Drugs and Reagents, Experimental Methods

(1) Main Instruments

721b spectrophotometer, Shanghai No.3 analytical instrument factory; 1-2 constant temperature magnetic stirrer, Shanghai sile instrument factory; 800 centrifugal precipitator, Shanghai surgical instrument factory; fa2004a electronic balance; infrared fast dryer; 250 W high pressure mercury lamp (wavelength 300 nm).

(2) Drugs and Reagents

K2 Cr2O7 (AR), nitric acid (AR), distilled water, DPC (AR), acetone (AR), salicylic acid (AR), TiO2

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(commercially available), WO3 (commercially available)

(3) Experimental Method

In this experiment, take different concentrations of test solution under normal temperature and pressure, respectively, add 0.5ml nitric acid (1:1), 5ml developer solution, about 0.100g catalyst (tio2:wo3 = 1:1), illuminate with 250W high pressure mercury light, take reaction solution every 10min, centrifugate for about 10min, take the upper clear solution to determine its absorbance, According to the abs-c standard working curve, find out the corresponding concentration and calculate its conversion rate.

3. Results and Discussion

3.1 Discussion on the Kinetics of Photocatalysis

In order to study the effect of different initial concentration on the photocatalytic reduction of Cr (Ⅵ) ion and the possible kinetic model of Cr (Ⅵ) ion photocatalytic reduction under the condition of mixed catalyst and strong acidity, The initial concentration of Cr (Ⅵ) of 1.5 × 10^{-5} mol / L, 1.25 × 10^{-5} mol / L, 1.0 × 10^{-5} mol / L, 0.75 × 10^{-5} mol / L, and 0.5 × 10^{-5} mol / L were selected to study the change of concentration and conversion rate with time. 0.50 × 10^{-5} mol / L, 0.75 × 10^{-5} mol / L, 1.00 × 10^{-5} mol / L, 1.25 × 10^{-5} mol / L, 1.50 × 10^{-5} mol / L, CC r (Ⅵ) The conversion rates under ion photocatalytic reduction were 59.26%, 51.35%, 48.00%, 47.93%, 48.00%, and the absolute amounts of degradation were 0.32 × 10^{-5} mol / L, 0.38 × 10^{-5} mol / L, 0.48 × 10^{-5} mol / L, 0.58 × 10^{-5} mol / L, 0.72 × 10^{-5} mol / L. According to this, the amount of degradation is related to the initial concentration of the reactants.The larger the initial concentration, the more the absolute amount of degradation.

It can be seen from the curve of concentration time of Cr (Ⅵ) ion photocatalytic reduction with different initial concentration in Figure 1, There is a linear relationship between the concentration and time in the reaction process, which is in line with the characteristics of zero order reaction. Therefore, the kinetic process of Cr (Ⅵ) photocatalytic reduction under the action of TiO2-WO3 mixed catalyst is zero order reaction, This is quite different from the L-H process of enzyme catalyzed reaction of Cr (Ⅵ) on TiO2 monomer catalyst reported in other literatures. This may be because in this experiment, the catalyst used is the composite catalyst made of TiO2 and WO3 powder by grinding and mixing, its reflection rate is reduced, and its photocatalytic activity is higher than that of TiO2 monomer catalyst, In this experiment, the acidity is very strong, and the pH value has a great influence on the reaction kinetics. Therefore, the kinetics of Cr (Ⅵ) on TiO2 monomer catalyst (pH > 3.8) is in line with the L-H process of enzyme catalytic reaction. In this experiment, it is converted to the zero order reaction kinetics process of surface catalytic reaction. The reaction rate equation and rate constant obtained from the experiment are CT = c0-0.0073t, K0 = 0.0073 Mo L- 1 /min.

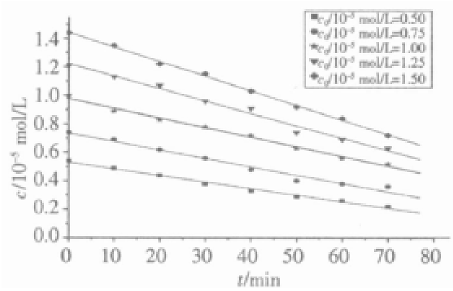

Fig.1 Concentration Time Curve of Photocatalytic Reduction of Cr (Ⅵ) with Different Initial Concentrations Tio2 + Wo3 is 2.5mg/Ml

3.2 Effect of Salicylic Acid on Photocatalytic Reduction of Cr (Ⅵ) Ion

From the perspective of the mechanism of photocatalytic reduction cycle, the redox process of metal ions as electron acceptors and organic compounds as electron donors is bound to be related. According to relevant literature, there is a strong synergistic effect between the photocatalytic oxidation of organic compounds and the photocatalytic reduction of metal ions.

(1) The Experiment Was Carried out by Adding the Same Amount of Salicylic Acid into Five Different Initial

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Concentrations of Cr (Ⅵ) Solution

It can be seen from Figure 2 that the concentration time curve of photocatalytic reduction of Cr (Ⅵ) ion with different initial concentration is similar to that of Cr (Ⅵ) ion with different initial concentration without adding organic matter. This shows that the photocatalytic reduction of Cr (Ⅵ) in TiO2 + WO3 composite catalyst is still zero order reaction in the presence of organic salicylic acid The reaction rate equation and rate constant obtained from the experiment are CT = c0-0.1115t, K0 = 0.1115mol L-1 / min. they are similar to those without salicylic acid. However, under the action of salicylic acid, the reduction reaction rate and reduction conversion rate are much higher than those without salicylic acid.

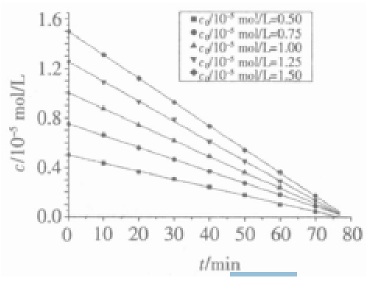

Fig.2 Concentration Time Curve of Photocatalytic Reduction of Cr (Ⅵ) with Different Initial Concentrations

(2) The Effect of the Amount of Salicylic Acid on the Photocatalytic Reduction of Cr (Ⅵ) with the Same Initial Concentration

The initial concentration of Cr (Ⅵ) ion is 1.00 × 10-5mo L / L, and the amount of salicylic acid is 5ml, 10ml, 15ml and 20ml respectively. The same light is applied for 70 min. in this way, the effect of the amount of salicylic acid added on the photocatalytic reduction of Cr (Ⅵ) ion with the same initial concentration is discussed. It can be seen from Figure 3 that with the increase of the amount of salicylic acid added, The conversion rate of Cr (Ⅵ) ion photocatalytic reduction increases gradually, which shows that the addition of salicylic acid can promote the photocatalytic reduction of Cr (Ⅵ) ion. This may be because salicylic acid is o-hydroxybenzoic acid, which belongs to aromatic compounds, and there are π electrons produced by orbital overlap, which are easy to conjugate with the reaction center and release the electrons to the positive charge center, Therefore, it has a synergistic effect with the hole produced by photoexcitation, which reduces the recombination of photogenerated hole and photogenerated electron, so that the photocatalyst has a strong reaction activity, so the aromatic compounds have a strong promotion effect on the photocatalytic reduction of Cr (Ⅵ) ions, which is consistent with the reports in the literature.

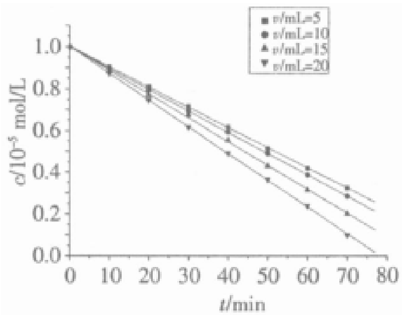

Fig.3 Different Amount of Salicylic Acid Added to the Same Initial Concentration

(3) Comparison of Photocatalytic Reduction of Cr (Ⅵ) under Different Reaction Conditions

In the whole reaction system, there may be homogeneous reaction of Cr (Ⅵ) and salicylic acid. In order to compare the influence of homogeneous reaction and dark state reaction on the photocatalytic reaction of Cr (Ⅵ), when the concentration of Cr (Ⅵ) and other conditions are fixed, the light without catalyst TiO2 + WO3 is used, According to Fig. 4, under the condition of Cr (Ⅵ) adding catalyst WO3-TiO2 but not light, the reduction rate of

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Cr (Ⅵ) ion is only 1.5% after 70 min reaction; under the condition of adding catalyst TiO2 + WO3 and adding catalyst TiO2 + WO3 but not light, the reduction rate of Cr (Ⅵ) ion is only 1.5%; under the condition of adding catalyst only water salicylic acid and light, The reduction rate of Cr (Ⅵ) in the same 70 min reaction is only about 1% respectively. Therefore, it can be seen from the above that the reaction rate of homogeneous reaction and dark state reaction is very slow. The conversion rate of Cr (Ⅵ) plus catalyst WO3-TiO2 and salicylic acid under light condition is 89.9%. The addition of salicylic acid greatly improves the reaction rate and conversion rate of Cr (Ⅵ) reduction by WO3-TiO2 composite catalyst[2].

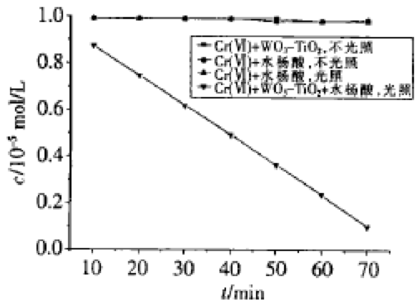

Fig.4 Photocatalytic Reduction of Cr (Ⅵ) under Different Reaction Conditions

4. Conclusion

Under strong acid conditions, TiO2 and WO3 powders are used as catalysts, which can effectively catalyze the reduction of Cr (Ⅵ) ions under the action of light. It can promote the photocatalytic reduction of Cr (Ⅵ) and greatly improve its reduction conversion rate.

References

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