*Journal of Environmental Sciences* Vol.14, No.3, pp.428—432, 2002 ISSN 1001—0742 CN11—2629/X

**Article ID**: 1001-0742(2002)03-0428-05 **CLC number**: X78 **Document code**: A

# Photocatalytic degradation of PCP-Na with $TiO_2$ photocatalysis loaded with platinum

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**Abstract**: Titanium dioxide($TiO_2$) samples of different crystal forms were prepared by hydrolysis tetrabutyl titanate in various water to alkoxide ratios and sintering the hydrolysis product at different temperatures. The photocatalysts coated on hollow glass beads and loaded with platinum varying from 0.2% to 2.4% by weight. The photocatalytic degradation rate of sodium pentachlorophenolate (PCP - Na) depends on the preparing conditions such as: sintering temperatures, water to alkoxide ratios($R$), platinum content and the size. The proper conditions of preparation photocatalysts are as follows: the ratio of $TiO_2$ : sodium silicate : hollow glass beads : platinum is 10:5:20:0.15(w/w), $R$ is 100, sintering temperature is 650℃, and the size of hollow glass is 0.5 - 1 mm. Under these conditions, the ratio between acatase and rutile of the photocatalyst is 2:1, and the photocatalytic activity is high.

**Keywords**: photocatalysts; tetrabutyl titanate hydrolysis; water to alkoxide ratios ($R$); sintering temperature; platinum; hollow glass beads; sodium pentachlorophenolate(PCP-Na)

## Introduction

Over the last 20 years the scientific and engineering interest in the application of $TiO_2$ as semiconductor photocatalysts has grown exponentially. Titanium alkoxides hydrolyse and photocatalysts loaded with noble metal have been investigated by some scientists(Bulent, 1986; Tsai, 1997; Michael, 1995). The hydrolysis reaction can be represented by the equation:

$$\equiv Ti\text{--}OR + H_2O \longrightarrow Ti—OH + R(OH), \quad (1)$$

$$\equiv Ti\text{--}OH + RO - Ti \longrightarrow \equiv Ti\text{--}OTi\equiv + R(OH). \quad (2)$$

Certain hydrolysis conditions, which include water to alkoxide ratios, molecular separation by dilution, hydrolysis medium, reaction temperature, alkyl groups in the alkoxide and sintering temperature, determine the molecular size and structure and affect photocatalysts activities (Richard, 1997). By changing these conditions, molecular size, morphology and crystallization can be optimized, titanium alkoxides hydrolyse is widely used in preparing photocatalysts, but because of its higher electron - hole recombination rate, the activity of the photocatalyst is not entirely perfect. To deal with this problem, load of the catalyst with noble metal is tried(Ranjit, 1996).

## 1 Methods

### 1.1 Experimental methods

A schematic diagram of the photocatalytic reactor is shown in Fig. 1. The photo-reactor was made from a quartz glass tank with a volume of 500 ml. The main wavelength of a high pressure mercury lamp is 365 nm and the power is 375W. The reactor was aerated through a high pressure oxygen mask. Sodium pentachlorophenolate wastewater and $Pt/TiO_2$ coated on hollow glass photo-catalysts were uniformly fed into the reactor, stirred by the magnetic force stirrer for 30 minutes before the lamp switched on. When adsorption equilibrium had been reached, the lamp was switched on and samples were taken from the reactor at intervals. The oxygen flux is 1.6 ml/s.

### 1.2 $Pt/TiO_2$ loaded on hollow glass photo-catalyst preparation

Foundation item: The National Key Science and Technology Project of Ninth Five-year Plan (No.96-909-05-02)

30 Vol (%) of tetrabutyl titanate in ethanol was added dropwise to deionized water while stirring vigorously. The precipitate formed was filtered off, washed, and dried at 120℃. $TiO_2$ thus prepared was sintered at different temperatures from 300℃ to 800℃ in air for 1h (Rivera, 1993).

Then, dispersed $TiO_2$ in sodium silicate solution with hollow glass beads. The solvent is subsequently removed by a supercritical drying step. Supercritical drying has the advantage of eliminating the liquid/vapor interface during drying and avoids partial collapse of the network structure which lead to loss of surface area and pore volume.

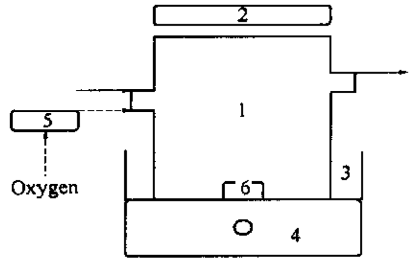


Fig.1 Scheme of the photocatalytic reactor
1. quartz glass tank; 2. high pressure mercury; 3. cooling water grove; 4. magnetic force stirrer; 5. air flowmeter; 6. stirrer

The metallized semiconductor catalysts were prepared by the impregnation method. The $K_2PtO_3Cl_7$ solution required for the loading was added to the required weight of $TiO_2$. The photocatalysts were dried at 100℃ for 12h and were subjected to a reduction in hydrogen. The samples were heated to 400℃ in a quartz glass reactor synchronously, given $H_2$ for 15h as 35 $cm^3$/min, finally supported $N_2$ for 2h.

### 1.3 Analytical methods

Sodium pentachlorophenolate solution sample was filtered off by 0.45 μm membrane and was measured by HPLC (Japan Shimadzu, Model LC Workstation Class-LC10). HPLC work conditions: ODS columniation C18T-5; columniation temperature 40℃; flow phase: methanol/deionized water ($v/v$: 60: 40); detect time: 8 min; detect wavelength: 270 nm; pump pressure: 8000—10000 kPa.

The platinum contents of the photo-catalysts were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES, Model 3410ARL) after calibration with standards containing known metal contents. The metal was extracted from the catalyst by boiling in aqua regia.

The BET surface areas were determined by physical adsorption of $N_2$ at liquid $N_2$ temperature by a BET instrument (Model Quantasorb, Quantasorb Company).

The $X$-ray diffraction patterns of photo-catalysis were recorded by the Beijing Institute of Nonferrous Metal.

## 2 Results and discussion

### 2.1 Effect of the water to alkoxide ratios ($R$) and sintering temperature

Table 1 shows that the alternant effects of $R$ and sintering temperature on photocatalytic activity of Pt/$TiO_2$ coated on catalysts of the photocatalytic oxidation experiments. The results were obtained under the following conditions: $TiO_2$: sodium silicate: platinum: hollow glass beads = 10: 5: 0.15: 20; PCP-Na concentration of the synthetic wastewater is 100 mg/L, air flow is 1.6 ml/s, and the irradiation time is 120 min.

**Table 1 Effects of $R$ and sintering temperature on photocatalytic activity**

| Water to alkoxide ratios, $R$ | Reaction constant $K$, $min^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 300℃ | 450℃ | 650℃ | 800℃ | 900℃ |
| 20 | 0.0072 | 0.0100 | 0.0106 | 0.0083 | 0.0065 |
| 100 | 0.0081 | 0.0109 | 0.0190 | 0.0074 | 0.0050 |
| 1000 | 0.0090 | 0.0012 | 0.0055 | 0.0025 | 0.0011 |

The results demonstrated that the PCP-Na degradation rate could be represented by the first-order rate equation: $\ln(C0/Ct) = Kt$ where $Kt$ is the reaction constant, and $Ct$ is the PCP-Na concentration at irradiation time $t$. The value of $Kt$ can be calculated to assess the photocatalytic activity of the Pt/$TiO_2$ coated catalysts. Table 1 shows that the effects of $R$, sintering temperature and their alternant effects to photocatalytic activity are prominent and indicates that there is an optimization of the prepared photocatalysts which is $R = 100$ and sintering temperature is 650℃. In this addition, $Kt$ is notable high.

## 2.2 Influence of sodium silicate quantity and the size of hollow glass beads granules

Table 2 shows the bonding agent quantity and the size of hollow glass beads granules on photocatalytic activity of Pt/$TiO_2$ coated catalysts. Conditions of the photocatalytic oxidation experiments are as follows: $R$ is 100 and sintering temperature is 650℃.

**Table 2 Effects of the bonding agent quantity and the size of hollow glass beads granules**

| $TiO_2$ : sodium silicate : platinum : glass beads | PCP-Na degradation rate(%) for 2h | | | |
|---|---|---|---|---|
| | 0.5 mm | 1.0 mm | 2.0 mm | 5.0 mm |
| 10:2.5:1:20 | 96.4 | 95.5 | 90.4 | 80.3 |
| 10:5:1:20 | 91.1 | 90.1 | 84.5 | 79.5 |
| 10:10:1:20 | 85.8 | 86.8 | 82.1 | 76.9 |

The experimental results demonstrated the PCP-Na degradation rate. The photocatalytic activity increased along with sodium silicate ratio increasing, in addition, when the sodium silicate ratio is too high, photocatalysts are seriously conglomerated during their preparation. However when the silicate ratio is too low, the coated catalysis are dispersed easily. It is prominent that photocatalytic activity increased along with the diameter of hollow glass beads decreasing.

## 2.3 Effect of the platinum content

Fig.2 illustrates the influence of the platinum content on photocatalytic degradation rate. A variety of platinum content photocatalysts have been used to degrade the PCP-Na synthetic wastewater. These experimental results were obtained under the following conditions: $TiO_2$ : sodium silicate : hollow glass beads = 10:5:20; $R$ is 100 and sintering temperature is 650℃. The diameter of hollow glass beads is 1 mm. The influent concentration of the PCP-Na synthetic wastewater is 100 mg/L, the air flow is 1.6 ml/s, and the irradiation time is 120 min.

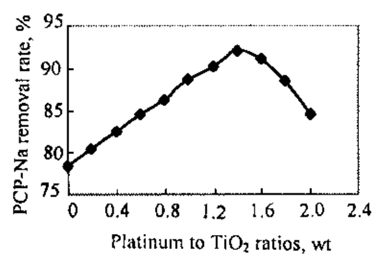


Fig.2 Effect of the platinum content on photocatalytic degradation rate

It indicates that loading platinum is effective to enhance the removal rate of PCP – Na and the optimized content is about 1.4% to 1.6%.

## 2.4 Crystal structure and surface areas

An analysis of the reaction product showed that the extent of polymerization was largely dependent on the number of moles of water added. When the $H_2O$/alkoxide ratio was low in the case of substoichiometric quantities of water, the hydrolysis of the alkoxide was not complete, and linear oligomers were obtained. When the $H_2O$/alkoxide ratio was in excess of that required for stoichiometry, hydrolysis was observed to approach completion and the time required for the formation of the gel also increased; the hydrolysis product was small and was sensitive to temperature. $X$-ray diffraction patterns of photo-catalysts sintered at different temperatures showed that the crystal form was anatase at a low sintering temperature and this transformed to rutile at various temperature according to $H_2O$/alkoxide ratio. This result is clearly indicated in Table 3.

Table 3 indicates that sintering temperature and $H_2O$/alkoxide ratios are interfactional. Considering Table 1, the maximum degradation rate of PCP-Na was related to the anatase content of $TiO_2$. It was demonstrated that anatase : rutile = 2 : 1 was the best for this effect. The crystal size of anatase and rutile was calculated by Scherrer's equation. It increased with the calcination temperature and decreased with the

$H_2O$/alkoxide ratio. The surface area decreased with the sintering temperature increasing. It may be concluded that photocatalytic activity is related with crastal and surface area. When anatase:rutile is 2:1, surface areas are large, the photocalytic activity is high.

Fig. 3 illustrates the alternant effects to anatase and rutile crystal structure. The difference between them is the degree of aberrance and the mode of coadjacent. The structure of rutile is not regular and slightly inclined to square crystal. The structure of anatase is the obvious aberrance inclined to the square crystal and having poor symmetry.

**Table 3 Effects of the $H_2O$/alkoxide ratios and sintering temperatures to crystal structures and surface areas of photocatalysts**

| Water to alkoxider ratios | Sintering temperature, ℃ | Surface area, $m^2/g$ | Crystal structures anatase / rutile |
|---|---|---|---|
| 20 | 300 | 367.9 | Non crystal structures |
| | 450 | 251.8 | Non crystal structures |
| | 650 | 130.1 | Anatase (100) |
| | 800 | 15.7 | Anatase (50) / rutile (50) |
| 100 | 300 | 560.9 | Non crystal structures |
| | 450 | 463.2 | Anatase (100) |
| | 650 | 322.8 | Anatase (67) / rutile (33) |
| | 800 | 130.0 | Rutile (100) |
| 1000 | 300 | 660.8 | Anatase (100) |
| | 450 | 210.2 | Anatase (65) / rutile (35) |
| | 650 | 100.3 | Rutile (100) |
| | 800 | 6.6 | Rutile (100) |

These different crystal structures lead to different mass density and conduction-band election. Rutile is easier to be excitated than anatase, however anatase is more difficult to recombine and has a good ability for adsorption electron acceptor (James, 1997). Thus combining anatase and rutile can enhance photoactivity.

## 2.5 Stability and application of the photocatalysts

The photocatalysts were prepared under such conditions: water to titanium alkoxides is 100, sintering temperature is 650℃, diameter of hollow glass beads is 1 mm, sodium silicate:$TiO_2$ is 10:1.5, platinum content of photocatalysts is about 1.5%. They were used for 10 times in the photocatalytic oxidation experiments and their photoactivity has little change, it indicates their photoactivity is stable(Xi, 2000).

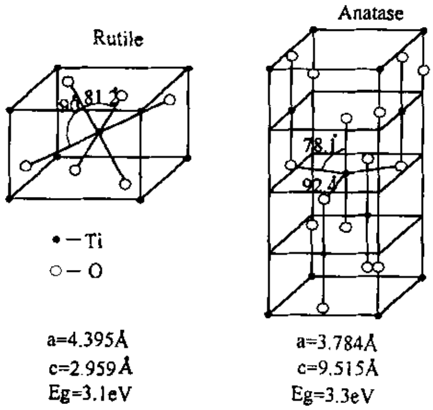


Fig.3 Crystal structure of anatase and rutile

# 3 Conclusions

The parameters that affected photoactivity of Pt/$TiO_2$ coated on hollow glass beads were investigated. The effect of crystal structure and surface area extends to water/titanium alkoxides ratios and sintering temperature. These influence photo-catalytic activity of Pt/$TiO_2$ coated catalysts, when anatase:rutile is 2:1, surface areas are large. The photocalytic activity is high.

The effect of bonding agent(sodium silicate) quantity, diameter of hollow glass beads and platinum content on PCP-Na degradation were examined. The optimization condition to prepare photocatalytic activity is that water to titanium alkoxides is 100, sintering temperature is 650℃, diameter of hollow glass beads is 1 mm, sodium silicate:$TiO_2$ is 10:1.5, platinum content of photocatalysts is about 1.4%—1.6%.

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(Received for review March 13, 2001. Accepted April 24, 2001)