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Original Research Paper

Preparation for Nano-titania Catalyst and Its Application for Benzene Decomposition

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ABSTRACT

In the experiment, nano-titania film was prepared by sol-gel method. The raw materials and experimental conditions were optimized for preparing TiO_2 thin film. We draw the conclusion as follows: n[Eth]:n[Ti(OBu)$_4$] = 18(Mole ratio), n[AcAc]:n[Ti(OBu)$_4$] = 1.2(Mole ratio), n[H_2O]:n[Ti(OBu)$_4$] = 2.5 (Mole ratio), pH = 3~5, hydrolysable temperature = 25~35°C, and heat treatment temperature = 450°C. Then the photocatalysts were packed into nonthermal plasma reactor, and a synergistic control experiment for benzene decomposition was carried out, that is, nano-titania photocatalyst with nonthermal plasma. The results show that benzene removal efficiency has an order of "with anatase photocatalyst in the plasma reactor > the mixture photocatalyst of anatase and rutileat > rutileat photocatalyst", and the effect of degradation was visible by added photocatalyst in the plasma reactor. When concentration of benzene was 1500 mg/m^3 and voltage was 30 kV, the removal efficiency was increased 19% higher with photocatalyst than without photocatalyst. Obviously, the synergistic effect of nano-TiO_2 catalyst and non-thermal plasma is very effective for benzene decomposition.

INTRODUCTION

As an emerging technology for environmental protection, there have been extensive researches on using non-thermal plasma (NTP) over the past 20 years (Muhamad & Jiang 2000). The major advantages of NTP technology include the moderate operating conditions (room temperature and atmospheric pressure), moderate capital cost, compact system, easy operations and short residence times, etc. as compared to the conventional technologies (Magureanu et al. 2005). In the field of air pollution control, the NTP technology has been tested for the abatement of various types of hazardous air pollutants such as volatile organic compounds (VOCs) (Subrahmanyam et al. 2007), SO_2 (Chang et al. 1991), NO_x (Young et al. 2004), odours (Chang & Tseng 1996), etc.

In order to further improve the removal efficiency of VOCs by the plasma, the cooperation with photocatalyst has been tested by some researchers (Kim et al. 2008). These studies showed that the combination of discharge plasma with catalyst is a very effective method for VOCs removal (Zhu et al. 2008, 2009).

In this paper, NTP coupled with nano-titania (TiO_2) photocatalyst film for benzene removal has been studied. In the experiment, nano-TiO_2 films were prepared by sol-gel method by improving the ratio of raw materials and the process control condition. On one hand, nano-TiO_2 film can fix the photocatalyst. On the other hand, because of its quantum size effect, small size effect, surface effect, quantum interface and limited domain effect as one of nanometer materials, nano-TiO_2 film can increase activity characteristics of the photocatalyst effectively.

MATERIALS AND METHODS

NTP system: The NTP system consisted of a tube-wire packed-bed reactor system, an AC power supply, a continuous flow gas supplying system and an electric and gaseous analytical system. The schematic diagram of NTP system is shown in Fig. 1. Dry air (78% N_2, 21% O_2) was used as a balance gas for benzene decomposition. Air supplied from an air compressor was divided into two air flows with each flow rate controlled by a mass flow controller (MFC). One dry air flow was introduced into a bottle of liquid benzene to produce saturated benzene. The vapour was then mixed with the other dry air flow in a blender so that benzene waste gas was diluted to a desired concentration. The voltage and current waves were measured by oscilloscope (Tektronix 2014). The voltage applied to the reactor was sampled by a 12500:1 voltage divider. Also, the current was determined from the voltage drop across a shunt resistor (R3 = 10kΩ) connected in series with the grounded electrode. In order to obtain the total charge and discharge power, simultaneously, a capacitor (Cm = 2μF) was placed instead of the shunt resistor. The electrical power provided to the discharge was measured using the Q–V Lissajous diagram.

The NTP packed-bed reactor is shown in Fig. 2. The coaxial cylindrical NTP reactor was made of an organic glass tube with an inner diameter of 32 mm and wall thickness of 3 mm wrapped by a copper mesh of 20 cm in length as a ground electrode. A tungsten wire (0.5 mm in diameter) was placed on the axis of NTP reactor which served as the inner discharge electrode. The relative humidity of 25% in NTP reactor was controlled by a thermohygrometer.

Materials preparation: Nano-TiO_2 films were prepared by the Sol-Gel method in the experiment. Flow chart on preparing nano-TiO_2 thin film by sol-gel method is given in Fig. 3.

Precursor solution**:** Tetrabutyl titanate ($Ti(OBu)_4$) (as precursor substance), ethanol (AcAc) (as solvent), Acetyiacetone (Eth) (as chelating reagent).

Droplet solution**:** Ethanol (AcAc) (as solvent), HNO_3 (as catalyzer), distilled water.

Detection methods. The conjugate chemical bonds of benzene (C_6H_6) locate on the same plane. Due to benzene possessing syntony stability, this kind of chemical bonds has more fastness and steady than common chemical bonds. So benzene was chosen as a kind of VOCs to decompose in the experiment because of its stabilized chemical structure. The plasma reactor employed an AC power supply of 60 Hz. The AC voltage was applied to the reactor in the radial direction, and the voltage extension lied from 0kV to 30kV. The benzene concentration was determined by gas chromatography (manufactured by American Thermo Finnigan Co., TRACE-GC ULTRA) with a flame ionization detector (FID) and a capillary column of DB-1. Reaction gas samples were taken by a syringe from the sampling ports of the reactor. The nanometer TiO_2 thin film was inspected and analysed by Scan Electric Mirror (SEM, made in Japan, S-2700). The experimental conditions were as atmospheric pressure (760 mmHg) and temperature (20°C). As evaluation criterion, the benzene removal efficiency (h) was calculated as follows:

$$h(\%) = \frac{[benzene]_{inlet} - [benzene]_{outlet}}{[benzene]_{inlet}} \times 100\% \qquad ...(1)$$

RESULTS AND DISCUSSION

The preparation parameters of nano-TiO_2 optimization: Nano-TiO_2 thin films were prepared by the sol-gel method in the experiment. Fig. 4 shows that the distilled water plays an important role in $Ti(OBu)_4$ hydrolysis. The gel time is shortest with $X = 4$, but the sol is the most unstable. When $X < 4$, the gel time becomes shorter with the quantity of distilled water increasing. When $X > 4$, the gel time becomes longer with the quantity of distilled water increasing. When $X < 1$, the sol can not be obtained.

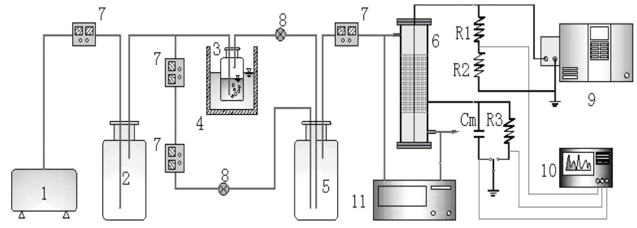

Fig. 1: Schematic diagram of NTP system for benzene removal. 1. air compressor, 2. buffer, 3. benzene liquid bottle, 4. attemperator, 5. blender, 6. NTP reactor, 7. mass flow meter, 8. needle valve, 9. high voltage, 10. oscukkograph, 11. gas chromatograph

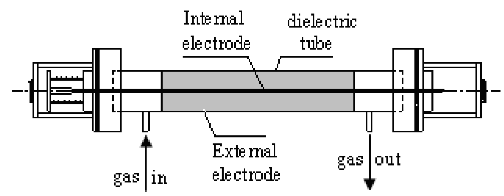

Fig. 2: NTP reactor
Reactor: organic-glass tube (i.d. 32mm, packed infilling length of packed materials of 200mm); Internal electrode: tungsten filament (i.d. 0.5mm); External electrode: dense steel mesh.

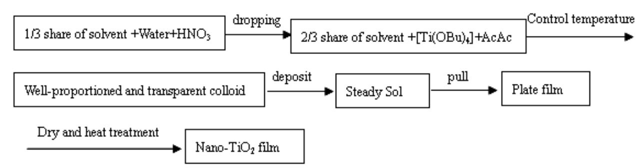

Fig. 3: Flow chart on preparing nano-TiO_2 thin film by sol-gel method.

Table 1: Physical characteristics of the packed materials.

Packed materials	Component (%)			Interspace rate(%)	Drink rate (%)
	Quartz	Al_2O_3	Non-crystal		
	15	15	70	1.8	0.8

Fig. 5 shows that the gel time extends with AcAc adding. Because AcAc can not only inhibit hydrolysis speed but also happen alcohol ester reaction.

Fig. 6 shows pH = 5 without HNO_3. When pH = 4 with HNO_3, the gel time has a peak value.

Fig. 7 shows that the sol is more unstable when hydrolysis temperature is higher and gel time is shorter. Under hydrolysis temperature of 293 ~ 313 K, the gelation time becomes short with the temperature increases rapidly. Under hydrolysis temperature of 313 ~ 323 K, the gel time remains unchanged. When the hydrolysis temperature is higher, the solution molecules move violently than before. So there are the greater chances to react each other to shorten the gel time. In addition, AcAc and water have different degrees of

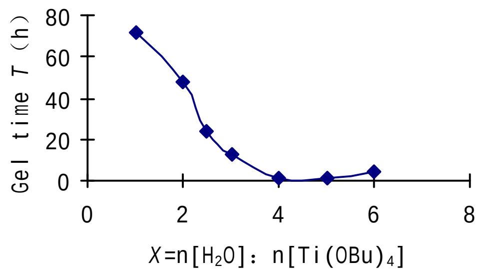

Fig. 4: Effect of water quantity on gelable time (n[Eth] : n[Ti(OBu)$_4$] = 21, n[AcAc] : n [Ti(OBu)$_4$] = 1, hypothetically, n[H_2O]:n[Ti(OBu)$_4$] = X (Mole ratio), gel time for T).

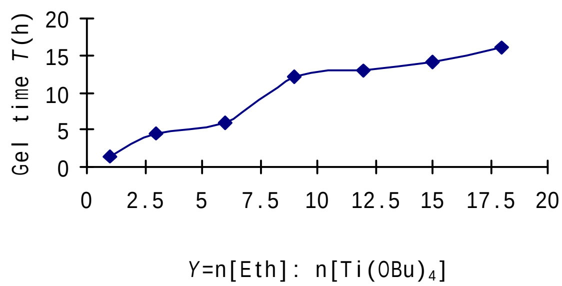

Fig. 5 Effect of solvent quantity on gelable time (With AcAc solvent, n[H_2O] : n[Ti(OBu)$_4$] = 3, n[AcAc] : n [Ti(OBu)$_4$] = 1, hypothetically, n[Eth] : n[Ti(OBu)$_4$] = *Y* (Mole ratio), gel time for T).

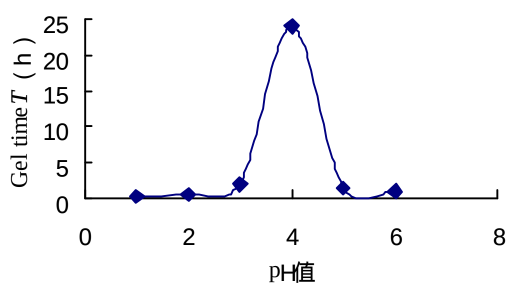

Fig. 6: Effect of pH on gelable time (with AcAc solvent, n[H_2O] : n[Ti(OBu)$_4$] = 2.5, n[NH(C_2H_5OH)$_3$] : n[Ti(OBu)$_4$] = 1, n[Eth] : n[Ti(OBu)$_4$] = 21. Through dropping HNO_3 to change pH value, the gelation time T was tested under different pH values).

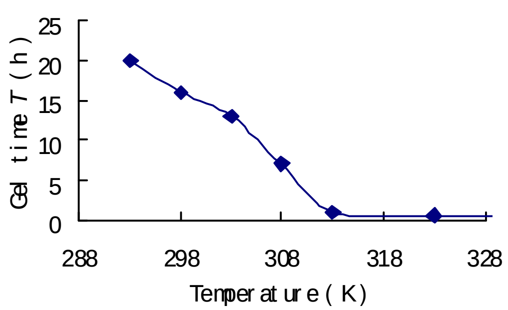

Fig. 7: Effect of hydrolysable temperature on gelable time (with AcAc solvent, n[H_2O] : n[Ti(OBu)$_4$] = 2.5, n[NH(C_2H_5OH)$_3$] : n[Ti(OBu)$_4$] = 1, n[Eth] : n[Ti(OBu)$_4$] = 21, pH = 3.5).

Fig. 8: SEM micrograph of TiO_2.

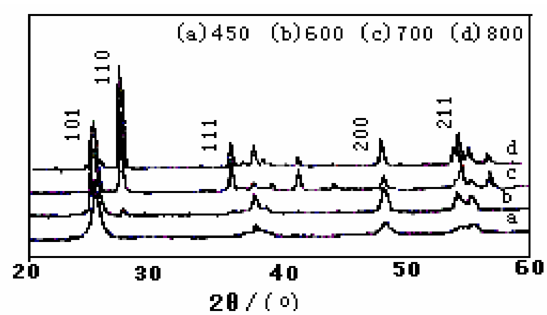

Fig. 9: XRD result of TiO_2 thin film by heat treatment.

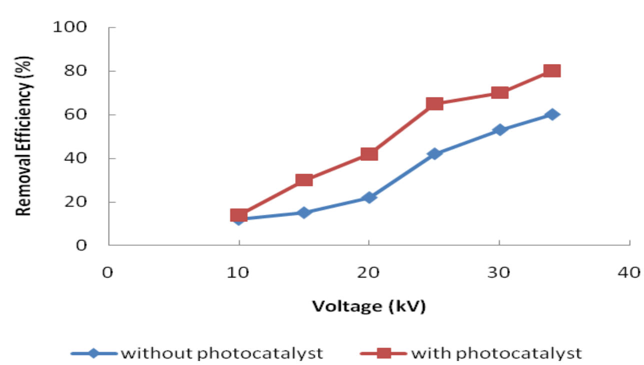

Fig. 10: Comparing bezene removal efficiency with or without photocatalyst in plasma reactor.
(benzene concentration is 1500 mg/m^3, the average voltage is 30 kV and gas flow rate is 14 mm/s)

volatilization with the temperature increasing. As a result, the gel time is shorter and the condensation polymerization process speeds up when the concentration of the reagent increases.

From Figs. 4-7, the preparation process of photocatalyst was optimized to form the next results as follows:

Precursor solution**:** 1mol tetrabutyl titanate (precursor substance) + 12mol ethanol (solvent) + 1.2mol acetyiacetone (chelating reagent).

Droplet solution**:** 6mol ethanol (solvent) + 1mol HNO_3 (catalyzer) + 2.5mol distilled water.

Droplet solution was dropped slowly into the original solution at 35°C and the whole solution was mixed well together. The steady sol would be obtained, and then the sol should be deposited at least 24 hours. The packed materials (i.d. 5 mm, thickness 3 mm, length 10 mm, raschig ceramic ring) must be washed by ultrasonic before they were immersed into the sol. The results of physical characteristics of the packed materials are given in Table 1. Later, the packed materials were pulled out from the sol at the speed of 1.5 mm/s to get the nanometer TiO_2 film.

The packed materials with nanometer film would be dried at 80°C for one hour before they were put into a muffle furnace to calcine at 450°C for two hours. At last, the film gradually refrigerated to ambient temperature.

The nanometer TiO_2 thin film was inspected and analysed by Scan Electric Mirror. The results of SEM micrograph showed that average particulate diameters of TiO_2 were less than 100 nm. SEM micrograph of the samples is shown in Fig. 8.

Comparing benzene removal efficiency with or without photocatalyst in plasma reactor: The relationship between benzene degradation and electrostatic field strength with or without photocatalyst is shown in Fig. 10. When benzene concentration is 1500 mg/m^3, the average voltage is 30 kV and gas flow rate is 14 mm/s, the destruction efficiency is higher at 19% with photocatalyst than without photocatalyst in the plasma reactor. The results indicate that photocatalyst enhanced the benzene decomposition efficiency obviously.

CONCLUSIONS

Using $Ti(OBu)_4$ as precursor, different complexation, solvent and catalyst, TiO_2 films were prepared by sol-gel method. The influence of changing the rates of raw materials and experimental conditions was explored and researched on preparing TiO_2 thin film. Then the optimum raw materials rates, process and controlled conditions of nano-TiO_2 thin film were obtained. If molar ratio of H_2O and $Ti(OBu)_4$ equals to 2.5; molar ratio of Eth and $Ti(OBu)_4$ equals to 18; molar ratio of complexation and $Ti(OBu)_4$ equals to 1.2; pH lies in 3~5; hydrolysable temperature lies in 25~35°C; and heat treatment temperature arrives at 450°C, the sol film will get better stabilization.

With nano-TiO_2 used as photocatalyst, a series of experiments were carried out. The results of synthesis effect showed that the effect of degradation was visible by added photocatalyst in the plasma reactor. When concentration of benzene was 600 mg/m^3 and electric field strength was 10 kV/cm, the removal efficiency was increased to 15% higher than without photocatalyst. Nano-TiO_2 crystal was anatase crystal in 450°C heat treatment is best for benzene removal.

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