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Experimental studies on photocatalytic oxidation of nitric oxides using titanium dioxide

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Abstract: In order to remove nitric oxides (NO) from flue gas, experimental studies on the photocatalytic oxidation (PCO) of NO are carried out in an efficient laboratory-scale reactor. Nano-sized TiO_2 particles loading on quartz sand are prepared and used as the photocatalyst. Effects of several key operating parameters on NO conversion are investigated, including operating temperature, NO inlet concentration, oxygen percentage, relative humidity and residence time. The results illustrate that the NO inlet concentration, the oxygen percentage and the relative humidity play an important role in the oxidation of NO. A lower NO inlet concentration and a higher oxygen percentage result in a higher NO conversion efficiency. When the relative humidity is 8%, the maximum value of NO conversion efficiency is achieved. In addition, the operating temperature and the residence time have a little effect on the conversion efficiency of NO.

Key words: photocatalytic oxidation; nitric oxides; titanium dioxide

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NO_x discharged from thermal power plants is harmful to humans, animals, plants and building materials through the acid deposition and photochemical smog[1-2]. The existing NO_x control methods and DeNO_x technologies have several shortcomings, such as low removal efficiency and high costs. The main reason is that NO (approximately 90% to 95% of NO_x) has low solubility and reactivity[3]. Therefore, it is necessary to develop environmentally friendly and economical technologies to treat NO_x.

Photocatalytic oxidation (PCO) is a newly developed technology which has the advantages of mild reaction conditions, simple equipment, low energy consumption and fewer secondary pollutants[4-7]. Titanium dioxide (TiO_2) is the most attractive photocatalyst, which is promising for decomposing pollutants from air and water. Ibusuki et al.[8] investigated the PCO of nitrogen oxides with the use of the TiO_2 photocatalyst in 1994. Devahasdin et al.[9] studied the transient behavior of the PCO of NO. Mahalakshmi et al.[10] reported the gas phase photocatalytic applications with TiO_2 and beta zeolite. Photocatalytic paints and mortar panels were studied at some cities in Europe[11]. It was reported that the anatase form of TiO_2 is the most active for photocatalytic reactions[12].

In the present paper, the reaction mechanism for the PCO of NO is discussed, and TiO_2 loading on quartz sand is applied to treat NO_x by the PCO. This paper focuses on some key factors influencing the conversion of NO, including operating temperature, NO inlet concentration, oxygen percentage, relative humidity and residence time.

1 Reaction Mechanism

TiO_2 is a kind of semiconductor with a wide band-gap energy of 3.2 eV. Fig. 1 shows the mechanism for photocatalytic reaction at the valence band and the conduction band of TiO_2. In order to make a valence band electron be promoted to the conduction band by illumination, the wavelength of light λ should meet the following condition:

$$h\nu = h\frac{c}{\lambda} > E_g$$

where h is the Planck constant (4.14×10^{-15} eV · s); ν is the frequency of light; c is the velocity of light (2.996×10^8 m/s); E_g is the band-gap energy of solid-state TiO_2 (3.2 eV). Substituting the corresponding values into the above formula, we can obtain that $\lambda < 387$ nm. Therefore, the TiO_2-based photocatalyst should be activated by a UV light source.

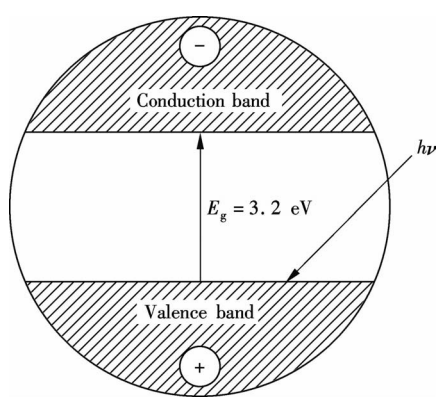

Fig. 1 Mechanism for photocatalytic reaction at valence band and conduction band of TiO_2

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From the above discussions, we can find that an electron-hole pair is generated when TiO_2 is subjected to the ultraviolet photon radiation ($\lambda < 387$ nm). The reaction mechanism of PCO is as follows:

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+)$$

The resulting electron-hole pair can take part in most of the oxidation and reduction chemical reactions. As a result, radical · OH and O_2^- are further generated from the reactions between the electron-hole pair and materials adsorbed on the surface of TiO_2, such as water and oxygen molecules. A possible reaction route of hole and electron is inferred as follows[13-14]:

Reactions of h^+

$$H_2O + h^+ \rightarrow \cdot OH + H^+$$
$$OH^- + h^+ \rightarrow \cdot OH$$

Reactions of e^-

$$O_2 + e^- \rightarrow O_2^-$$
$$O_2^- + H_2O \rightarrow HO_2 \cdot + OH^-$$
$$2HO_2 \cdot \rightarrow O_2 + H_2O_2$$
$$HO_2 \cdot + H_2O + e^- \rightarrow H_2O_2 + OH^-$$
$$H_2O_2 + e^- \rightarrow \cdot OH + OH^-$$

These intermediate products possess strong oxidization. Radical · OH and O_2^- can oxidize NO to NO_2. Then, partial NO_2 will be further oxidized to nitric acid. Negishi et al.[15] reported that the formation of HNO_3 was postulated as the final product in the PCO of NO_x.

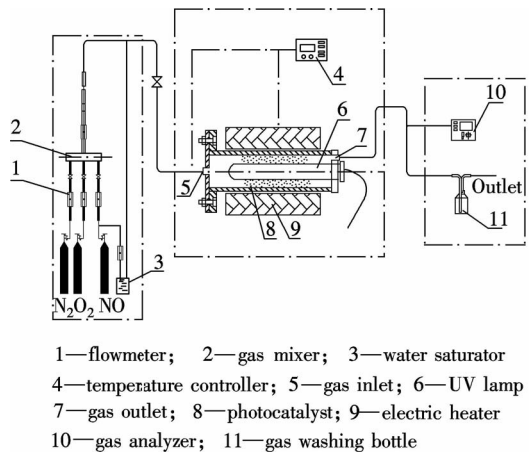
2 Experimental

2.1 Photocatalyst preparation

First, 3 g nano-sized TiO_2 with a crystal phase of anatase and a mean diameter of 10 nm (Nanjing High Technology Nano Material Co., Ltd.) is mixed with de-ionized water to prepare a slurry with the use of a magnetic stirrer (DF-Ⅱ, China). Secondly, 117 g quartz sand with a mean diameter of 3 to 4 mm, which has high UV light transmittance, is immersed in the resulting slurry for 1 h with an ultrasonic generator (GL-600SD, China), which is used to excite ultrasonic wave (15 kHz) to well coat TiO_2 on the support. Finally, the coated support is put into an oven (160 ℃) for drying to obtain the photocatalyst sample we need.

2.2 Experimental setup

The schematic experimental setup is shown in Fig. 2. The experiments for studying the conversion of NO by PCO are carried out in a laboratory-scale reactor with an inner diameter of 47 mm and a length of 600 mm. The artificial flue gases, N_2 gas, O_2 gas and NO gas from the cylinders are mixed to obtain the desired concentration and the photocatalyst is set into the reactor. The influent mixture gas is heated to the desired operating temperature by an electric heater while being fed into the reactor which is then irradiated with a UV lamp of 15 W (Nanjing Huaqiang Electronics Co., Ltd.). The temperature of the reactor is adjusted by a temperature controller. The concentration of the remaining NO is measured by a gas analyzer (DELTA65, Germany). A washing bottle containing an aqueous sodium hydroxide solution is used to absorb the untreated NO_x.



1—flowmeter; 2—gas mixer; 3—water saturator
4—temperature controller; 5—gas inlet; 6—UV lamp
7—gas outlet; 8—photocatalyst; 9—electric heater
10—gas analyzer; 11—gas washing bottle

Fig. 2 Schematic diagram of the experimental setup

3 Results and Discussion

3.1 Blank test

The blank test is conducted first on the condition that the reactor is illuminated by the UV lamp without the photocatalyst. Fig. 3 gives the conversion efficiency of NO. In this case, the total gas flow rate is 1.06 L/min; the concentration of NO at the gas inlet is 620 mg/Nm^3; the volume fraction of oxygen is 6%; the relative humidity is 8%; and the temperature of the reactor is 125 ℃.

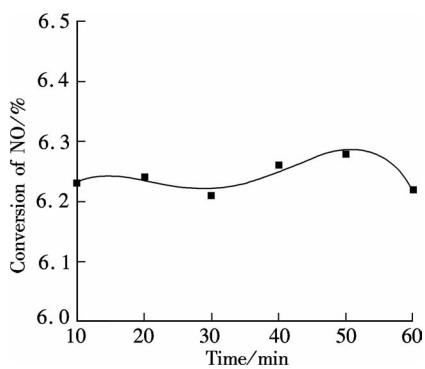


Fig. 3 NO conversion efficiency with the illumination of UV lamp only

It can be found that the NO conversion efficiency is close to 6.25% with the illumination of the UV lamp only. The main reason is that some photodegradation reactions may occur under this condition. Therefore, it is concluded that the presence of the UV lamp causes the oxidation of a small amount of NO.

In the next experiments, the effects of several operating parameters such as operating temperature, NO inlet concentration, oxygen percentage, relative humidity and residence time on the NO conversion efficiency are studied. Detailed experimental parameters are given in Tab. 1.

Tab. 1 Experimental parameters

Operating temperature/℃	NO inlet concentration/ (mg · Nm^{-3})	Oxygen percentage/%	Relative humidity/%	Residence time/min
40, 80, 120, 160, 200	620	6	8	1
125	400, 600, 800, 1 000, 1 200, 1 400, 1 600, 1 800, 2 000	6	8	1
125	620	2, 4, 6, 8, 10	8	1
125	620	6	2, 4, 6, 8, 10, 12	1
125	620	6	8	0.5, 1, 1.5, 2, 2.5

3.2 Effect of operating temperature

Fig. 4 shows the NO conversion efficiency profile under different operating temperatures. The total gas flow rate is 1.06 L/min; the concentration of NO at the gas inlet is 620 mg/Nm^3; the volume fraction of oxygen is 6%; and the relative humidity is 8%.

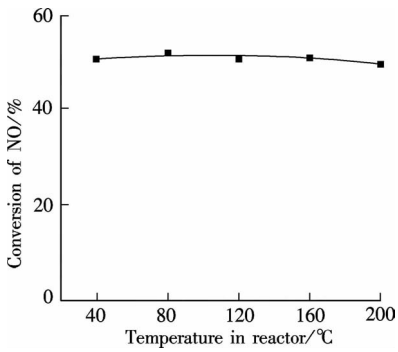


Fig. 4 Effect of operating temperature on NO conversion efficiency

The experimental results show that the conversion efficiency of NO changes a little when the operating temperatures range from 40 to 200 ℃. In this experiment (see Fig. 4), the NO conversion efficiency is around 50%.

Zhao et al.[14] carried out experiments to evaluate the effect of operating temperature on NO conversion efficiency. Their results also show that the operating temperature has less effect on the conversion efficiency of NO.

3.3 Effect of NO inlet concentration

The effect of NO inlet concentration is shown in Fig. 5. The total gas flow rate is 1.06 L/min; the volume fraction of oxygen is 6%; the relative humidity is 8%; and the operating temperature is 125 ℃.

It is found that the NO inlet concentration has a remarkable effect on the conversion efficiency of NO. Higher initial concentration leads to a lower oxidation efficiency. The NO conversion efficiency declines from 56.8% to 24.8% when the NO inlet concentration increases from 400 to 2 000 mg/Nm^3.

3.4 Effect of oxygen percentage

The effect of oxygen percentage is shown in Fig. 6.

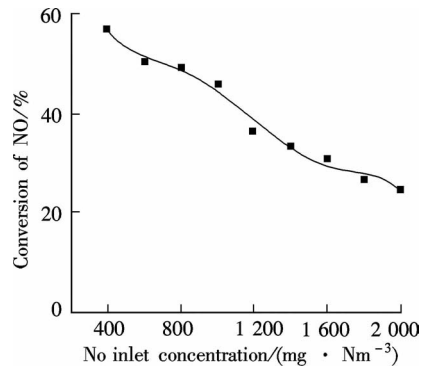


Fig. 5 Effect of NO inlet concentration on NO conversion efficiency

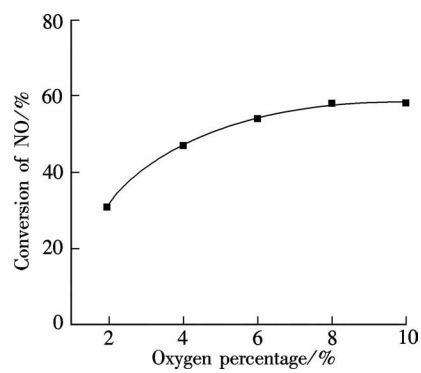


Fig. 6 Effect of oxygen percentage on NO conversion efficiency

The total gas flow rate is 1.06 L/min; the concentration of NO at the gas inlet is 620 mg/Nm^3; the relative humidity is 8%; and the operating temperature is 125 ℃.

The experimental results show that the percentage of oxygen plays an important role on the NO conversion efficiency. In general, the NO conversion efficiency increases with the oxygen percentage increasing. When the volume fraction of oxygen is 8%, the value of NO conversion efficiency is close to 55%.

The oxygen is very important in this system as it takes part in the corresponding reactions as an electron acceptor, which can effectively prevent the recombination between h^+ and e^-[16]. Furthermore, the resulting O_2^- can also promote the oxidation of NO. In conclusion, the presence of oxygen is beneficial for the PCO of NO.

3.5 Effect of relative humidity

The effect of relative humidity on the NO conversion efficiency is also investigated. Water vapor generated by a water saturator is sent to the air pipe to meet the corresponding requirements of the experiments.

Fig. 7 shows the effect of relative humidity. The total gas flow rate is 1.06 L/min; the concentration of NO at the gas inlet is 620 mg/Nm^3; the volume fraction of oxygen is 6%; and the operating temperature is 125 ℃.

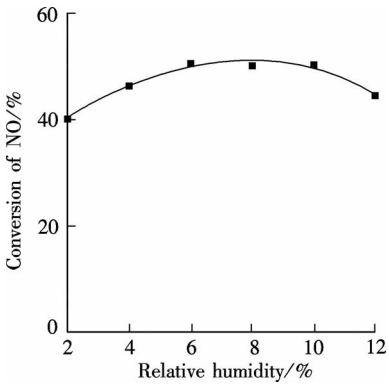


Fig. 7 Effect of relative humidity on NO conversion efficiency

When the relative humidity is below 8%, the NO conversion efficiency increases with the value of the relative humidity increasing. Then, the maximum value of the NO conversion efficiency is achieved when the relative humidity is 8%, but the NO conversion efficiency decreases when the relative humidity is above 8%.

Water molecules are also important materials in the PCO system as H_2O can react with both h^+ and e^-. More water molecules result in more · OH radical and O_2^-, which contributes to the oxidation of NO. However, too many water molecules will lead to competition adsorption, causing a declining NO conversion efficiency.

3.6 Effect of residence time

The effect of residence time is shown in Fig. 8. The total gas flow rates are 0.53, 1.06, 1.59, 2.12 and 2.65 L/min, respectively; the concentration of NO at the gas inlet is 620 mg/Nm^3; the volume fraction of oxygen is 6%; the relative humidity is 8%; and the operating temperature is 125 ℃.

The experimental results show that the effect of residence time on NO conversion efficiency is rather modest. The NO conversion efficiency fluctuates around 50.5% when the residence time ranges from 0.5 to 2.5 min.

It is reported that the PCO reactions are completed in a very short time (10^{-3} s)[17-18]. Therefore, the residence time of artificial flue gas in the reactor is enough for the completion of the PCO of NO. As a result, the NO conversion efficiency changes a little at different residence times.

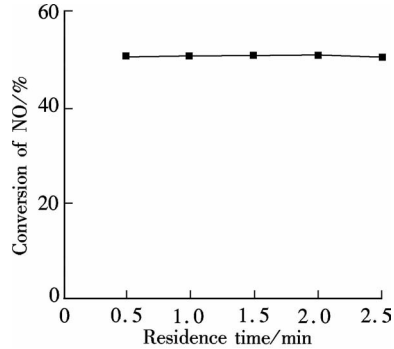


Fig. 8 Effect of residence time on NO conversion efficiency

4 Conclusion

Experimental studies on the photocatalytic oxidation of NO are carried out in a laboratory-scale reactor. Nano-sized TiO_2 particles (anatase) loading on quartz sand are used the as photocatalyst. The NO conversion efficiencies are measured at different operating temperatures, NO inlet concentrations, oxygen percentages, relative humidities and residence times. It is concluded that: A lower NO inlet concentration and a higher oxygen percentage will result in higher NO conversion efficiency; when the relative humidity is 8%, the maximum value of NO conversion efficiency is achieved; the operating temperature and residence time have a little effect on the conversion efficiency of NO.

References

[1] Allen G C, El-Turki A, Hallam K R, et al. Role of NO_2 and SO_2 in degradation of limestone [J]. *British Corrosion Journal*, 2000, **35**(1): 35 - 48.

[2] Ballari M M, Yu Q L, Brouwers H J H. Experimental study of NO and NO_2 degradation by photocatalytically active concrete [J]. *Catalysis Today*, 2010, **161**(1): 175 - 180.

[3] Radojevic M. Reduction of nitrogen oxides in flue gases [J]. *Environmental Pollution*, 1998, **102**(1): 685 - 689.

[4] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode [J]. *Nature*, 1972, **238** (5358): 37 - 38.

[5] Augugliaro V, Voluccia S, Loddo V, et al. Photocatalytic oxidation of gaseous toluene on anatase TiO_2 catalyst: mechanistic aspects and FT-IR investigation [J]. *Applied Catalysis B*: *Environmental*, 1999, **20**(1): 15 - 27.

[6] Takeda N, Torimoto T, Sampath S, et al. Effect of inert supports for titanium dioxide loading on enhancement of photodecomposition rate of gaseous propionaldehyde [J]. *Journal of Physical Chemistry*, 1995, **99**(24): 9986 - 9991.

[7] Shigwedha N, Hua Z Z, Chen J. A new photon kinetic-measurement based on the kinetics of electron-hole pairs in photodegradation of textile wastewater using the UV-H_2O_2FS-TiO_2 process [J]. *Journal of Environmental Sciences*, 2007, **19**(3): 367 - 373.

[8] Ibusuki T, Takeuchi K. Removal of low concentration of nitrogen oxides through photoassisted heterogeneous catalysis [J]. *Journal of Molecular Catalysis*, 1994, **88**(1):

93 - 102.
[9] Devahasdin S, Fan C, Li K Y, et al. TiO_2 photocatalytic oxidation of nitric oxide transient behavior and reaction kinetics [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2003, **156**(1/2/3): 161 - 170.
[10] Mahalakshmi M, Priya S V, Arabindoo B, et al. Photocatalytic degradation of aqueous propoxur solution using TiO_2 and Hβ zeolite-supported TiO_2 [J]. *Journal of Hazardous Materials*, 2009, **161**(1): 336 - 343.
[11] Maggos T, Plassais A, Bartzis J G, et al. Photocatalytic degradation of NO_x in a pilot street canyon configuration using TiO_2-mortar panels [J]. *Environmental Monitoring and Assessment*, 2008, **136**(1/2/3): 35 - 44.
[12] Linsebigler A L, Lu G Q, Yates J T. Photocatalysis on TiO_2 surfaces-principles, mechanisms, and selected results [J]. *Chemical Reviews*, 1995, **95**(3): 735 - 758.
[13] Laufsa S, Burgeth G, Duttlinger W, et al. Conversion of nitrogen oxides on commercial photocatalytic dispersion paints [J]. *Atmospheric Environment*, 2010, **44**(19): 2341 - 2349.
[14] Zhao Y, Han J, Zhao L, et al. Experimental studies on simultaneous desulfurization and denitrification of flue gas by photocatalysis with TiO_2 [J]. *Journal of Power Engineering*, 2007, **27**(3): 411 - 414. (in Chinese)
[15] Negishi N, Takeuchi K, Ibusuki T. Surface structure of the TiO_2 thin film photocatalyst [J]. *Journal of Materials Science*, 1998, **33**(24): 5789 - 5794.
[16] Subramanian V, Wolf E, Kamat P V. Semiconductor-metal composite nanostructures. To what extent do metal nanoparticles improve the photocatalytic activity of TiO_2 films? [J]. *Journal of Physical Chemistry*, 2001, **105**(46): 11439 - 11446.
[17] Tomkiewicz M. Scaling properties in photocatalysis [J]. *Catalysis Today*, 2000, **58**(2/3): 115 - 123.
[18] Hoffmann M R, Martin S T, Choi W Y, et al. Environmental application of semiconductor photocatalysis [J]. *Chemical Reviews*, 1995, **95**(1): 69 - 96.

二氧化钛光催化氧化一氧化氮的试验研究

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摘要:为脱除烟气中的一氧化氮(NO),在小试实验装置上进行了光催化氧化(PCO)烟气中 NO 的实验研究. 制备出负载在石英砂上的纳米级 TiO_2 颗粒作为光催化剂,通过试验分别考察了操作温度、NO 初始浓度、氧气含量、相对湿度、停留时间这 5 个重要因素对 NO 转化效率的影响. 研究结果表明,NO 初始浓度、氧气含量和相对湿度对 NO 的光催化氧化效率影响显著. NO 初始浓度越低、氧气含量越高时,NO 转化效率越高;当烟气相对湿度为 8% 时,NO 转化效率达到最高. 此外,操作温度和停留时间对 NO 转化效率影响甚微.

关键词:光催化氧化;一氧化氮;二氧化钛

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