Application of and research on TiO₂ photocatalysis technology

Wu Mengjie^{1*}, Liu Kun²

¹School energy and power engineering, Wuhan university of technology, Wuhan, Hubei, 430063, China

²School of navigation, Wuhan university of technology, Wuhan, Hubei, 430063, China

Abstract. Nano-TiO₂ photocatalysis technology is a new environmental pollutant purification technology, but its application is very extensive. This paper introduces the photocatalytic properties of nano-TiO₂, and summarizes the research progress of nano-TiO₂ in industrial wastewater, marine pollution, solid waste degradation, air purification and sterilization. At the same time, it is pointed out that the nano-TiO₂ photocatalytic technology has not fully reached the practical application level, and the development trend of nano-TiO₂ photocatalytic materials is prospected. Photocatalytic oxidation (PCO) using nanomaterials is a promising technology for removing pollutants, especially in deodorization, degradation of volatile organic compounds (VOCs) and sterilization. The mechanism of nanometer photocatalysis was reviewed in this paper. The influence factors including initial concentration of pollutants, reaction time, light intensity, humidity, surface area and catalyst activity were discussed. Furthermore, the application in photocatalytic removal of gas phase contaminants was summarized, and the future development of its application was proposed based on the existing problems.

1 INTRODUCTION

With the increasing air pollution, the problem of purification and removal of gaseous pollutants in the air, especially volatile organic compounds, has become an urgent environmental problem. To this end, many techniques such as filtration, adsorption, low temperature plasma, photocatalysis, and catalytic oxidation have been studied. Among them, photocatalytic oxidation technology is an emerging and potential gas phase pollutant purification technology that has received increasing attention in recent years, and has a generally good degradation effect on VOCs.

Volatile organic compound emissions have caused global atmospheric environmental problems such as photochemical smog, urban ash, acid rain, which seriously threaten human health and safety. NO and NO₂, which are often harmful to the human body in the air, can bind to hemoglobin in the blood, causing the same hypoxia as CO at high concentrations, and affecting the respiratory system and the nervous system. NO₂ is 45 times more toxic than NO, and has a strong stimulating effect on human respiratory organs. It has a strong corrosive effect on lung tissue after entering the lungs. The hazards of nitrogen oxides are slowly accumulated unconsciously, and their damage is hidden and long-lasting. NO_x is also known as the “invisible killer”. The commonly used methods for removing nitrogen oxides include physical adsorption method, catalytic reduction method, photocatalysis method, etc. At present, the method for removing NO_x is a catalytic reduction method, but this method is limited to the removal of nitrogen oxides from pollution sources. It is not suitable

for indoor use. Although the physical adsorption method has good adsorption capacity, it has the disadvantages of easy saturation of adsorbent and secondary pollution caused by desorption of adsorbed products.

Among various single or complex photocatalysts such as TiO₂, ZnO, CdS, and Fe₃-TiO₂, TiO₂-based photocatalysts are currently recognized as excellent photocatalytic materials. TiO₂ has non-toxic, low-cost and thermal stability. In this paper, the photocatalytic oxidation mechanism, influencing factors and application of gas phase pollution in air have been reviewed for TiO₂ photocatalysis technology.

2 EXPERIMENTAL PART

2.1 Reagents and instruments

Powder coconut shell activated carbon, industrial grade; butyl titanate, absolute ethanol, glacial acetic acid, concentrated hydrochloric acid are analytically pure. GZX9140 MBE digital display blast drying oven; CJJ781 magnetic heating stirrer; HC-B type electronic balance; LD88A type pelleting machine; YC-D205 ultrasonic humidifier; PTH-A type precision temperature and humidity inspection instrument; GDYK206S type formaldehyde Tester, etc

2.2 Preparation of activated carbon/TiO₂ sol

Measure 100 mL of butyl titanate and slowly add it to 300 mL of absolute ethanol, stir rapidly, and mix well to obtain A solution. Then, 10 mL of deionized water, 10

* Corresponding author: 804612350@qq.com

mL of concentrated hydrochloric acid, 10 mL of glacial acetic acid, and 100 mL of absolute ethanol were uniformly mixed and stirred to obtain a B solution. Add 50 g of powdered activated carbon to the solution A, stir well, then slowly drop the B solution into the solution A, and continue to stir for 1 h to prepare a sol, which is sealed and gelled at room temperature. Dry at 100 °C for 12 h.

3 PRINCIPLE OF PHOTOCATALYTIC OXIDATION OF NITROGEN OXIDES

Photocatalysts are mostly N-type semiconductor materials, such as TiO₂, ZnO₂, CdS, etc. Among them, TiO₂ is highly valued due to its high activity, good chemical stability, non-toxic and harmless, and can be loaded onto walls, ceramic tiles, glass, etc. a photocatalyst. The forbidden band width of TiO₂ is 3.2eV. When it absorbs photons with a wavelength less than or equal to 387.5nm, the surface of the semiconductor will generate electron e⁻ and hole h⁺, which interact with H₂O, O₂ to form hydroxyl OH and peroxy anion. The O₂-equivalent oxidizing substance oxidizes and removes the contaminants adsorbed on the surface of the catalyst.

It has been found that in the presence of oxygen, ultraviolet light irradiates TiO₂ to produce a peroxy anion O₂⁻, which is then reacted with nitrogen oxides to form nitric acid. It can be speculated that the reaction mechanism equation of nitrogen oxides is as follows:

Under certain energy, electrons and holes generated by TiO₂ semiconductors are separated and migrated to the surface of the nanoparticles. Among them, photogenerated electrons (e⁻) have strong reducing ability, which can reduce electron acceptors such as O₂ adsorbed on the surface of nano-semiconductors; photogenerated holes (h⁺) have strong oxidizing ability and can capture organic substances or solvents adsorbed on the surface of semiconductors. The electrons in the medium activate H₂O in the air to form a strong oxidizing hydroxyl radical ·OH. The active OH can oxidize the organic matter in the air into inorganic substances such as CO₂ and H₂O.

4 Factors affecting photocatalytic oxidation of oxides

4.1 Initial concentration / residence time

Previous studies have shown that the photocatalytic method is more efficient for low-concentration contaminants. When the reaction reaches steady state, the efficiency of TiO₂ photocatalytic oxidation of nitrogen oxides increases with the decrease of initial

concentration. The method of reducing the gas flow rate and prolonging the residence time can be used to increase the conversion efficiency of photocatalytic oxidation of NO, that is, to extend the contact time between NO_x and TiO₂, so that the nitrogen oxides have sufficient time to react with the catalyst to increase the conversion rate.

The optimum residence time varies depending on the reaction system and experimental conditions used in the experiment. As shown in Figure 1, at a relative humidity of 50%, the conversion of NO at different initial concentrations reached a maximum at 12 s.

figure 1

4.2 Temperature

One of the advantages of the photocatalytic method is that the reaction can occur at room temperature. It has been found that the efficiency of oxidative removal of NO by TiO₂ increases with increasing temperature (about 320K to 500K). In the temperature range of 0~25 °C, the photocatalytic oxidation efficiency increases with the increase of temperature, while the temperature in the range of 25~60 °C has no significant effect on the photocatalytic reaction efficiency. This may be due to the fact that the photocatalytic oxidation reaction is related to the diffusion and migration of the reactant molecules or intermediates on the catalyst surface and the desorption of the reaction products at the active center in the temperature range of 0 to 25 °C.

4.3 Humidity

Water is indispensable for photocatalytic reaction. Water molecules provide hydroxyl groups that can capture photogenerated holes, and then produce highly oxidic hydroxyl radicals OH· to oxidize and decompose pollutants adsorbed on the catalyst surface. It is good for oxygen-absorbing light and, in most cases, accelerates the photocatalytic reaction. Studies have shown that within a certain humidity range, the NO_x conversion rate increases with the increase of relative humidity, but when the humidity exceeds a certain range, the increase of humidity has little effect on the efficiency of photocatalytic oxidation or even lowers the efficiency. When studying the photocatalytic oxidation of nitrogen oxides in automobile exhaust gas, it was found that when the volume flow rate of NO₂ gas was 0.5L/min and the concentration was 0.35mg/m³, the relative humidity was in the range of 60% to 72%, and photocatalysis of NO₂

gas. The oxidation efficiency drops sharply with increasing gas humidity, from 95% to 45%. The reason is that excessive water molecules may compete with NO_x at the active sites on the surface of the photocatalyst, and at the same time act with NO_2 , which weakens the adsorption of NO_2 by photocatalysts. The water adsorbed on the surface of TiO_2 makes photoelectrons and holes easier to recombine.

4.4 Light intensity

When the intensity of the incident light is greater than a certain value, the photogenerated carriers can be excited and a photocatalytic reaction occurs. The TiO_2 photocatalyst itself has a large band gap ($E = 3.2 \text{ eV}$). As the intensity of the UV light increases, the reaction rate increases. The efficiency of photocatalytic oxidation is related to the initial concentration of pollutants, and the effect on low concentration is not significant. For higher concentrations of nitrogen oxides, the efficiency of photocatalytic oxidation increases with the increase of light intensity, due to ultraviolet light. The increase in intensity increases the energy of the excitation photocatalyst, so that the number of electron-holes generated by the excitation per unit time is increased, thereby improving the photocatalytic oxidation efficiency. In addition, proper intensity of light can promote the separation of electron-hole pairs on the catalyst surface and increase the number of photogenerated electron holes, thereby increasing the active adsorption sites on the surface of the photocatalyst, resulting in an increase in photocatalytic oxidation efficiency.

5 Effective ways to improve the performance of TiO_2 photocatalytic treatment of gaseous pollutants

Due to the limitation of the forbidden band width, TiO_2 can only absorb ultraviolet light, and the content of ultraviolet light in sunlight is less than 5%. The formed electron-hole pairs can be recombined during the reaction, which affects the photocatalytic efficiency of TiO_2 . The currently studied modification methods mainly include precious metal loading, metal / non-metal element doping, semiconductor compounding, etc.

5.1 Precious metal load

Precious metal loading is an effective method to enhance the photocatalytic performance of TiO_2 . Many studies have shown that by enriching electrons in the Schottky barrier conduction band, depositing metal nanoparticles on TiO_2 can significantly improve its photocatalytic oxidation efficiency and effectively inhibit The recombination of photogenerated electron-hole pairs further improves the photoelectric activity of TiO_2 . At present, the precious metals commonly used in research are Pt, Ru, Pd, Au, and Ag. However, the use of precious

metals to support TiO_2 is relatively expensive and has not been widely used.

5.2 Metal doping

Metal doping is the introduction of impurity metal ions into the TiO_2 lattice, which results in a change in crystallinity or a trap to capture electrons, reducing the recombination rate of photogenerated electron-hole pairs, thereby improving the photocatalytic activity of TiO_2 .

5.3 Non-metal doping

The essence of non-metal doping is that non-metal elements replace some of the oxygen in the TiO_2 lattice, doped in the semiconductor, and introduce defect levels or impurity levels into the band gap of TiO_2 to reduce the band gap of TiO_2 and widen the light Degradation catalyst photoresponse wavelength range, thereby improving photocatalytic efficiency. Among them, C, B, S, N, F, etc. are the more common doping elements.

6 Conclusion

Although photocatalysis technology has received extensive attention and research in recent decades, there are still many problems to be solved. Due to the low efficiency of PCO reaction light utilization, most of the current PCO technology only stays in the laboratory stage. To be widely used, it is necessary to improve the spectral wavelength response range, increase the contact specific surface area of the device, and develop catalyst immobilization technology. Key technologies are key to tackling key issues.

The light-efficiency efficiency of PCO technology for removing gaseous pollutants such as VOCs is still very low, and its single application is greatly limited by a single PCO technology. In the future, combined with low-temperature plasma, adsorption and other technologies to achieve high efficiency, low energy consumption, plasma catalytic combined processing technology to remove VOCs and purify air will be the key development direction. The integrated air purifier developed based on such photocatalytic combined technology is very It may become a new generation of air purifiers in the future. In order to promote the technological advancement of PCO air purification technology, more in-depth research should be conducted on the synergistic methods of photocatalysis and low-temperature plasma, the synergistic mechanism, and the dynamics model for co-degradation of VOCs.

In order to create a high-quality indoor environment, scientists have done a lot of research on the removal of indoor and outdoor nitrogen oxides. Among many air purification methods and methods for removing nitrogen oxides from pollution sources, TiO_2 photocatalysis has obvious advantages and is suitable for the purification of indoor low-concentration nitrogen oxides, which has broad application prospects. However, the mechanism of nitrogen oxide photocatalytic reaction, influencing

factors, and improving conversion efficiency and deactivation of catalysts still need further research.

TiO₂ is an environment-friendly catalyst, and has broad application prospects in the treatment of atmospheric environmental pollution. However, the photocatalytic oxidation technology also has some limitations, including the recombination of electrons and holes in the catalyst, the low utilization of solar light sources, the high cost of some catalyst modification technologies, and the inability to achieve large-scale promotion and application.

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