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# Photocatalytic Removal of NO from Flue Gas by $TiO_2$ Loaded on Semi-coke Prepared by Sol-gel Method

SUN Sheng-nan[1], LI Chun-hu[1,2**], YANG Wei-wei[1], YAN Xin[1], ZHENG Yu[1], WANG Liang[1], BIAN Jun-jie[1]

(1. *College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao* 266100, *China*; 2. *Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Qingdao* 266100, *China*)

**Abstract**: $TiO_2$ supported on activated semi-coke (ASC) is prepared by the ultrasonic assisted sol-gel method, tetra-n-butyl titanate as precursor. The effects of $TiO_2$ loading amount, calcination temperature and time, and water vapor on the activity of photocatalytic oxidation of NO have been investigated. Prepared photocatalysts are characterized by X-ray diffraction (XRD), FT-IR, scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). With the optimum $TiO_2$ load, 5.22%, calcinated at 500 ℃ for 1 h, $TiO_2$/ASC photocatalyst performs the best photocatalytic activity with more than 70% NO conversion after a 3-hour reaction. Results indicate that the hydroxyl radical, $\cdot OH$, and superoxide radical, $\cdot O_2^-$, are responsible for NO photocatalytic oxidation while photodenerated hole has little effect in photocatalytic reaction. Regeneration test results show that the photocatalysts perform high stability and high-temperature with vapor in is an optimum regeneration method.

**Key words**: sol-gel method; $TiO_2$; photocatalysts; NO removal; activated semi-coke

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Since Fujishima and Honda[1] discovered the photocatalytic decomposition of water on titanium dioxide electrode in 1972, scientific and engineering interests in semiconductor photocatalysis have grown significantly. Subsequently, revolutionary research studies have been published in prestigious journals[1-5]. As is reported, photocatalysis shows the potential in meeting clean energy demands and tackling environmental through photocatalytic hydrogen or oxygen production[3, 5-8] and photocatalytic degradation of pollutant in polluted air and wastewater[9-12], respectively. Specifically, $TiO_2$ is considered to be the most attractive photocatalyst because of its high oxidative power, photostability, low cost and low toxicity. However, its large band gap energy (3.2 eV) and the fast recombination of photogenerated electron-hole pairs on the surface or in the lattices of $TiO_2$ result in low efficiency in practical applications[11, 13]. Activated carbon materials, such as activated carbon, activated carbon fiber (ACF), carbon nanotubes (CNTs), fullerene, and graphene with high surface area have been utilized in photocatalytic system in order to deal with these disadvantages and to thus extend the industrial applications[11, 14-16]. Furthermore, activated carbon materials provide a promising alternative for air purification, especially for the control of $NO_x$ emission[17-20]. Toma and his coworkers[21] studied the removal of nitrogen oxides pollutants via $TiO_2$ Degussa P25 power by photocatalysis, and found that $TiO_2$ was a kind of efficient photocatalyst for the removal of nitrogen oxides. Matsuda et. al[22] worked on the photocatalytic removal of $NO_x$, and discussed the mechanism of the $NO_x$ removal

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**First author**: Sun Sheng-nan(1986-), female, PhD. E-mail: ssn86_pumpkin@163.com.

* **Corresponding author**: LI Chunhu, lichunhu@ouc.edu.cn.

by the photocatalyst, which was thought to be divided into oxidation and adsorption processes, and the adsorption was regarded as more important than the oxidation processes in the experimental system. Many researchers[23-29] have worked hard to study the photocatalytic removal of NO and made significant achievements. However, utilizing $TiO_2$ on semi-coke photocatalyst made by sol-gel method for NO removal from flue gas has never been discussed. Professor Li and his team[30-32] have done a lot of work on removal of NO from flue gas by catalysts based on semi-coke, one of the most efficient carbon materials with excellent absorbency to NO. As same as other carbon materials, poor water resistance is the bottleneck problem for activated semi-coke removal of NO. Our previous work results[33] have indicated that $TiO_2$ loaded on activated semi-coke (ASC) is an efficient and new way to overcome water resistance.

This paper concentrates on using $TiO_2$ loaded on activated semi-coke as a photocatalyst for removing NO from flue gas. And in this paper, we have investigated the effect of loading amount of $TiO_2$ on activated semi-coke, calcination temperature and time for $TiO_2$ respectively. We have found that when the mass fraction of $TiO_2$ to activated semi-coke was 5.22% and $TiO_2$ was calcined at 500 ℃ for 1 h, the photocatalyst performed the best photocatalytic activity. Results indicate that the hydroxyl radical, $\cdot OH$, and superoxide radical, $\cdot O_2^-$, are responsible for NO photocatalytic oxidation while photodenerated hole has little effect in photocatalytic reaction. The stability of the re-prepared photocatalysts was detected by regeneration in different ways.

# 1 Experimental

## 1.1 Preparation of catalysts

The raw material of Ordos's semi-coke was activated by the nitric acid activation and hydrothermal activation. After then, semi-coke was washed by distilled water and dried at 110 ℃ overnight. $TiO_2$ was prepared by sol-gel method, tetra-n-butyl titanate used as titanium source, and then activated semi-coke was impregnated in sol for 24 h at room temperature. Ultrasonic stirring instead of conventional magnetic stirring was utilized in sol-gel method. The obtained mixture was dried at 110 ℃ overnight and calcined at different temperature in nitrogen for certain time. The loading of $TiO_2$ was varied by the volume of tetra-n butyl titanate in sol-gel process, such as 14, 12, 10, 8 and 6 mL, corresponding to the loading of $TiO_2$ 9.38%, 7.82%, 6.66%, 5.22%, and 3.96%. The calcination temperature and time were parameters tested in this experiment. Activated semi-coke with the optimal amount of $TiO_2$ loaded were calcined at 400, 450, 500, 550, and 600 ℃ for 1 h and calcined for 0.5, 1, 1.5 and 2 h at the optimal temperature, respectively. The prepared photocatalysts were noted as $TiO_2$/ASC. The partical size of raw semi-coke used in this paper is 0.90 ~ 0.45 mm. The specific surface area of raw semi-coke and activated semi-coke is 27 $mg/m^3$ and 364 $mg/m^3$, respectively.

## 1.2 Catalysts characterization

The scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) photos were carried out by HITACHI S-4800. FT-IR spectra (4 $cm^{-1}$ resolution) of samples were recorded on Nicolet iN10 + iZ10 (Thermo) at a spectral resolution of 4 $cm^{-1}$ and accumulating 32 scans over the spectral range of 400 ~ 4 000 $cm^{-1}$. The crystallinity of those photocatalysts was identified by X-ray diffraction (XRD) with a diffractometer (type Bruker D2-CRYSO) employing Cu $K_\alpha$ radiation. The accelerating voltage and the applied current were 30 kV and 10 mA, respectively.

## 1.3 Activity measurement

The photocatalytic reactor utilized in this experiment process was customized, as shown in Fig. 1. 50 mL photocatalysts was filled into the cylindrical reactor, with 50 mL quartz particles on the bottom, for per test. It has been proved that quartz particles have no obvious effect on de-NO. The reaction gas mixture was consisted of 300 $mg/m^3$ NO, 8% $H_2O$, 5% $O_2$ and $N_2$ in balance, while the gas hourly space velocity (GHSV) was 800 $h^{-1}$ and reaction covered at 100 ℃. An 18 W mercury lamp (254 nm) was used as UV-light source in this system. The feed and product con-

centrations were carried out by combustion analyzer, and the activity was shown as NO conversion which was calculated as follows:

$$NO\ conversion(\%) = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\% \quad (1)$$

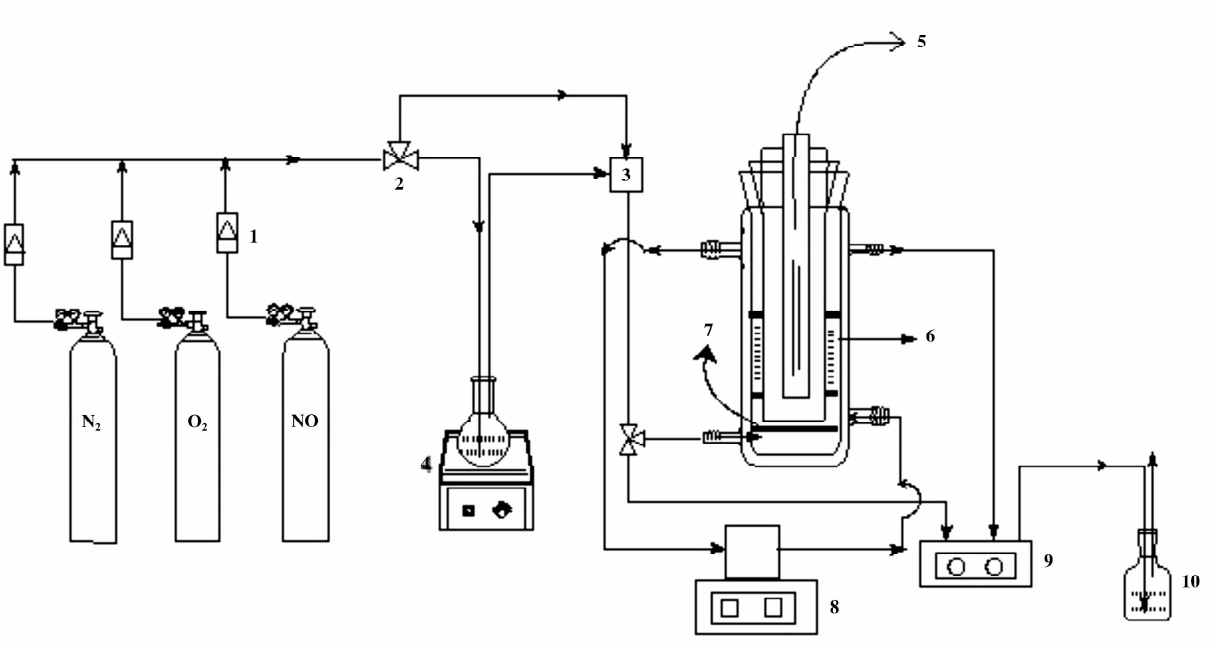


Fig. 1 Apparatus for photocatalytic removal of NO.

1: rotameter; 2: triple valves; 3: gas mixer; 4: humidifier; 5: mercury lamp; 6: photocatalyst; 7: gas-distribution plate; 8: circulator; 9: flue gas analyzer; 10: tail gas absorption solution

## 2 Results and discussion

### 2.1 Scanning electron microscope (SEM)

Fig. 2 shows the morphological characteristics of $TiO_2$/ASC calcined at different temperature for 1 h. And Fig. 3 shows the morphological characteristics of $TiO_2$/ASC calcined at 500 ℃ for different time. It reveals that $TiO_2$ film is obtained other than nano-particles in this experimental process, and calcination temperature and time affect the fracture extent of $TiO_2$ film. It is clearly that higher calcination temperature and longer calcination time make more thorough fracture of $TiO_2$ film. EDS (Fig. 4) further confirmed that the fracture on activated semi-coke surface was $TiO_2$. Ca and Al elements detected by EDS belong to impurities in semi-coke and C element is also from semi-coke. If no special instructions, the content of $TiO_2$ in $TiO_2$/ASC samples remained at about 5%.

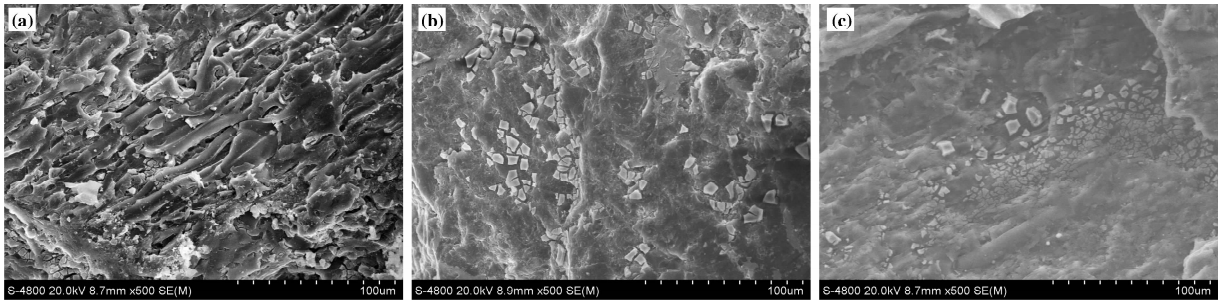


Fig. 2 SEM images of photocatalysts calcined at (a) 400 ℃, (b) 500 ℃, and (c) 600 ℃ for 1 h, respectively

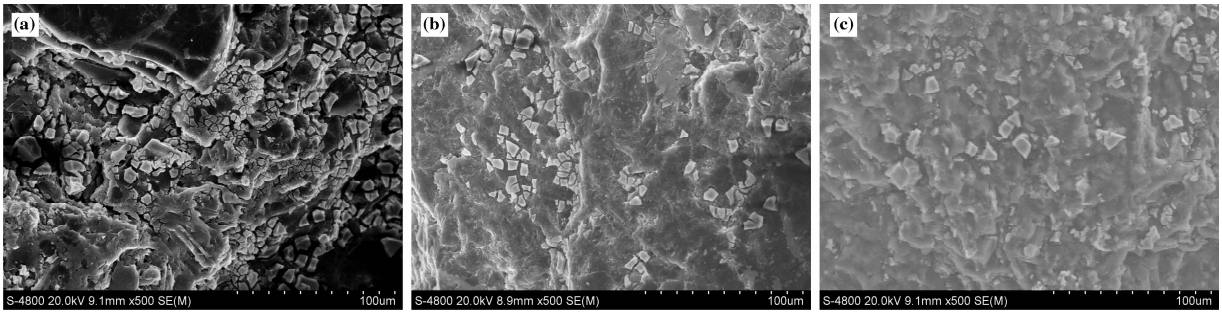


Fig. 3 SEM images of photocatalysts calcined at 500℃ for 0.5h (a), 1 h (b), and 1.5 h (c), respectively

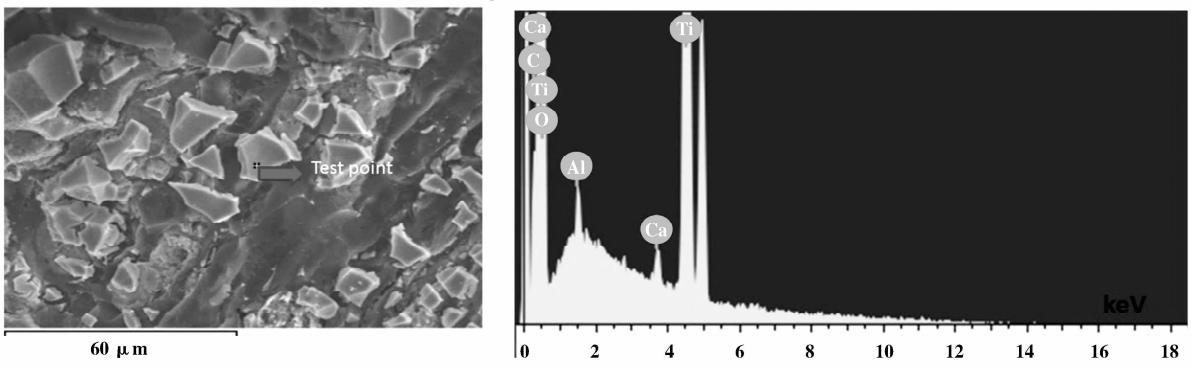


Fig. 4 Energy spectrum results of $TiO_2$/ASC calcined at 500 ℃ for 1 h

## 2.2 XRD study

Fig. 5 and Fig. 6 display the effect of calcination temperature and time on the crystal structure of $TiO_2$ films loaded on activated semi-coke, respectively. Fig. 5 exhibits that, with the calcination temperature increasing from 400 to 600 ℃, the intensity and the width of the diffraction peaks of anatase become higher and narrower, respectively. Barely rutile $TiO_2$ was observed at 600 ℃, and the reason is that the activated semi-coke inhibited the phase transition and thus the phase temperature of anatase to rutile was higher than pure $TiO_2$[16, 34]. With the calcination time increasing from 0.5 h to 2 h at 500 ℃, the trend is similar to that with the calcination temperature increasing.

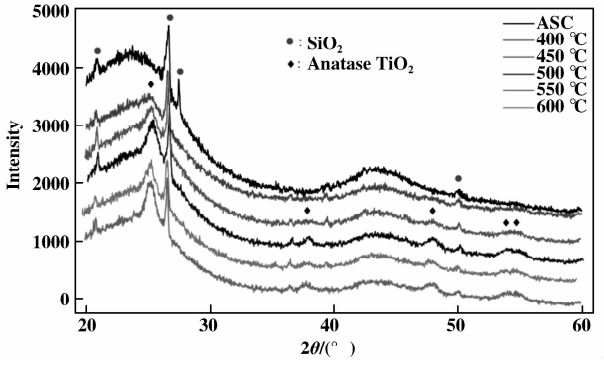


Fig. 5 XRD patterns of activated semi-coke and $TiO_2$/ASC calcined at different temperature for 1h, respectively

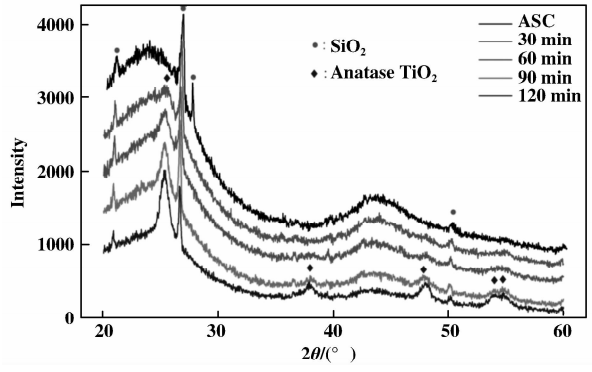


Fig. 6 XRD patterns of activated semi-coke and $TiO_2$/ASC calcined at 500 ℃ for different time, respectively

## 2.3 FT-IR spectrum

Fig. 7 reports the IR spectra of $TiO_2$/ASC, calcined at 500 ℃ for 1 h, before and after photocatalytic removal of NO. In order to eliminate the influence of water vapor adsorption on $TiO_2$/ASC catalysts, blank

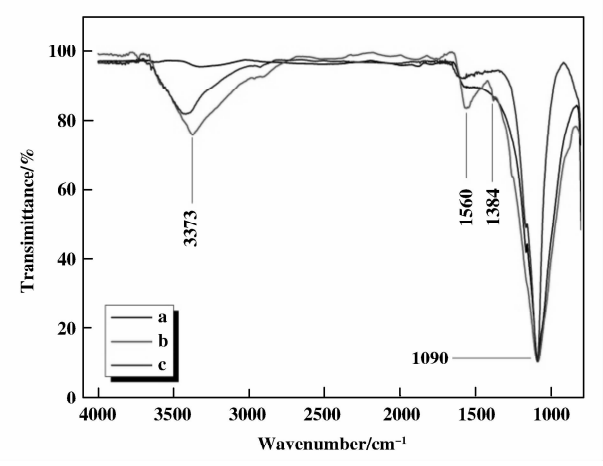


Fig. 7 FT-IR spectra of $TiO_2$/ASC photocatalyst before (a), after (b) photocatalytic removal of NO and blank test (c)

test was carried out at the same time. $TiO_2$/ASC catalysts were exposed to reaction mixed gas for 2 h in dark. 3 373 $cm^{-1}$ is due to the OH stretching band in the $TiO_2$/ASC catalysts after reaction IR spectra and blank test, which means that both adsorbed water and hydroxyl radical exit at the same time. Nitrate symmetric and antisymmetric stretching vibration peak appear at 1 560 $cm^{-1}$ and 1 384 $cm^{-1}$, respectively. The presence of these peaks proves that NO was oxided into $NO_2$ during the photocatalytic reaction. 1 085 $cm^{-1}$ can be described to be ether groups, which has barely changes during the reaction.

## 2.4 Photocatalysts activities

Fig. 8 exhibits the photocatalytic activities of removal of NO on different loads of $TiO_2$/ASC photocatalysts calcined at 500 ℃ for 1 h. When 8mL tetra-n-butyl titanate was added into the solution in the sol-gel method, the photocatalyst obtained exhibited better de-NO activities than other photocatalysts, with more than 70% conversion after 3 h photocatalytic reaction. The photocatalytic activities of removal of NO order are following: 5.2% > 4.0% > 6.7% > 9.4% > 7.8%. As shown in Fig. 8, 5.2% $TiO_2$ loaded on activated semi-coke performs the best effect on photocatalytic removal of NO in this experimental process. Activated semi-coke, with 0% $TiO_2$ loaded, exhibits better activities even than 7.8% $TiO_2$, and that is acceptable because of the strong capacity of activated semi-coke on removal of NO[30].

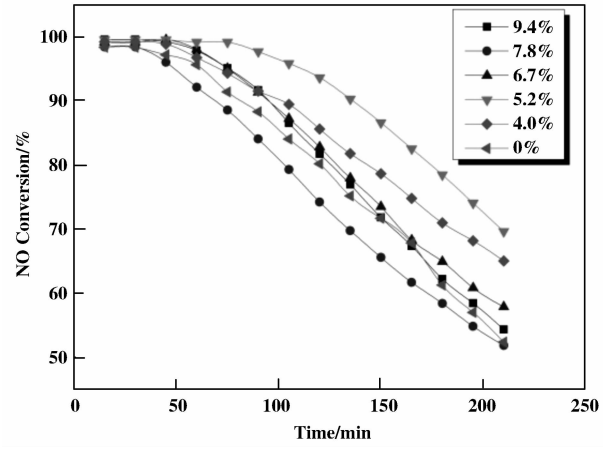


Fig. 8 The de-NO activities of photocatalysts with different amount of $TiO_2$ loaded on semi-coke

Fig. 9 reveals that photocatalysts calcined at 500 ℃ provides better de-NO activities than others. The

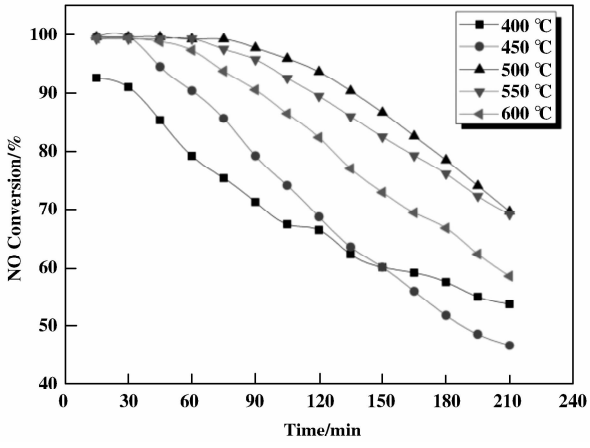


Fig. 9 The de-NO activities of photocatalysts calcined at different temperatures for 1 h

de-NO activities of photocatalysts increases with increase of calcination temperature from 400 to 500 ℃, but decreases with increase of calcination temperature from 500 to 600 ℃. It is clearly seen from Fig. 10 that photocatalyst calcined at 500 ℃ for 1 h exhibits better de-NO activities, which is in good agreement with XRD results. As calcination temperature and time affect the crystal structure thus effect the photocatalytic activity, there is another explanation for the photocatalytic activity increases with the increasing calcination temperature and time and then showed the opposite trend, decreases with the increasing calcination temperature and time. It has been well reported that sur-

face bound OH groups play a vital role in photocatalytic reactions over titanium dioxide[35], and the surface density of molecular water and hydroxyl groups on $TiO_2$ and activated semi-coke decreased as calcination temperature and time were increased[25].

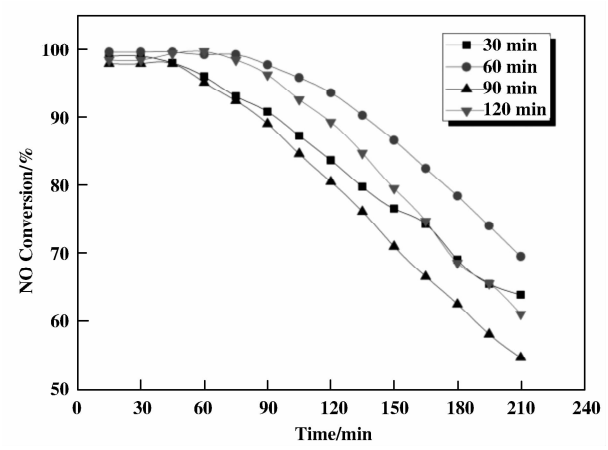


Fig. 10 The de-NO activities of photocatalysts calcined at 500 ℃ for different time

The mechanism of photocatalysis has been discussed in different ways, especially by fluorescence technique[37-39]. Salicylic acid (SA), triethanolamine (TEA) and p-benzoquinone (PBQ) are the common trapping agent of the hydroxyl radicals ( $\cdot OH$ ), the photogenerated hole ( $h^+$ ) and atomic oxygen radical anion ( $\cdot O_2^-$ ) respectively. We test the de-NO activities of $TiO_2$/ASC by adding SA, TEA and PBQ into humidifier, respectively, and the results are shown in Fig. 11. In the first 90 min reaction process, humidifier is filled with pure water but 0.1% salicylic acid, 5% triethanolamine and 5% p-benzoquinone aqueous solutions in the next 60 min reaction process, respectively. The NO conversion decreased sharply after salicylic acid and p-benzoquinone aqueous, $\cdot OH$ and $\cdot O_2^-$ trapping agent, were added into humidifier while no obvious fluctuations were detected when triethanolamine, $h^+$ trapping agent, was added into humidifier. The results have confirmed that $\cdot OH$ and $\cdot O_2^-$ radicals are responsible for NO oxidation in this reaction process other than $h^+$.

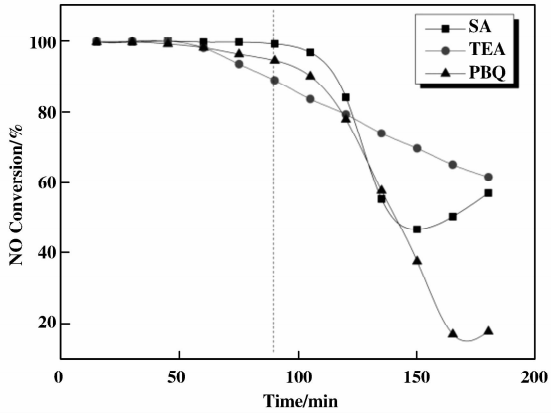


Fig. 11 The de-NO activities of $TiO_2$/ASC with addition of $\cdot OH$, $h^+$ and $\cdot O_2^-$ trapping agents in reaction system, respectively

As reported in literature, the surface bound $\cdot OH$ radicals act as efficient trapping sites for the photogenerated holes, thereby suppressing the energy wasting electron-hole recombination process, and yielding an increased lifetime for the photogenerated electron, the mobile charge carrier[40], which is then migrate to the surface of the photocatalyst particle and undergo a redox reaction with an adsorbed electron acceptor molecule[25]. Based on our previous work, activated semi-coke has preferable ability on adsorption and catalytic removal of NO. According to the results, we discuss the mechanism of photocatalytic removal of NO by $TiO_2$/ASC and it can be described that NO adsorbs on the surface of $TiO_2$/ASC and then transforms into $NO_2$ with oxidation by $\cdot OH$ and $\cdot O_2^-$. The schematic diagram of $TiO_2$/ASC catalysts photocatalytic removal of NO is shown in Fig. 12. The process can be detailed by the following equations.

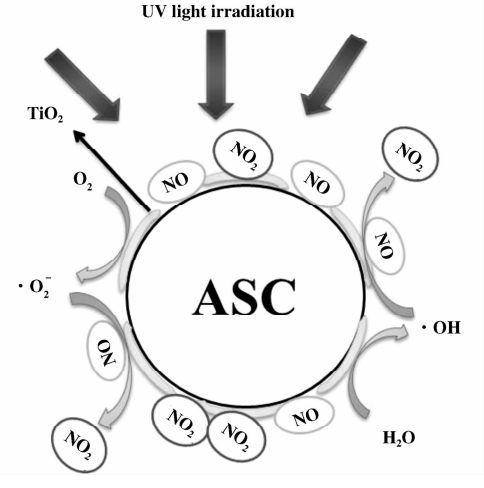


Fig. 12 Schematic diagram of $TiO_2$/ASC photocatalytic removal of NO

$$TiO_2 + hv \rightarrow h^+ + e^- \quad (2)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (3)$$

$$O_2 + e^- \rightarrow \cdot O_2^- \quad (4)$$

$$\cdot O_2^- + H_2O \rightarrow \cdot HO_2 + OH^- \quad (5)$$

$$\cdot HO_2 + H_2O \rightarrow H_2O_2 + \cdot OH \quad (6)$$

$$H_2O_2 \rightarrow 2 \cdot OH \quad (7)$$

$$NO + \cdot O_2^- \rightarrow NO_3^- \quad (8)$$

$$NO_3^- + H^+ \rightarrow HNO_3 \quad (9)$$

$$NO + \cdot OH \rightarrow HNO_2 \quad (10)$$

$$HNO_2 + \cdot OH \rightarrow NO_2 + H_2O \quad (11)$$

As photogenerated hole has little effect in photocatalytic removal of NO by $TiO_2$/ASC, eq. (3) can be ignored. Some of the photogenerated holes recombined with photogenerated electrons to liberate heat and others were caught by π-bond electrons of carbocyclic ring on semi-coke surface to finish nonradiative recombination.

As the stability is one of the most important reference points, regeneration test is carried out. Three regeneration method, ammonia, high temperature (400 ℃), high temperature (400 ℃) with 8% vapor, were utilized to measure the stability of the photocatalyst with loading 5.2% $TiO_2$ calcined at 500 ℃ for 1 h. In ammonia regeneration, photocatalysts were steeped in 2.28 mol/L hartshorn compounded by ammonia and distilled water for 24 h, and then washed by distilled water. In high temperature regeneration, photocatalysts were calicined at 400 ℃ in $N_2$ for 1 h. 8% vapor was added in high temperature with vapor regeneration. These three regeneration methods perform different regenerated capacity shown in Fig. 13. High temperature with 8% vapor could be the best regeneration method of these three methods. Photocatalytic activities of removal NO scarcely changed after one-time regeneration. Multiple time regeneration was put on and the results were shown in Fig. 14.

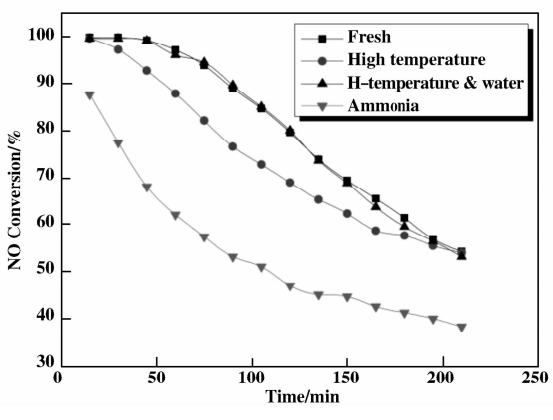


Fig. 13 The de-NO activities of photocatalysts with different regeneration methods

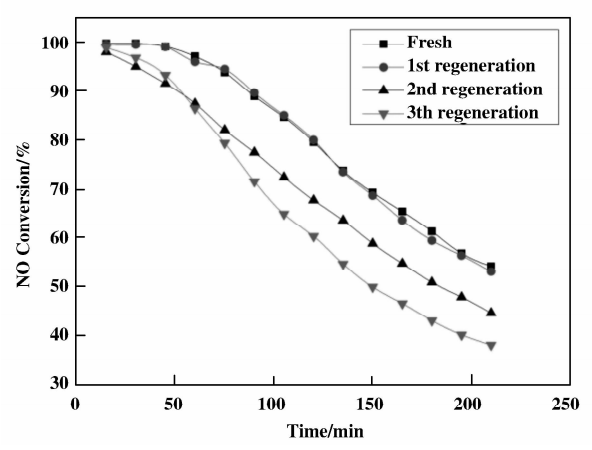


Fig. 14 The de-NO activities of photocatalysts after different regeneration times

## 3 Conclusion

$TiO_2$ supported on activated semi-coke is an effective stable photocatalyst on photocatalytic oxidation of NO and displays a promising application prospect. The activity can maintain for more than 3 h with NO conversion 70%. The photocatalytic reaction mechanism can be regarded that NO is adsorbed on the surface active sites of activated semi-coke or titanium dioxide and then oxided by hydroxyl radical and active oxide. The results observed in this paper can be further evidence support that the hydroxyl radical and atomic oxygen radical anions play a vital role in photocatalytic reaction over titanium dioxide while photogenerated hole has little effect in photocatalytic removal of NO.

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# 溶胶-凝胶法制备 $TiO_2$ 负载活化半焦光催化烟气脱硝

孙圣楠[1*], 李春虎[1,2,**], 杨微微[1], 闫 欣[1], 郑 昱[1], 王 亮[1], 卞俊杰[1]

(1. 中国海洋大学化学化工学院, 山东 青岛 266100;
2. 中国海洋大学海洋化学工程理论与技术教育部重点实验室, 山东 青岛 266100)

**摘要:** 利用超声辅助溶胶-凝胶法, 以钛酸正丁酯为钛源, 制备了 $TiO_2$ 负载于活化半焦的光催化剂. 考察了 $TiO_2$ 负载量, 煅烧温度和时间, 以及水对光催化脱硝活性的影响. 利用 X 射线衍射(XRD), BET, FT-IR, 扫描电镜(SEM)以及能谱分析(EDS)等方法对催化剂进行了表征分析. 实验结果表明, $TiO_2$ 负载量为 5.22%, 煅烧温度 500 ℃, 煅烧时间为 1 h 时, $TiO_2$/ASC 光催化脱硝剂效果最好, 反应 3 h 后脱硝率仍高于 70%. 通过添加自由基捕获剂的方法确定 $TiO_2$/ASC 光催化脱硝过程中起主要作用的活性物种为 $\cdot OH$ 和 $\cdot O_2^-$, 而空穴在本实验的光催化过程中几乎不起作用. 对催化剂的再生研究发现, 高温(400 ℃)水热一次再生可恢复催化剂脱硝活性至新鲜催化剂的 100%, 3 次再生效果仍为新鲜催化剂脱硝率的 80%.

**关键词:** 溶胶-凝胶法; 二氧化钛; 光催化; 脱硝; 活化半焦