

## Gas Phase Photolysis of Volatile Organic Compounds and Its Photolysis in Metal Ion Solution

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**Keywords:** Volatile organic compounds (VOCs); Photo-catalytic oxidation (PCO) in gas phase; Metal ion solution; Photolysis study;

**Abstract:** In recent years, fog pollution and indoor air quality problems have become more and more serious. Volatile organic pollutants (VOCs) have been widely used as one of the main sources of pollution of fog and indoor air pollution. Taking phenol as an example, the photolysis reaction of gas phase and its photolysis at different metal ion concentrations were studied. The results show that phenol can be photolyzed rapidly and reacted to produce CO<sub>2</sub> under ultraviolet light irradiation at 245 nm. Titanium dioxide photo-catalysts were prepared by doping with Cu<sup>2+</sup> and Fe<sup>2+</sup>, respectively. The photo-catalytic degradation experiments of phenol-containing wastewater were carried out in a self-made photo-catalytic reactor using the above two catalysts. The research results make it possible to design and construct a highly active titanium dioxide catalyst under visible light, which provides a theoretical basis and technical reference for the search for practical photo-catalysts for degrading water pollution.

### 1. Introduction

In the 21st century, with the rapid development of science and technology and social economy, the sustainable development of resources, environment, population and human society has become a major research topic of great concern. Water and the atmosphere are important resources for human survival. However, the rapid development of social economy has brought about an increasing pollution of resources [1]. Among them, the pollution of water and air caused by toxic and harmful volatile pollutants produced by chemical and chemical industries has become the focus of academic, industrial and even human society. How to minimize the pollution hazard of production to water and atmospheric environment and realize the sustainable use and protection of resources has become a practical problem that needs to be solved urgently [2].

Phenol is the simplest cool organic substance that reacts chemically with proteins in cells, destroys the properties of proteins, causes proteins to coagulate or locally damage them, and relies on strong penetrating power to penetrate deep tissues, causing serious consequences [3] [4]. Cool compounds can enter the body through skin and mucous membrane contact, inhalation of the respiratory tract and entry into the digestive tract through the mouth. Acute poisoning of cool types occurs mainly in production accidents, which can cause coma and even death. Skin contact with a lot of cool liquid can cause severe burning, local grayish white and soften, then turn red or even black and lead to skin necrosis. Because Phenol is an important synthetic material and has a large demand, it is widely used in wastewater from petroleum, chemical, mechanical processing and printing industries. Because phenol has obvious toxic effects on organisms, it is highly affected in environmental management [5].

In this paper, phenol was used as an example to study the photolysis in the gas phase and the catalytic photolysis in the metal ion solution. It provides a theoretical basis and technology for the photo-catalyst to find practical phenol degradation of water reference.

## 2. Experimental study on gas phase photolysis of VOCs

### 2.1 Experimental methods

The gas phase photolysis and photo-catalytic reactions were carried out in the reactor shown in Fig. 1. Volatile organic compounds (VOCs) vapors are passed through a vacuum static gas distribution, that is, the reactor is first evacuated, and the organic liquid is injected into the reactor, and after it is completely vaporized, air is introduced and mixed. When performing gas phase photo-catalytic reaction. Firstly, mix a certain amount of  $P_{25}TiO_2$  with a small amount of deionized water, evenly spread on a quartz glass of the same size as the light window. After natural air drying, the side with the catalyst is away from the light irradiation direction and fixed under the quartz light window. Simultaneous sampling and analysis with a gas mass spectrometer while turning on the light.



Fig.1. Photochemical reactor

After the experiment was completed, the gas and mass spectrometer (Omni Star TM, Balzers, Switzerland) was used to continuously analyze the vapor and gas concentrations during the reaction by MCD (Multiple Concentration Detection) and MID (Multiple Ion Detection). The detector was CHTRON, secondary electron multiplier (SEM) voltage is 1000V [6].

### 2.2 Experimental results and discussion

#### 2.2.1 Photolysis and Photo-catalytic Degradation of Phenol Vapor

The degradation of phenol is greatly affected by the wavelength of light and the catalyst. Under the irradiation of sterilizing light with a dominant wavelength of 245 nm, the phenol vapor can be photolyzed rapidly. In 1 min, the phenol vapor is degraded by 99.9%; In the black light of 365 nm, the phenol vapor did not degrade significantly. After the introduction of the photo-catalyst, the reaction rate when irradiated with a germicidal lamp with a dominant wavelength of 245 nm was slightly faster than that with a black light [7].

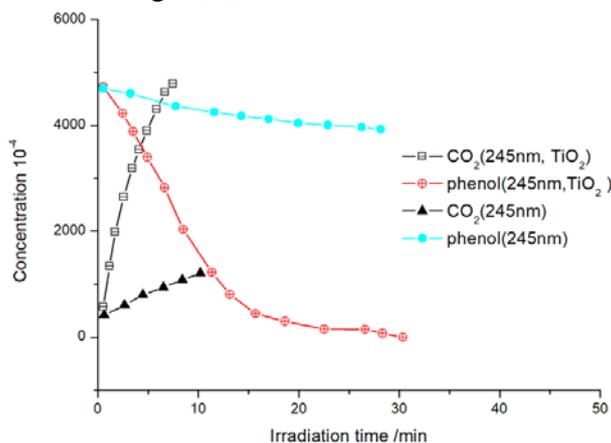


Fig.2. Photolysis of phenol

### 2.2.2 Preliminary study on photolysis and photo-catalytic reaction mechanism of VOCs

We used a gas mass spectrometer to perform on-line qualitative analysis of the components of the gas phase during the reaction. It was found that in the photolysis and photo-catalytic reactions of phenol, in addition to generating a large amount of CO<sub>2</sub> and HCl, Cl<sub>2</sub>, phosgene and a small amount of chloroform were formed [8]. These products are in good agreement with the products initiated by Cl radicals reported in the literature [9]. Therefore, we believe that the photolysis and photo-catalytic reactions of trichloroethylene are controlled by the mechanism of Cl radical initiation. The initial reaction is OH. Free radicals or Cl radicals will produce a large amount of Cl radicals during the reaction, so the reaction is ultimately controlled by Cl radicals [10].

Through the research and analysis of the photolysis and photo-catalytic degradation behavior of the above organic substances, we believe that there are four main ways to cause decomposition of organic matter:

(1) The organic molecules themselves absorb photons and produce energy level transitions, triggering further photochemical reactions.

(2) Light can activate the O<sub>2</sub> and H<sub>2</sub>O molecules in the air, which in turn produces active components with higher oxidation properties. The reaction of these active components with organic compounds can lead to the degradation of organic matter, such as toluene.

(3) Photo-catalytic oxidation. Mainly photo-activated catalyst, which generates holes and O H radicals to further oxidize organic molecules. In addition to carbon tetrachloride, other substances in the above organic matter can be photo-catalyzed.

(4) Photo-catalytic reduction. Mainly photo-activated catalyst, which generates electrons on the valence band and reduces organic matter by photoelectron. The reaction is usually difficult to carry out in an air medium, and an electron donor is introduced into the reaction system to capture photo-generated holes. It can be carried out, such as photo-catalytic degradation of CCl<sub>4</sub> is this mechanism.

Therefore, the CCl<sub>4</sub> in the aqueous phase can be photo-catalyzed, mainly because water can be used as an electron donor. Similarly, the introduction of an electron donor in the gas phase can also cause photo-catalytic degradation of CCl<sub>4</sub>.

### 3. Photolysis of VOCs in metal ion solution

The trace addition of Fe<sup>2+</sup> ions in the reaction system promotes the photo-catalytic activity of the titanium dioxide photo-catalyst prepared by noble metal doping. Because Fe<sup>2+</sup> ions are sensitive to light, they are relatively unstable. In the photo-catalytic reaction process, they can become shallow traps of photo-generated holes and combine with photo-generated holes to form Fe<sup>3+</sup> ions. Fe<sup>3+</sup> ions can also be captured by photo-generated electrons. Thus, Fe<sup>2+</sup> ions and Fe<sup>3+</sup> ions are present on the surface of the titanium dioxide photo-catalyst, which can effectively suppress the recombination of holes and electrons and improve the photo-catalytic performance. Then, for the Cu<sup>2+</sup> ion doped titanium dioxide photo-catalyst prepared by the sol-gel method, this part investigates whether the addition of trace Fe<sup>2+</sup> ions in the reaction system can also improve the photo-catalytic activity to some extent. The reaction steps are as follows:

(1) 350 ml of simulated phenol-containing wastewater with a concentration of 55 mg/L was added to two photo-catalytic reaction cells with an area of 600 cm<sup>2</sup>, and labeled as a and b reaction cells, respectively.

(2) According to the amount of catalyst of 310 mg TiO<sub>2</sub> / L, the mass fraction of the self-doped Cu<sup>2+</sup> ions is 0.4% of the titanium dioxide photo-catalyst, and then placed in the a and b reaction cells respectively. At the same time, a low concentration of Fe<sup>2+</sup> (1.5mg / L) was added to the reaction system in the reaction cell.

(3) The above two reaction cells were placed in a reactor, and the photo-catalytic reaction was carried out under a 9 W ultraviolet lamp for 8 hours, sampled every two hours, centrifuged, and the phenol ion content was measured to calculate the degradation rate.

The experimental results are shown in Table 1.

Table.1. Effect of the addition of iron ions in the reaction system on the degradation rate

Time	Degradation rate (%)	
	A reaction pool	B reaction pool
	Add Fe <sup>2+</sup>	do not add
2	51.2	46.5
4	76.5	66.8
6	92.1	81.3
8	100	92.6

The results show that the addition of trace amounts of Fe<sup>2+</sup> ions to the reaction system, the doped titanium dioxide photo-catalyst has a significant increase in the degradation rate of phenol-containing wastewater, that is, the degradation rate can reach 100% within 8 hours, and the phenol-containing wastewater will be Completely degraded, It has also been confirmed that the carrier can be effectively separated after the addition of Fe<sup>2+</sup> ions, which is more favorable for the transfer of photo-generated electrons and holes to cyanide ions, thereby accelerating the progress of the entire photo-catalytic reaction and improving the degradation efficiency.

#### 4. Conclusion

In this paper, the photolysis reaction of phenol in the gas phase was studied. It was concluded that phenol vapor can be photolyzed and photo-catalyzed by UV light at 245 nm. The reaction process is controlled by Cl radical and is volatile. The organic matter is photo-catalyzed and degraded by a large amount of CO<sub>2</sub>, so the degradation is more complete than the photolysis reaction. The photolysis of phenol in metal ion solution was also studied. It was confirmed by experiments that a low concentration of photo-sensitive metal ion Fe<sup>2+</sup> was added to the reaction system to form a TiO<sub>2</sub>/UV+Fe<sup>2+</sup> system, which was beneficial to photo-catalytic oxidation and reduction of titanium dioxide. Simultaneously, the degradation efficiency of the phenol-containing wastewater is effectively improved. At the same time, the addition of inorganic anions, positive ion and surfactants to the reaction system has little effect on the degradation rate of phenol ions, and it is considered that the photo-catalytic reaction will not be disturbed in practical application.

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