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Article

High-humidity tolerance of porous TiO₂(B) microspheres in photothermal catalytic removal of NO_x

He Ma, Changhua Wang *, Songmei Li, Xintong Zhang #, Yichun Liu

Key Laboratory of UV-Emitting Materials and Technology of Chinese Ministry of Education, Northeast Normal University, Changchun 130024, Jilin, China

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ABSTRACT

Semiconductor oxides are widely used to achieve photocatalytic removal of NO_x (NO and NO₂) species. These materials also exhibit enhanced oxidation ability in thermally assisted photocatalysis; however, many of them tend to be deactivated at high relative humidity (RH) levels. In the case of the benchmark P25 TiO₂ photocatalyst, we observe a significant decrease in non-NO₂ selectivity from 95.02% to 58.33% when RH increases from 20% to 80%. Interestingly, the porous TiO₂(B) microspheres synthesized in this work exhibit 99% selectivity at 20% RH; the selectivity remains as high as 96.18% at 80% RH. The high humidity tolerance of the TiO₂(B) sample can be ascribed to its strong water desorption capacity and easy O₂ adsorption at elevated temperatures, which reflects the fact that the superoxide radical is the main active species for the deep oxidation of NO_x. This work may inspire the design of efficient photothermal catalysts with application in NO_x removal in hot and humid environments.

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1. Introduction

Semiconductor oxide photocatalysis (PC) is a promising approach to eliminate NO_x (NO + NO₂) species in ambient air [1–11]. These applications require NO to be removed by photooxidation, while the generation of NO₂ would be inhibited [12–15]. In order to achieve a high non-NO₂ selectivity, the dominant reactive oxygen species should be represented by superoxide radicals (O₂^{•−}), rather than hydroxyl radicals (OH[•]) [16]. However, when the photocatalyst is exposed to high relative humidity (RH) conditions, its surface is mostly covered by adsorbed water [17]. As the oxidation of NO is controlled by hydroxyl radicals, a high selectivity toward the formation of more toxic NO₂ species is unfortunately exhibited [18]. Therefore, the removal of NO_x over oxide photocatalysts with high

non-NO₂ selectivity at high RH levels remains a challenge.

Recent studies showed that photothermal catalysis (PTC) helps activating the lattice oxygen atoms of semiconductor oxide photocatalysts, resulting in enhanced oxidation ability [19]. Nevertheless, a conflicting situation emerges when a photothermal catalyst is used for NO oxidation. In terms of reaction rate, an increase in reaction temperature leads to a decreased NO oxidation rate [20]; hence, a higher reaction temperature hinders NO oxidation [21]. However, in terms of reaction selectivity, heating leads to desorption of water from the catalyst surface and to an increased amount of superoxide radicals [22,23]; therefore, a higher temperature is beneficial to achieve a higher non-NO₂ selectivity. Based on these premises, the reaction rate and selectivity should be carefully balanced. This task would require the optimization of the system temperature

* Corresponding author. Tel/Fax: +86-431-85099772; E-mail: wangch100@nenu.edu.cn

Corresponding author. E-mail: xtzhang@nenu.edu.cn

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during photothermal catalysis and an improved structural design of the photothermal catalyst.

In recent years, $\text{TiO}_2(\text{B})$ has drawn limited attention due to its widely reported lower activity than anatase [24,25]. It should also be noted that the less active $\text{TiO}_2(\text{B})$ usually exhibits low surface area and poor crystallinity [26]. Moreover, $\text{TiO}_2(\text{B})$ has been reported to exhibit a unique layered structure. The thermal diffusivity of lattice oxygen species, which play a key role in thermally assisted photocatalytic oxidation, is expected to be higher than those of other TiO_2 phases such as anatase and rutile. In this work, we assess the potential application of $\text{TiO}_2(\text{B})$ as a model photothermal catalyst to achieve high non- NO_2 selectivity at high RH levels. We aim to synthesize high-surface area and highly crystalline $\text{TiO}_2(\text{B})$ samples, which can not only facilitate water desorption, but also inhibit charge recombination at elevated temperatures. The performance of $\text{TiO}_2(\text{B})$ is compared with that of the P25 benchmark at high RH. A high non- NO_2 selectivity of 96.18% is achieved for $\text{TiO}_2(\text{B})$ microspheres at 80% RH and 60 °C; this selectivity is much higher than that of the 58.33% value obtained for P25 under the same conditions. This result indicates that $\text{TiO}_2(\text{B})$ can be a promising photothermal catalyst for NO_x removal under hot and humid conditions.

2. Experimental

2.1. Chemicals

All solvents and chemicals were of analytical grade and used without further purification. Titanium tetrachloride (TiCl_4) and glycolic acid were purchased from Aladdin Chemical Reagent Co., Ltd. (China), while aqueous ammonia, hydrogen peroxide, sulfuric acid, and ethyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Nitric oxide (10 ppm in N_2) was obtained from Beijing Chemical Co.

2.2. Preparation of $\text{TiO}_2(\text{B})$ microspheres

$\text{TiO}_2(\text{B})$ microspheres were prepared by a two-step method. First, 0.8 mL TiCl_4 was added to 45 g ice in a plastic beaker; then, 5 mL aqueous ammonia, 60 mL deionized water, and 10 mL hydrogen peroxide were added to the beaker. After the ice dissolved completely, 0.5 g glycolic acid was added to the mixture. The as-obtained transparent yellow solution was heated at 80 °C until a yellow gel was formed. The gel was diluted to 50 mL with deionized water. At the same time, 2 mL sulfuric acid was added dropwise into the above solution. The resulting solution was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 50 min. After cooling down, the white solid products were centrifuged from the solution and washed several times with deionized water and ethanol to remove the residue acid and other impurities. Finally, the wet powder was dried at 80 °C overnight.

2.3. Photothermal catalytic experiments

The photothermal catalytic experiments were carried out in

Scheme 1. Schematic illustration of the continuous photocatalytic reactor for NO removal.

a continuous rectangular reactor at 60 °C on a hot plate, as shown in Scheme 1. The target NO gas (0.35 ppm) was supplied by a gas cylinder with compressed NO (10 ppm, N_2 balance). The compressed gas was diluted by a pure air stream with a total airflow of 1 L/min and fed into a stainless steel reactor (20 cm × 10 cm × 1.6 cm) covered with a quartz glass. Two pieces of 6.5 × 6.5 cm² clean glass coated by 80 mg of catalyst were placed in the center of the reactor. Four commercial halogen tungsten lamps of 1 mW/cm² intensity and 365 nm central wavelength were placed vertically above the reactor. The concentrations of NO and NO_2 were continuously measured every 1 min by a chemiluminescence air pollution monitor (Horiba APNA-370). For comparison, photocatalytic tests were performed at room temperature, while the other conditions were kept the same as those applied in the photothermal catalysis experiments.

The NO conversion ratio, NO_2 release ratio, and selectivity for non- NO_2 species were calculated as follows [27,28]:

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

$$\text{NO}_2 \text{ release (\%)} = ([\text{NO}_2]_{\text{out}} / [\text{NO}]_{\text{in}}) \times 100 \quad (2)$$

$$\text{non-NO}_2 \text{ selectivity} = 1 - ([\text{NO}_2]_{\text{out}} - [\text{NO}_2]_{\text{in}}) / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) \times 100 \quad (3)$$

where $[\text{NO}]_{\text{in}}$, $[\text{NO}]_{\text{out}}$ and $[\text{NO}_2]_{\text{in}}$, $[\text{NO}_2]_{\text{out}}$ are the concentrations of NO and NO_2 at the inlet and outlet, respectively.

2.4. Characterization of materials

The microstructure and surface morphologies of the microspheres were inspected by field-emission scanning electron microscopy (SEM, FEI Quanta 250, USA) and transmission electron microscopy (TEM, JEOL JEM-2100, Japan). The crystal phase composition was analyzed by X-ray diffraction (XRD), using $\text{Cu K}\alpha$ radiation at a scan rate of 5°/min ($\lambda = 0.1542 \text{ \AA}$, 40 kV, 100 mA, Rigaku D/max-2500), as well as Raman spectroscopy with an excitation wavelength of 488 nm (Horiba LabRAM HR Evolution). A nitrogen adsorption apparatus (ASAP 2020, USA) was used to obtain the Brunauer-Emmett-Teller (BET) surface areas of the samples degassed at 200 °C prior to the analysis. A UV-vis spectrometer (Hitachi UH-4150, Japan) equipped with an integrating sphere was used to obtain the diffuse reflectance UV-vis spectra of the different catalysts. The optical adsorption spectra were measured from 300 to 800 nm.

Fig. 1. XRD patterns (a), Raman spectra (b), SEM image (c), and HRTEM image (d) of the TiO₂(B) microspheres.

The electron spin resonance (ESR) signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were recorded on a Bruker EMXnano spectrometer. ESR measurements were performed after mixing the samples in a 25 mM DMPO solution tank (aqueous dispersion for DMPO-•OH and methanol dispersion for DMPO-•O₂⁻) and irradiating them with UV light at room temperature or 60 °C. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed with a Nicolet iZ10 Fourier transform infrared (FTIR) spectrometer at 4 cm⁻¹ resolution with 32 co-added scans.

3. Results and discussion

3.1. Phase composition and morphology

XRD measurements were performed to determine the crystal phase composition. Fig. 1(a) shows the diffraction pattern of the synthesized sample. The characteristic peaks at 14.19°, 24.93°, 28.64°, 33.32°, 43.53°, 58.32°, 62.27° and 67.91° can be ascribed to the monoclinic TiO₂(B) phase, in agreement with

the standard powder diffraction card (JCPDS No. 46-1238) [29]. The structure of the synthesized TiO₂(B) was also confirmed by Raman spectroscopy. The characteristic bands of TiO₂(B) at 127.9, 147.9, 193.7, 247.3, 346.7, 408.3, 484.8, 549.6, 633.5, and 861.6 cm⁻¹ can be clearly detected in the Raman spectra shown in Fig. 1(b) [30]. No additional bands corresponding to other TiO₂ phases were observed, further confirming the single-phase nature of the as-synthesized sample.

The detailed morphological and structural characteristics of the synthesized TiO₂(B) were inspected by SEM and TEM. The SEM image in Fig. 1(c) reveals that the sample consisted of microspheres with diameters of 1–2 μm. Fig. 1(d) shows the HRTEM image of a typical microsphere. The microspheres were composed of nanoparticles. Interplanar spacings corresponding to the (200) and (001) planes (*d*(200) = 0.602 nm and *d*(001) = 0.643 nm) are clearly observed in the image and can be ascribed to the TiO₂(B) phase, in good agreement with the XRD and Raman results.

3.2. BET surface areas and optical properties

Figs. 2(a) and (b) show the nitrogen adsorption-desorption isotherms and corresponding pore size distributions of the TiO₂(B) microspheres. For better comparison, commercial P25 nanoparticles were also characterized. As shown in Fig. 2(a), the TiO₂(B) microspheres showed typical type IV isotherms with a specific area of 220.3 m²/g, indicating the presence of mesopores. Fig. 2(b) highlights a narrow pore size distribution with an average pore size of 3.9 nm. On the other hand, P25 exhibited a specific surface area of 50.1 m²/g and a wide pore distribution.

The optical absorption spectra of the samples were investigated by UV-vis diffuse reflectance spectroscopy (DRS), as shown in Fig. 2(c). The absorption band edges of the TiO₂(B) microsphere and P25 samples were 392 and 405 nm, corresponding to band gaps of 3.16 and 3.06 eV, respectively. No visible light absorption was observed, suggesting that no impurities or defects existed in the TiO₂(B) sample.

Fig. 2. N₂ adsorption-desorption isotherms (a), pore size distributions (b), and UV-vis diffuse reflectance spectra (c) of the TiO₂(B) microsphere and P25 samples.

Fig. 3. Concentrations of NO and NO₂ measured for the TiO₂(B) microsphere and P25 samples under 1 mW/cm² irradiation (RH = 40%) and comparison of removal ratios and non-NO₂ selectivities in photocatalysis (a–c) and photothermal catalysis (d–f) experiments.

3.3. Photocatalytic and photothermal catalytic activities under UV light irradiation

Fig. 3 shows the variation of the concentrations of NO and NO₂ gases over TiO₂(B) and P25 at 40% RH. The non-NO₂ selectivity was also calculated. The NO conversion ratio and non-NO₂ selectivity of the TiO₂(B) photocatalyst were 51.1% and 78.29%, respectively, whereas P25 exhibited a NO conversion ratio and a non-NO₂ selectivity of 69.58% and 78.86%, respectively. The comparison shows that TiO₂(B) exhibited a lower NO conversion ratio and non-NO₂ selectivity, indicating that it is less active than P25 in the photocatalytic removal of NO. After switching to photothermal catalysis, TiO₂(B) exhibited NO conversion ratio and non-NO₂ selectivity values of 70.01% and 93.73%, respectively, while the corresponding values for P25 were 71.59% and 77.56%, respectively. In particular, a higher concentration of NO₂ was released over P25. To better understand these results, the data obtained for the TiO₂(B) sphere and P25 samples in the photocatalysis and photothermal catalysis experiments are summarized in Table 1. TiO₂(B) showed a NO conversion ratio comparable to that of P25, but also a significantly higher non-NO₂ selectivity. This indicates that TiO₂(B) can be a better candidate than P25 for the photothermal catalytic removal of NO, despite its inferior performance in photocatalysis. We also measured the radical concentrations at room temperature and 60 °C. As shown in Fig. 4, after increasing the temperature to 60 °C, P25 and

TiO₂(B) were selectively enriched with hydroxyl and superoxide radicals, respectively. This confirms that superoxide radicals are the dominant active oxygen species in the thermally assisted photocatalysis process.

For a more comprehensive assessment of the photothermal catalytic activity of TiO₂(B), we performed catalytic tests at different RH levels. As shown in Figs. 5 and 6, when the RH decreased from 40% to 20%, both TiO₂(B) and P25 exhibited enhanced oxidation ability. This enhancement was observed for both photocatalysis and photothermal catalysis, and indicates that a lower RH is beneficial for a higher non-NO₂ selectivity. On the other hand, when the RH increased from 40% to 60% and 80%, P25 exhibited no obvious change in NO conversion ratio. However, the concentration of NO₂ drastically increased and the non-NO₂ selectivity significantly decreased. This shows that the oxidation ability of the catalyst decreased with increasing RH, which is consistent with previous results [31]. Different from P25, TiO₂(B) did not show a significant decrease in NO conversion ratio or increase in NO₂ evolution at higher RH levels. More importantly, the non-NO₂ selectivity

Table 1

Comparison of removal and mineralization ratios of TiO₂(B) and P25 in 60 °C photothermal catalysis experiments.

	TiO ₂ (B)		P25	
	40% PC	40% PTC	40% PC	40% PTC
NO conversion ratio (%)	51.1	70.01	69.58	71.59
NO ₂ release ratio (%)	11.63	4.55	15.11	17.09
Non-NO ₂ selectivity ratio (%)	78.29	93.73	78.86	77.56

Fig. 4. ESR signals of hydroxyl (a) and superoxide radicals (b) for $\text{TiO}_2(\text{B})$ sphere and P25 samples under dark and UV light conditions in 25 mM DMPO aqueous or methanol solutions.

Fig. 5. Photocatalysis and photothermal catalysis experimental concentrations of NO (a, d) and NO_2 (b, e) under 1 mW/cm^2 irradiation for different relative humidity levels; (c, f) NO conversion, non- NO_2 selectivity, and NO_2 release ratio of $\text{TiO}_2(\text{B})$ microspheres in photocatalysis (c) and photothermal catalysis (f) experiments.

showed a slight increase when the RH was increased above 40%, and reached 96.18% at 80% RH. Therefore, it is safe to conclude that the $\text{TiO}_2(\text{B})$ microspheres are highly active and robust photothermal catalysts. The activity of the $\text{TiO}_2(\text{B})$ microspheres shows high tolerance to the RH and exceeds that of commercial P25.

To better understand the mechanism of the deep NO oxidation reaction, we measured the ESR signals of the radicals at room temperature and 60°C . As shown in Fig. 7, when the

temperature was increased to 60°C , P25 and $\text{TiO}_2(\text{B})$ showed selective enrichment in hydroxyl and superoxide radicals, respectively. Therefore, we can confirm that superoxide radicals are the dominant active oxygen species in the thermally assisted photocatalysis process.

In order to understand the superior performance of the $\text{TiO}_2(\text{B})$ microspheres in photothermal catalysis, the adsorption and desorption of water on the surface of $\text{TiO}_2(\text{B})$ were monitored by mass measurements. The original mass of the sample

Fig. 6. Photocatalysis and photothermal catalysis experimental concentrations of NO (a, d) and NO₂ (b, e) under 1 mW/cm² irradiation for different relative humidity levels; NO conversion, non-NO₂ selectivity, and NO₂ release ratio of P25 in photocatalysis (c) and photothermal catalysis (f) experiments.

Fig. 7. ESR signals of hydroxyl (a) and superoxide radicals (b) for TiO₂(B) sphere and P25 samples under photocatalysis and photothermal catalysis conditions, in 25 mM DMPO aqueous or methanol solutions.

was 0.080 g. After exposure to the flow of reaction gas at room temperature for 15 min, the sample was immediately removed from the reactor and transferred to a glove box purged with dry N₂. At this stage, the mass of the sample was 0.0936 g. Then, the sample was heated on a hot plate at 60 °C for 20 min. The mass gradually decreased within 5 min and remained at 0.084 g in the following 15 min. Accordingly, the amounts of adsorbed water at room temperature and desorbed water at 60 °C were 0.0136 and 0.0096 g, respectively. In addition, the mass change of P25 before and after heating was monitored

under the same conditions; the results show that the amounts of adsorbed water at room temperature and desorbed water at 60 °C were 0.0102 and 0.0060 g, respectively. Using the specific surface areas of TiO₂(B) (220.3 m²/g) and P25 (50.1 m²/g), along with the average cross-sectional area of a water molecule ($S_{\text{water}}, 1.25 \times 10^{-17} \text{ cm}^2$), the water coverage θ can be calculated as follows:

$$\theta = \{n_{\text{water}} \times N_A \times S_{\text{water}}\} / \{m_{\text{catalyst}} \times S_{\text{catalyst}}\} \times 100 \quad (4)$$

where $n_{\text{water}} \times N_A$ represents the number of water molecules adsorbed on the catalyst surface, m_{catalyst} is the mass of catalyst,

TiO₂(B) is different from P25 in terms of surface area and crystal phase. The higher surface area of TiO₂(B) is believed to be beneficial for water desorption at elevated temperatures. A higher surface area promotes the dispersion of water, and smaller water droplets are formed on the surface of the microspheres. According to the Kelvin equation for the vapor pressure at a curved interface, smaller droplets produce a higher vapor pressure. Therefore, the smaller droplets on the TiO₂(B) surface can be evaporated more easily and enable the adsorption of higher number of O₂ and NO molecules for the deep oxidation of NO, as illustrated in Scheme 2.

We then obtained the *in situ* FT-IR spectra of the TiO₂(B) sphere and P25 samples. As shown in Fig. 8(a), during the adsorption process, the peaks ascribed to NO₃⁻ (bidentate), NO₃⁻ (monodentate), NO₂⁻, NO₂⁻ (chelated), and NO₃⁻ (chelated) groups appeared at 1190, 1260, 1298, 1457, and 1580 cm⁻¹, respectively. However, no obvious NO₂ peaks were observed in the spectra. After irradiation, the products detected over P25 in both photocatalysis and photothermal catalysis remained largely unchanged, as shown in Figs. 8(b) and (c). Turning to the TiO₂(B) spheres, Fig. 8(d) shows that peaks attributed to NO₂ (ads), NO₂⁻ (chelated), and NO₃⁻ (chelated) groups were detected at 1316, 1414, and 1577 cm⁻¹, respectively, in the adsorption process. After irradiation at room temperature (Fig. 8(e)), the peak intensities of NO₂ (ads) and NO₂⁻ (chelated) species produced on the surface of the catalyst showed no obvious change. However, the intensity of the NO₃⁻ peak increased with the irradiation time, indicating that higher

amounts of NO were transformed into the stable NO₃⁻. On the other hand, after irradiation at 60 °C (Fig. 8(f)), the peak intensity corresponding to the NO₂ (chelated) species decreased, whereas the intensity of the NO₃⁻ (chelated) peak increased with time. This result suggests that higher numbers of unstable N-containing species will transform into stable NO₃⁻ in the case of photothermal catalysis. The *in situ* FT-IR results thus show that the TiO₂(B) spheres are more effective than P25 at promoting the deep oxidation of NO in photothermal catalysis.

Besides the surface area, we also investigated whether the different crystal phase contributes to the observed difference in activity. We synthesized two other products composed of pure TiO₂(B) phase, according to previous studies on TiO₂(B) nanosheets and nanotubes [37,38]. As shown in Fig. 9, the XRD and Raman analyses confirm the single-phase nature of the as-synthesized products. The surface areas of the TiO₂(B) nanosheet and nanotube samples were 334.5 and 51.71 m²/g, respectively. Photothermal catalytic tests showed that the NO conversion ratio over the TiO₂(B) nanosheet and nanotube samples was 68.6% and 69.58%, respectively, whereas the corresponding non-NO₂ selectivities were 98.27% and 88.47%, respectively. Since the NO conversion ratio and non-NO₂ selectivity are not completely dependent on the surface area, the TiO₂(B) phase is expected to play an important role in the highly efficient elimination of NO. Further studies on the relationship between TiO₂(B) and water desorption in photothermal catalysis are in progress. In addition, we compared the activity of TiO₂(B) with those of pure anatase and rutile phases.

Fig. 9. XRD patterns (a), Raman spectra (b), and PTC experimental concentration curves (c, d) of NO (c) and NO₂ (d) under 1 mW/cm² irradiation (RH = 50%) for different types of TiO₂(B) samples; (e, f) PTC results over different TiO₂ phases.

Fig. 10. Experimental concentrations of NO (a) and NO₂ (b) for photothermal catalysis experiments over TiO₂(B) microspheres at different temperatures (RH = 50%).

As shown in Figs. 9(e) and (f), the photothermal catalytic activity of TiO₂(B) is greater than that of the other two phases in terms of higher NO removal and lower NO₂ evolution. The superior performance of TiO₂(B) may be due to its unique layered structure, which is beneficial for the thermal diffusivity of lattice oxygen.

Finally, to evaluate the applicability of the TiO₂(B) microspheres at different temperatures, we also tested their photothermal catalytic activity towards NO oxidation at 50% RH. The results in Fig. 10 show that the highest NO conversion ratio in photothermal catalysis (76.07%) was obtained at 60 °C, whereas the highest non-NO₂ selectivity (97.17%) was achieved at 40 °C. Compared to photocatalysis at room temperature, a slight temperature increase to 40 °C significantly improved the non-NO₂ selectivity from 71.19% to 97.17%, demonstrating that the TiO₂(B) microspheres are particularly suitable for photothermal catalysis. More importantly, the TiO₂(B) microspheres investigated in this work represent promising candidates for NO photooxidation in outdoor natural environments.

4. Conclusions

In this study, we investigated the application of TiO₂(B) microspheres for the photocatalytic and photothermal catalytic removal of NO under UV light. The photothermal catalytic activity of TiO₂(B) was far superior to its photocatalytic activity, despite a slight increase in the system temperature. Moreover, the photothermal catalytic activity of TiO₂(B) was higher than that of P25. The superiority of TiO₂(B) became more evident at high RH levels. A high non-NO₂ selectivity of 96.18% was obtained for TiO₂(B) at 80% RH, benefiting from the higher water desorption capability of the TiO₂(B) surface at elevated temperatures. As the desorption and evaporation of water in the photothermal catalysis process inhibit the production of hydroxyl radicals, superoxide radicals become the dominant ac-

tive oxygen species, which leads to a deeper oxidation of NO to NO₃⁻ and hence a higher non-NO₂ selectivity. This work suggests that TiO₂(B) is a promising candidate for NO removal under outdoor hot and humid conditions.

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Graphical Abstract

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High-humidity tolerance of porous $\text{TiO}_2(\text{B})$ microspheres in photothermal catalytic removal of NO_x

He Ma, Changhua Wang*, Songmei Li, Xintong Zhang#, Yichun Liu
Northeast Normal University

The photothermal catalytic activity of $\text{TiO}_2(\text{B})$ is superior to its photocatalytic activity at elevated temperatures. Moreover, the photothermal catalytic activity of $\text{TiO}_2(\text{B})$ is higher than that of P25. The superior activity of $\text{TiO}_2(\text{B})$ becomes more evident at high RH levels.

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$\text{TiO}_2(\text{B})$ 多孔微球高湿光热催化降解 NO_x 性能

马 贺, 王长华*, 李松美, 张昕彤#, 刘益春

东北师范大学物理学院, 紫外发射材料与技术教育部重点实验室, 吉林长春130024

摘要: 近年来, 半导体氧化物光催化技术由于反应条件温和, 在消除环境空气中氮氧化物 $\text{NO}_x(\text{NO}+\text{NO}_2)$ 方面得到了广泛的关注. 然而, 随着反应过程中湿度的逐渐增加, 催化剂表面水的覆盖率也逐渐增加, 从而导致许多光催化材料高湿失活. 因此研发高湿条件下仍具有高活性的催化剂成为高效脱除大气环境中 NO_x 的关键. 本文制备了粒径为1–2 μm , 结晶度较高的单斜相 $\text{TiO}_2(\text{B})$ 微球催化剂. BET和孔结构分析发现, $\text{TiO}_2(\text{B})$ 微球具有高比表面积的多孔结构. 催化性能测试发现, $\text{TiO}_2(\text{B})$ 多孔微球在相对湿度为20%时, 光热催化下的非 NO_2 选择性高达99%; 当相对湿度增至80%时仍保持在96.18%. 相比之下, 当反应气相对湿度从20%增加到80%时, 标准商用二氧化钛P25的非 NO_2 选择性却由95.02%降至58.33%, 可见, $\text{TiO}_2(\text{B})$ 多孔微球在光热催化反应中具有较强的耐湿性. 进一步研究发现, 光热反应中, 水在催化剂表面的覆盖率明显减少, 从而促进了超氧自由基的形成. ESR自由基捕获实验表明, 相较于室温下的光催化反应, 光热条件下 $\text{TiO}_2(\text{B})$ 微球的超氧自由基含量

明显提升,更多的超氧自由基更有利于NO的深度氧化以及抑制毒副产物NO₂的生成,从而有效提高了NO_x的去除效率,并明显提升了非NO₂选择性.原位红外光谱表明,相比于标准P25在光催化和光热催化过程中硝酸根与亚硝酸根含量与暗吸附过程中基本保持不变的情况,TiO₂(B)微球在光催化过程中硝酸根的含量相较于暗吸附过程随时间的增加而明显增加,表明在光催化过程中更多的NO在TiO₂(B)微球表面生成了更为稳定的含氮化合物;而在光热催化过程中,随反应时间的增加,催化剂表面的亚硝酸根含量逐渐减少,硝酸根含量明显增加,由此表明在光热催化条件下,TiO₂(B)微球对NO的深度氧化促进作用明显优于标准商用P25.本文有助于耐湿性光热催化剂的设计,为炎热高湿气候下NO_x的脱除提供了参考.

关键词: TiO₂(B)多孔微球; 光催化剂; 光热催化; 耐湿性; NO降解

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*通讯联系人. 电话/传真: (0431)85099772; 电子信箱: wangch100@nenu.edu.cn

#通讯联系人. 电子信箱: xtzhang@nenu.edu.cn

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