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Synergistic photo-thermal catalytic NO purification of $\text{MnO}_x/\text{g-C}_3\text{N}_4$: Enhanced performance and reaction mechanism

Peng Chen, Fan Dong *, Maoxi Ran, Jiarui Li

Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China

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ABSTRACT

Both MnO_x and $\text{g-C}_3\text{N}_4$ have been proved to be active in the catalytic oxidation of NO, and their individual mechanisms for catalytic NO conversion have also been investigated. However, the mechanism of photo-thermal catalysis of the $\text{MnO}_x/\text{g-C}_3\text{N}_4$ composite remains unresolved. In this paper, $\text{MnO}_x/\text{g-C}_3\text{N}_4$ catalysts with different molar ratios were synthesized by the precipitation approach at room temperature. The as-prepared catalysts exhibit excellent synergistic photo-thermal catalytic performance towards the purification of NO in air. The $\text{MnO}_x/\text{g-C}_3\text{N}_4$ catalysts contain MnO_x with different valence states on the surface of $\text{g-C}_3\text{N}_4$. The thermal catalytic reaction for NO oxidation on MnO_x and the photo-thermal catalytic reaction on 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$ were investigated by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). The results show that light exerted a weak effect on NO oxidation over MnO_x , and it exerted a positive synergistic effect on NO conversion over 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$. A synergistic photo-thermal catalytic cycle of NO oxidation on $\text{MnO}_x/\text{g-C}_3\text{N}_4$ is proposed. Specifically, photo-generated electrons (e^-) are transferred to MnO_x and participate in the synergistic photo-thermal reduction cycle ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$). The reverse cycle ($\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$) can regenerate the active oxygen vacancy sites and inject electrons into the $\text{g-C}_3\text{N}_4$ hole (h^+). The active oxygen (O^-) was generated in the redox cycles among manganese species ($\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$) and could oxidize the intermediates (NOH and N_2O_2^-) to final products (NO_2^- and NO_3^-). This paper can provide insightful guidance for the development of better catalysts for NO_x purification.

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1. Introduction

NO_x (NO and NO_2) contribute to serious environmental problems, such as acid rain, ozone depletion, and photochemical smog [1–4]. Efficient NO_x removal technology is urgently needed owing to the increased emission from transport sectors and power plants. Selective catalytic reduction (SCR) has been widely adopted to eliminate NO_x pollution [5,6]. Normally, the

SCR catalysts exhibit excellent activity for removal of high-concentration NO (200–2000 ppm) at high temperatures ($>200^\circ\text{C}$) [7]. Along with the report by Kapteijn *et al.* describing NO_x SCR by MnO_x in 1994, research interest in the development of MnO_x -driven SCR has increased. Over the last few decades, MnO_x has been widely applied to NO removal. Kang *et al.* [8] prepared MnO_x catalyst by a precipitation technique and found that the MnO_x catalyst exhibited excellent activity for SCR

* Corresponding author. Tel/Fax: +86-23-62769785; E-mail: dfctbu@126.com

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of NO_x with NH₃ at low temperatures. Unfortunately, the SCR activity for NO_x removal was still unsatisfactory at lower temperatures (<100 °C). Thus, developing advanced techniques for efficient NO_x removal at lower temperature has become a research challenge.

Photocatalysis has gained considerable attention for solar-energy utilization and environmental remediation in view of mild reaction conditions [9,10]. Many photocatalysts were developed to meet the requirement of various applications, e.g., photocatalytic hydrogen evolution, photodegradation of RhB solutions, and NO_x removal [11–13]. In particular, as a metal-free layered conjugated semiconductor, g-C₃N₄ has become a new subject of research focus in the area of environmental remediation due to its appealing electronic structure, physico-chemical stability, and natural abundance [14–19].

Dong *et al.* [17] immobilized polymeric g-C₃N₄ on structured ceramic foam for efficient photocatalytic air purification and proposed the corresponding reaction mechanism of photocatalytic NO oxidation. Yu *et al.* [20] revealed the mechanism of photocatalytic oxidation of NO over g-C₃N₄-based carbon nanofibers at room temperature. Recently, Cui *et al.* [18] steered the interlayer energy barrier and charge flow via bi-oriented transportation channels in g-C₃N₄ and revealed the reaction mechanism by a combined density functional theory (DFT) calculation with DRIFTS.

Although NO purification on MnO_x and g-C₃N₄ has been extensively investigated, combining them to construct a photo-thermal catalyst has not been reported to the best of our knowledge. Furthermore, the photo-thermal catalytic mechanism of NO oxidation remains unresolved. In the work reported here, MnO_x/g-C₃N₄ hybrids were fabricated via precipitation at room temperature. MnO_x/g-C₃N₄ was applied to remove NO with a low concentration of 500 ppb in air under ultraviolet-visible-light (UV-Vis) irradiation. The mechanisms of NO adsorption and NO catalytic oxidation over MnO_x and 1:5 MnO_x/g-C₃N₄ at 60 °C were proposed through a systematic *in situ* DRIFTS investigation. Based on the experimental results, a significant synergistic photo-thermal catalytic cycle was proposed for MnO_x/g-C₃N₄ hybrids. The NO could first be adsorbed on the surface of the hybrid to form some intermediates (NOH and N₂O₂⁻), and then reacted with active oxygen (O⁻) generated in the redox cycles between manganese species (Mn⁴⁺/Mn³⁺/Mn²⁺) to oxidize intermediates to NO₃⁻ or NO₂⁻. Specifically, during the synergistic photo-thermal reduction cycle (Mn⁴⁺→Mn³⁺→Mn²⁺), photo-generated electrons (e⁻) are transferred to MnO_x and captured by surface-adsorbed oxygen to generate active oxygen (O⁻). Furthermore, the reverse cycle (Mn²⁺→Mn³⁺→Mn⁴⁺) can regenerate the active oxygen vacancy sites and inject electrons into the g-C₃N₄ hole (h⁺). Thus, there will be abundant O⁻ generated to participate in NO oxidation and enhance the synergistic photo-thermal catalytic performance of MnO_x/g-C₃N₄ catalysts for NO removal.

2. Experimental

2.1. Materials and synthesis

All chemicals employed were of analytical grade and were used without further treatment. First, 10 g of thiourea was placed into a crucible and heated at 550 °C for 2 h to obtain g-C₃N₄. Second, the MnO_x/g-C₃N₄ samples were synthesized via room-temperature precipitation. In the typical procedure, 30 mL of distilled water and 30 mL of ethanol was added into a 100-mL beaker and stirred using a magnetic stirrer. A certain amount of g-C₃N₄ was then added into above mixed solution and stirred for 30 min. According to the molar ratios (1:3, 1:5, and 1:10) of MnO_x/g-C₃N₄, a certain amount of KMnO₄ was also added into a beaker and stirred using a magnetic stirrer until it was completely dissolved. Next, 0.0378 g of NaBH₄ was added into the ethanol solution. Finally, the KMnO₄ solution was added dropwise into above mixed solution and stirred for another 24 h. Then, after precipitation for 30 min, the resulting samples were obtained by centrifugation, and washed with water and ethanol four times, and dried at 60 °C in a vacuum drying oven. The obtained samples were labeled as 1:3 MnO_x/g-C₃N₄, 1:5 MnO_x/g-C₃N₄, and 1:10 of MnO_x/g-C₃N₄, respectively.

2.2. Materials characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with Cu K_α radiation (Model D/max RA, Rigaku Corp., Japan). UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained for the dry-pressed disk samples using a scanning UV-Vis spectrophotometer (UV-Vis DRS, UV-2450, Shimadzu Corp., Japan) equipped with an integrating sphere assembly to investigate the optical properties of the samples. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 110 °C for 4 h before measurements. X-ray photoelectron spectroscopy (XPS) with Al K_α X-ray radiation (hν = 1486.6 eV) operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. Electron paramagnetic resonance (EPR) measurements were carried out on a spectrometer (Bruker ESP 500, USA) and was used to study the electronic properties. Transmission electron microscopy (TEM, JEM-2010, JEOL Corp., Japan) was used to characterize the morphology and structure.

2.3. Evaluation of photocatalytic activity

Gas-phase catalytic performance was evaluated through the removal ratio of a low concentration of NO with ppb levels (500 ppb) in a continuous-flow reactor (rectangular reactor, 30 cm × 15 cm × 10 cm). 0.1 g samples were taken in two small beakers, into each of which 20 mL of distilled water was added, and then the resulting solution was transferred to two glass dishes (12.0 cm in diameter) after ultrasonic dispersion for 5 min, followed by drying at 60 °C in advance of catalytic activity tests. A 150-W commercial tungsten halogen lamp (average light intensity 0.16 W/cm²) was vertically placed outside and above the reactor, and then turned on when adsorption-desorption equilibrium was achieved. A reactor outlet was connected to the NO_x analyzer (Thermo Scientific, 42i-TL). An opening light source was applied after the NO concentration was stable at intervals

of 1 min and recorded with a NO_x analyzer. The removal ratio (η) of NO was calculated as $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet stream and feeding stream, respectively.

2.4. *In situ* DRIFTS study of visible-light-photocatalytic-NO-oxidation process

The *in situ* DRIFTS measurements were conducted using a TENSOR II FTIR spectrometer (Bruker Corp.) equipped with an *in situ* diffuse reflectance cell (Harrick) and a high-temperature reaction chamber (HVC), as shown in Scheme 1. The reaction chamber was equipped with three gas ports and two coolant ports. High-purity He, high-purity O₂, and 100 ppm of NO (in He) mixtures could be fed into the reaction system, and a three-way ball valve was used to switch between the target gas (NO) and the purge gas (He). The total gas-flow rate was 100 mL/min, and the concentration of NO was adjusted to 50 ppm by dilution with O₂. The chamber was enclosed with a dome having three windows, two for IR light entrance and detection, and one for illuminating the photocatalyst. The observation window was made of UV quartz, and the other two windows were made of ZnSe. A Xe lamp (MVL-210, Japan) was used as

Scheme 1. Reaction system designed for *in situ* IR signal recording.

the irradiation light source. In this work, prepared samples were pretreated for 20 min at 110 °C before measurements. In addition, the temperature was kept at 60 °C throughout the measurements.

3. Results and discussion

3.1. Crystal structure

As revealed by the XRD patterns in Fig. 1(a) and (b), the crystallinity of all the MnO_x/g-C₃N₄ samples are lower than that

Fig. 1. XRD spectra for the samples (a, b) and TEM for 1:5 MnO_x/g-C₃N₄ (c, d); Field emission scanning electron microscopy energy dispersive X-ray (FESEM-EDX) elemental mapping of 1:5 MnO_x/g-C₃N₄ (e, f, g, h).

of the pristine g-C₃N₄. Two characteristic diffraction peaks, at 13.1° for the (100) plane and at 27.4° for the (002) plane of g-C₃N₄, can be observed. The former arises from the in-plane structural repeating motifs of the aromatic systems, and the latter originates from the interlayered graphite-like structure [21,22]. The diffraction peaks of MnO_x appearing in Fig. 1(b) are weak and broad, which can be ascribed to the low crystallinity of MnO_x in the hybrids.

For 1:5 MnO_x/g-C₃N₄ sample, there are several characteristic lattice fringes, as shown in Fig. 1(c). These lattice fringes may be assigned to different kinds of MnO_x with different valence states, corresponding to the results of the Mn 2p spectrum in Fig. 2(c). The lattice-fringe spacings of 0.127, 0.157, and 0.246 nm correspond to the (321), (151), and (021) planes of MnO (PDF #04-0326), respectively. The lattice-fringe spacings of 0.186 and 0.222 nm are assigned to the (024) and (113) planes for Mn₂O₃ (PDF #33-0900), respectively. The lattice-fringe spacings of 0.121, 0.143, and 0.239 nm belong to the (332), (002), and (211) planes for MnO₂ (PDF #44-0141), respective-

ly. More importantly, two characteristic diffraction peaks of MnO₂ at 37.5° for the (211) plane and 65.1° for the (002) plane (PDF #44-0141) can be noticeably observed in Fig. 1(b). However, the diffraction peak of Mn₂O₃ or MnO cannot be clearly found in Fig. 1(b), which suggests that the concentration of MnO₂ in the hybrids is higher than that of Mn₂O₃ or MnO, corresponding to the concentration of Mn⁴⁺ surpassing that of Mn³⁺ or Mn²⁺ for fresh 1:5 MnO_x/g-C₃N₄ in Fig. 3(b). Furthermore, C, N, Mn, and O signals can be detected in the element mapping of 1:5 MnO_x/g-C₃N₄ (Fig. 1(e)–(h)), indicating the uniform dispersion of Mn and O elements across the catalyst.

3.2. Surface species analysis

The chemical structure and composition of samples were examined by XPS measurements. In XPS survey spectra (Fig. 2(a)–(d)), C 1s, N 1s, K 2p, Mn 2p, and O 1s can be observed for 1:5 MnO_x/g-C₃N₄. Fig. 2(a) suggested that the binding energies of C 1s at 284.6 and 288.1 eV can be ascribed to the sp² C–C

Fig. 2. C 1s (a) and N 1s (b) XPS spectra for g-C₃N₄ and 1:5 MnO_x/g-C₃N₄; Mn 2p XPS spectra for fresh and used MnO_x and 1:5 MnO_x/g-C₃N₄ (c); O 1s XPS spectra for MnO_x and 1:5 MnO_x/g-C₃N₄ (d).

Fig. 3. Percentage of core electron spectra for fresh and used MnO_x (a) and 1:5 MnO_x/g-C₃N₄ (b).

bonds and *sp*²-bonded carbon in the N-containing aromatic rings (N=C=N), respectively [23,24]. Conspicuously, for 1:5 MnO_x/g-C₃N₄, there are another two binding energies of C 1s centered at 292.7 and 295.5 eV, corresponding to the orbital of K 2*p*. The N 1s spectra in Fig. 2(b) reveal that the main peak centered at 398.8 eV originates from the *sp*²-bonded N involved in the triazine rings (C=N=C), and the weak peak located at 400.4 eV can be ascribed to the tertiary nitrogen N-(C)₃ groups in both g-C₃N₄ and 1:5 MnO_x/g-C₃N₄ [24,25]. The N-C=N, N-(C)₃, and C=N=C groups constitute the basic substructure units and construct the heptazine heterocyclic ring (C₆N₇) units of g-C₃N₄ polymers.

As shown in Fig. 2(c), the Mn 2*p* spectra exhibit two peaks, 2*p*_{3/2} and 2*p*_{1/2} (resulting from the spin-orbit splitting), located at 642.2 and 653.9 eV, respectively. For Mn 2*p*_{3/2}, the peak fitting was carried out [4,25]. For fresh (or used) MnO_x, Mn 2*p*_{3/2} can be deconvoluted into Mn³⁺ and Mn⁴⁺ with the characteristic binding energy at 641.5 (641.3) and 643.0 eV (642.6 eV), respectively. However, for the used MnO_x, the Mn-nitrate species appears with the binding energy at 644.6 eV, and can be attributed to the adsorption of NO oxidation. However, Mn 2*p*_{3/2} can be deconvoluted into Mn²⁺, Mn³⁺, and Mn⁴⁺ for fresh (or

used) 1:5 MnO_x/g-C₃N₄, with the characteristic binding energy at 640.5 (640.7), 641.7 (641.8) and 643.2 eV (643.1), respectively [4,26–28], which indicates that the introduction of g-C₃N₄ could affect the formation of various valence states of Mn in MnO_x via precipitation.

In the high-resolution O 1s XPS spectra, MnO_x and 1:5 MnO_x/g-C₃N₄ can be fitted to the two groups as shown in Fig. 2(d). The lattice oxygen O₂²⁻ (denoted O_β) is located in the range 529.8–530.1 eV. The peaks at 531.0–531.3 eV can be assigned to surface-adsorbed oxygen (denoted O_α), such as O₂⁻ and O⁻ due to defect-oxide or hydroxyl-like groups [4,29–31]. O_α was often considered beneficial for NO oxidation to NO₂ due to its higher mobility than O_β [4,29], which correctly corresponds to the detected signal intensity of the electron-deficient surface oxygen anion O⁻ in EPR spectra (Fig. 4(b)).

Additionally, the elemental composition for fresh and used samples are compared and listed in Fig. 3(a) and (b). The experimental results imply that the concentration of Mn⁴⁺ surpasses that of Mn³⁺ for the fresh MnO_x and 1:5 MnO_x/g-C₃N₄ samples. Moreover, the concentration of Mn³⁺ and Mn⁴⁺ decreased, while the concentrations of the Mn-Nitrate increased after reaction for used MnO_x, as shown in Fig. 3(a). Fig. 3(b)

Fig. 4. N₂ adsorption-desorption isotherm (a) and pore-size distributions (b) of the MnO_x/g-C₃N₄ samples.

Table 1

Summary of the specific surface areas and pore parameters of the as-prepared samples.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
g-C ₃ N ₄	26	0.19	24.5
MnO _x	157	0.39	9.6
1:3 MnO _x /g-C ₃ N ₄	81	0.31	14.9
1:5 MnO _x /g-C ₃ N ₄	64	0.27	17.2
1:10 MnO _x /g-C ₃ N ₄	51	0.22	17.4

shows that the concentration of Mn³⁺ decreased, while the concentrations of Mn²⁺ and Mn⁴⁺ increased after the reaction for used 1:5 MnO_x/g-C₃N₄. These results correspond with NO oxidation reactions over MnO_x and 1:5 MnO_x/g-C₃N₄, and constitute favorable evidence for the elucidation of the photo-thermal catalytic reaction (PTCR) mechanism.

3.3. Surface area and pore structure

The specific surface area of a catalyst is another important parameter for photocatalysis. The morphological properties of the as-obtained catalysts are determined by N₂ physisorption, and the parameters are summarized in Table 1. In contrast to the pristine g-C₃N₄, both the specific surface areas and pore volumes of MnO_x/g-C₃N₄ conspicuously increased, while the average size decreased. These results may suggest that the excellent pollutant adsorption capacity of MnO_x/g-C₃N₄ can be ascribed to the introduction of MnO_x. In addition, the N₂ adsorption-desorption isotherms are typical type-IV isotherms with a hysteresis loop at $p/p_0=0.6-1.0$ [32], which indicates the formation of mesoporous structure, as illustrated in Fig. 4(a). Moreover, Fig. 4(b) shows that the pore size of 1:3 MnO_x/g-C₃N₄ and 1:10 MnO_x/g-C₃N₄ changes in the range 20–60 nm. In addition, the peak pore size of 1:5 MnO_x/g-C₃N₄ disappeared in the range 3–4 nm, which can be attributed to the fact that MnO_x particles are located in the porous structure of g-C₃N₄.

3.4. Optical and electronic properties

UV-Vis DRS is carried out to investigate the optical properties. As presented in Fig. 5(a), compared to g-C₃N₄, the MnO_x/g-C₃N₄ shows more intensive absorption over the entire range of wavelengths. This is because the MnO_x possesses strong absorption in the UV-Vis light region, which contributes to the very high light-harvesting efficiency of MnO_x/g-C₃N₄ hybrid.

The electronic properties of MnO_x and 1:5 MnO_x/g-C₃N₄ were examined by solid-state electron paramagnetic resonance (EPR) at room temperature. The signal intensity of the electron-deficient surface oxygen anion O^{•−} ($g_{\perp}=2.036$) can be detected in EPR spectra (Fig. 5(b)) [33]. For MnO_x, the EPR signal intensity of O^{•−} barely changes in the dark or under visible light irradiation. This result suggests that light irradiation does not affect the electronic property of MnO_x and cannot accelerate the charge transportation. Importantly, for the 1:5 MnO_x/g-C₃N₄ sample, the EPR signal intensity of O^{•−} is enhanced both in the dark and under visible light irradiation, indicating that the combination MnO_x and g-C₃N₄ could widen the band distribution, boosting the oxygen ion (O^{•−}) mobility, and accelerating the charge transportation. In contrast to the dark situation, the signal intensity of O^{•−} under visible light irradiation is obviously increased for 1:5 MnO_x/g-C₃N₄, indicating the excellent electron-migrating ability of 1:5 MnO_x/g-C₃N₄. More importantly, the boosted electron mobility and accelerated charge transportation could induce the formation of more active oxygen (O^{•−}), so 1:5 MnO_x/g-C₃N₄ might show outstanding performance in NO purification under visible light irradiation. The enhanced light adsorption ability (Fig. 5(a)) and the boosted oxygen-ion (O^{•−}) mobility should be contributed from the combination of MnO_x and g-C₃N₄. Thus, 1:5 MnO_x/g-C₃N₄ can be expected to an excellent photo-thermal catalyst.

3.5. UV-Vis-light-induced photo-thermal catalytic NO oxidation

As shown in Fig. 6, the temperature increases gradually with irradiation time and is stabilized at approximately 60 °C under

Fig. 5. UV-Vis spectra for MnO_x/g-C₃N₄ samples(a) and room-temperature solid-state EPR spectra of MnO_x and 1:5 MnO_x/g-C₃N₄ (b).

Fig. 6. Photo-thermal catalytic activity towards NO removal under UV-Vis light irradiation.

UV-Vis light irradiation for 1 h, providing the photo-thermal condition for NO removal. In contrast to the pristine MnO_x and $\text{g-C}_3\text{N}_4$, the photocatalytic activity for NO removal is significantly enhanced on the $\text{MnO}_x/\text{g-C}_3\text{N}_4$ hydride. Among the various samples, the 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$ sample exhibits the most efficient performance for NO removal, with a NO removal ratio of 44%, exceeding that of the MnO_x (27%) and $\text{g-C}_3\text{N}_4$ (36%). This result suggests that the $\text{MnO}_x/\text{g-C}_3\text{N}_4$ might demonstrate a special photo-thermal catalytic effect (PTCE) ascribed to the enlarged specific surface (Fig. 4), the enhanced light adsorption (Fig. 5(a)) by introducing MnO_x , and the boosted oxygen-ion (O^-) mobility by introducing $\text{g-C}_3\text{N}_4$ (Fig. 5(b)).

3.6. In situ DRIFTS investigation and synergistic photo-thermal catalytic mechanism

To reveal the conversion pathways and mechanisms of NO oxidation at 60 °C with MnO_x and 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$, *in situ* DRIFTS is carried out to dynamically monitor the reaction intermediates and products over the catalyst surface in time sequence. Tables 2 and 3 summarize the assignment of the observed bands.

As shown in Fig. 7(a) and (b), the strong absorption band at 1247 cm^{-1} and the weak band at 1028 cm^{-1} can be assigned to bidentate nitrate [34–36]. The peak at 1388 cm^{-1} is possibly indexed to free nitrate ions bonded to Mn^{n+} [37]. In addition, the peak located at 1446 cm^{-1} is assigned to the Mn-NO₂ group [38,39]. Moreover, the adsorption band at 1536 cm^{-1} is as-

Table 2

Assignments of the infrared (IR) bands observed during NO adsorption and NO oxidation at 60 °C over MnO_x .

Wavenumber (cm^{-1})	Possible assignment	Reference
1028, 1247	bidentate nitrate	[34–36]
1388	free nitrate ion, possibly bonded to Mn^{n+}	[37]
1446	Mn-NO ₂ group	[38,39]
1536	$\nu_{\text{as}}(\text{NO}_3^-)$ split	[40]
1624	$\delta(\text{HOH})$	[39]
3590	H-bonded OH group	[41]

Table 3

Assignments of the IR bands observed during NO adsorption and NO oxidation at 60 °C over 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$.

Wavenumber (cm^{-1})	Possible assignment	Reference
1227	$\nu_{\text{as}}(\text{NO}_3^-)$ split	[39]
1300	$\nu_{\text{as}}(\text{NO}_2^-)$	[44]
1104, 1375	N_2O_2^-	[37]
2420–2900	mostly assigned to NO_3^- (nitrates)	[39,45,46]
~3400	$\text{H}_2\text{O}(\text{ads})$	[40]
3565	$\nu(\text{OH})$ of NO–H	[41]
3608	H-bonded OH group	[41]

signed to the $\nu_{\text{as}}(\text{NO}_3^-)$ split and the peak at 1624 cm^{-1} is assigned to NO_3^- (bridged) [39,40]. The peak at 3590 cm^{-1} is attributed to H-bonded OH groups [41]. These results suggest that the amounts of nitrate in different forms are formed through NO oxidation over MnO_x , corresponding to the increased Mn-nitrate species after reaction for used MnO_x as shown in Fig. 3(a). The electron transfer between Mn^{3+} and Mn^{4+} ions is expressed in Eqs. (1)–(3) [4]. Moreover, the intensities of all peaks are conspicuously increased in Fig. 7(a), while the intensities of the corresponding peaks are unchanged in Fig. 7(b). These results reveal that MnO_x demonstrates the TCR of NO oxidation at 60 °C with a weak effect of light irradiation.

According to these results and the literature on the thermal catalytic mechanism with MnO_x [4,42–45], a possible mechanism of NO adsorption and oxidation over MnO_x is proposed in Scheme 2. The process could be described as follows. First, NO is adsorbed on the metal sites, and then the nitrosyls are formed. Simultaneously, the adsorption of O_2 molecules is activated by the redox cycles between manganese species ($\text{Mn}^{4+}/\text{Mn}^{3+}$) in the oxygen vacancy, and active oxygen (O^-) radicals are generated. Subsequently, the nitrosyls are converted to nitroxyls via interaction between nitrosyls and O^- . Then, nitroxyls are transformed to NO_2 due to the interaction between nitroxyls and H_2O . Ultimately, a large proportion of NO_2 would be oxidized to nitrates via the reaction with O^- . Furthermore, abundant nitrates cannot be decomposed, but instead are bonded to MnO_x , corresponding to the appearance and increased concentration of Mn-nitrate over used MnO_x observed in Fig. 3(a).

Fig. 7(c) and (d) reveal the process of NO adsorption and oxidation over 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$. The peaks at 1227, 3400, and 3608 cm^{-1} can be assigned to the $\nu_{\text{as}}(\text{NO}_3^-)$ split [39], $\text{H}_2\text{O}(\text{ads})$ [45], and H-bonded OH groups [41], respectively. Obviously, the absorption band at 1300 cm^{-1} is observed and can be assigned to $\nu_{\text{as}}(\text{NO}_2^-)$ [44]. Furthermore, the absorption bands at 1104 and 1375 cm^{-1} indexing to N_2O_2^- are observed, and their intensity increases gradually with light irradiation [37]. Simultaneously, the broad peak at 2420–2900 cm^{-1} , assigned to nitrates [39,45,46], could be found, and the intensity distinctly increases, as shown in Fig. 7(d). In addition, the peak at 3565 cm^{-1} decreases gradually with time, and it can be assigned to NOH [39]. In contrast to the NO absorption band in Fig. 7(c),

Fig. 7. *In situ* DRIFTS spectra of NO adsorption and photo-thermal catalytic reaction processes over MnO_x (a, b) and 1:5 $\text{MnO}_x/\text{g-C}_3\text{N}_4$ (c, d).

Scheme 2. Mechanism of NO adsorption without light and NO oxidation with light over MnO_x at 60 °C.

the intensity of the peak at 3565 cm^{-1} (NOH) decreases rapidly under UV-Vis light irradiation, while the peaks at 3400 and 3608 cm^{-1} become obviously strong.

According to these results and previous work on NO ad-

sorption over MnO_x and $\text{g-C}_3\text{N}_4$ [17,18,39,43,47,48], the possible adsorption and PTCR processes are proposed as shown in Scheme 3. The two-dimensional geometry and surface hydroxyl groups of $\text{g-C}_3\text{N}_4$ could facilitate the adsorption of NO. There-

Scheme 3. Mechanism of NO adsorption without light and NO oxidation with light over 1:5 MnO_x/g-C₃N₄ at 60 °C.

fore, the appearance of N₂O₂⁻ and NOH may be attributed to the reaction of NO on the surface of g-C₃N₄. During the adsorption process, the reduced metal centers and oxygen defects are created thermally on MnO_x and are sites of O₂ adsorption and activation. That is, the oxygen transfer from molecular oxygen to the active oxygen (O⁻) of Mn⁴⁺ (MnO₂) or Mn³⁺ (Mn₂O₃) or Mn²⁺ (MnO) could achieve the activation of molecular oxygen. O⁻ would then react with the intermediates (NOH and N₂O₂⁻), generating nitrate species. Interestingly, during the PTCR process, the g-C₃N₄ produced a large amount of photo-generated electron-hole pairs (e⁻-h⁺) under UV-Vis light irradiation, which could participate in the catalytic cycles, thus accelerating the transformation of NOH and N₂O₂⁻ to form nitrate species (NO₃⁻ or NO₂⁻). The MnO_x/g-C₃N₄ interlayer areas provide important interfaces where the photo-generated electron-hole pairs (e⁻-h⁺) could greatly accelerate charge transfer between Mn⁴⁺, Mn³⁺, and Mn²⁺ species, and increase the generation of active oxygen (O⁻). This is consistent with the EPR signal intensity of the electron-deficient surface oxygen anion O⁻ over 1:5 MnO_x/g-C₃N₄ under light irradiation in Fig. 5(b). Specifically, photo-generated electrons (e⁻) are transferred to MnO_x and participate in the reduction of manganese species (Mn⁴⁺→Mn³⁺→Mn²⁺), which is called the synergistic photo-thermal reduction cycle. During this reduction cycle, electrons (e⁻) are inclined to transfer to oxygen vacancies and be captured by surface-adsorbed oxygen to generate active oxygen (O⁻). Simultaneously, the oxidation of manganese species (Mn²⁺→Mn³⁺→Mn⁴⁺) can regenerate the active oxygen vacancy sites and inject electrons into the g-C₃N₄ hole (h⁺), which is called the synergistic photo-thermal regeneration cycle. These redox cycles can be also verified via the weakly changed concentrations of Mn ions over used 1:5 MnO_x/g-C₃N₄ in Fig. 3(b). As a result, a greater amount of active oxygen (O⁻) can be sustainably produced to participate in NO oxidation, thus enhancing the catalytic performance of MnO_x/g-C₃N₄ catalyst for NO removal.

4. Conclusions

MnO_x/g-C₃N₄ catalysts with different molar ratios were prepared by precipitation at room temperature. The results show that the samples demonstrate low crystallinity with various manganese oxides (e.g., MnO, MnO₂, or Mn₂O₃). The 1:5 MnO_x/g-C₃N₄ catalyst showed relatively stable and synergistic photo-thermal catalytic activity towards NO purification under

UV-Vis light irradiation. *In situ* DRIFTS was carried out to dynamically monitor the reaction intermediates and products over the catalyst surface in a time sequence and revealed the conversion pathways and mechanisms of NO oxidation at 60 °C with MnO_x and 1:5 MnO_x/g-C₃N₄. For NO adsorption and NO oxidation over MnO_x, the NO conversion process is mainly assigned to TCR. NO could be adsorbed in the form of bidentate or monodentate nitrites by reacting with the generated active oxygen (O⁻) in the redox cycles between manganese species (Mn⁴⁺/Mn³⁺). For the NO adsorption and NO oxidation over 1:5 MnO_x/g-C₃N₄, the NO conversion process under light irradiation can be attributed to PTCR. First, NO and O₂ molecules will be adsorbed on the surface of g-C₃N₄ and transformed into the intermediates (NOH and N₂O₂⁻). The O₂ molecules could be transformed to active oxygen (O⁻) through the redox cycles between manganese species (Mn⁴⁺/Mn³⁺/Mn²⁺). When g-C₃N₄ was irradiated under light, the electron-hole pairs (e⁻-h⁺) would be produced and participate in the oxygen activation and oxygen transfer over MnO_x and generate a significant catalytic cycle. The catalytic cycle will accelerate charge transportation and produce more active oxygen (O⁻). Specifically, during the synergistic photo-thermal reduction cycle (Mn⁴⁺→Mn³⁺→Mn²⁺), photo-generated electrons (e⁻) are transferred to MnO_x and captured by surface-adsorbed oxygen to generate active oxygen (O⁻). Furthermore, the reverse cycle (Mn²⁺→Mn³⁺→Mn⁴⁺) can regenerate the active oxygen vacancy sites and inject electrons into the g-C₃N₄ hole (h⁺). Finally, there will be abundant O⁻ generated to react to intermediates (NOH and N₂O₂⁻) and generate abundant final products (NO₃⁻ or NO₂⁻). Thus, the synergistic photo-thermal performance of MnO_x/g-C₃N₄ catalysts for NO removal will be enhanced. In this work, we proposed reaction mechanisms for the TCR process over MnO_x and the PTCR process over 1:5 MnO_x/g-C₃N₄, which can provide useful guidance for the development of better catalysts towards NO_x purification in the future.

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Graphical Abstract

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Synergistic photo-thermal catalytic NO purification of $\text{MnO}_x/\text{g-C}_3\text{N}_4$: enhanced performance and reaction mechanism

Peng Chen, Fan Dong *, Maoxi Ran, Jiarui Li
Chongqing Technology and Business University

During the adsorption process, the reduced metal centers and oxygen defects are created thermally on MnO_x and are sites of O_2 adsorption and activation. During the PTCR process, $\text{g-C}_3\text{N}_4$ produces a large amount of photo-generated electron-hole pairs (e^- - h^+) under UV-Vis light irradiation, which could participate in the catalytic cycles to generate abundant O^- and regenerate the active oxygen vacancy sites, thus accelerating the transformation of NOH and N_2O_2 to form nitrate species (NO_3^- or NO_2^-).

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MnO_x/g-C₃N₄光热协同催化净化NO的性能增强和反应机理

陈 鹏, 董 帆*, 冉茂希, 李佳芮

重庆工商大学环境与资源学院, 重庆市催化与环境新材料重点实验室, 重庆400067

摘要: 许多研究表明, MnO_x和g-C₃N₄均有催化氧化NO的活性, 并且探索了它们各自的转化机理. 然而, MnO_x/g-C₃N₄复合材料的光热催化机理仍然是一个未解决的问题. 我们通过室温沉淀法直接合成不同摩尔比的MnO_x/g-C₃N₄, 并发现其表现出良好的光热协同催化氧化NO的性能. MnO_x/g-C₃N₄催化剂在g-C₃N₄表面含有不同价态的MnO_x. 通过原位红外光谱在60 °C下研究了紫外-可见光诱导的MnO_x热催化NO的机理以及MnO_x/g-C₃N₄光热协同催化NO的机理. 结果表明, 光照对MnO_x热催化NO的过程几乎没有影响, 但对MnO_x/g-C₃N₄光热协同催化NO产生积极作用并且形成重要的催化循环机制. 具体过程是光生电子(e⁻)转移到MnO_x上参与光热协同的还原循环(Mn⁴⁺→Mn³⁺→Mn²⁺), 且低价Mn离子易给出电子(e⁻)与光生空穴(h⁺)相结合而诱导逆向的循环(Mn²⁺→Mn³⁺→Mn⁴⁺), 使活性氧空位再生. 通过MnO_x(Mn⁴⁺/Mn³⁺/Mn²⁺)变价而产生的活性氧(O⁻)可将中间产物(NOH和N₂O₂⁻)氧化为终产物(NO₂⁻和NO₃⁻). 这将为开发更好的净化NO_x的催化剂提供重要的指导意义.

XRD表征结果表明, MnO_x/g-C₃N₄复合催化剂的结晶度较低. TEM和XPS表征结果表明, g-C₃N₄表面含有多种低结晶度的MnO_x, 主要含有MnO, MnO₂和Mn₂O₃. 此外, 通过对比MnO_x和1:5 MnO_x/g-C₃N₄催化净化NO的XPS结果, 发现反应后的MnO_x含有大量Mn-Nitrate且Mn³⁺和Mn⁴⁺大幅度减少; 同时, 反应前后1:5 MnO_x/g-C₃N₄的Mn²⁺, Mn³⁺和Mn⁴⁺的含量变化微弱. BET-BJH测试结果显示, MnO_x/g-C₃N₄复合催化剂的比表面积和孔容均高于纯g-C₃N₄. UV-Vis DRS测试结果显示, MnO_x/g-C₃N₄复合催化剂显示了良好的可见光吸收能力. 紫外-可见光催化去除NO的测试结果表明, 1:5 MnO_x/g-C₃N₄(44%)的光催化活性明显高于MnO_x(28%)和g-C₃N₄(36%). ESR测试结果表明, 参与反应的主要活性物种为•O₂⁻自由基. EPR测试结果表明, 1:5 MnO_x/g-C₃N₄的氧空位明显多于MnO_x, 丰富的活性氧空位更有利于电子的迁移且促进Mnⁿ⁺(n = 2, 3和4)的变价而诱导O₂分子形成活性氧(O⁻). 以上结果清晰地表明1:5 MnO_x/g-C₃N₄表现出不同的理化特性.

可见光催化氧化NO的原位红外光谱表明, 光照前后MnO_x催化氧化NO的过程没有明显的变化, 表明其属于典型的热催化过程. 综合上述表征结果发现MnO_x的氧缺陷是Mnⁿ⁺(n = 3和4)变价的活性位点, 可诱导O₂产生活性氧催化氧化NO为硝酸盐吸附在MnO_x上; 光照前后1:5 MnO_x/g-C₃N₄催化氧化NO的过程有明显不同, 光照前主要表现为g-C₃N₄表面MnO_x的热催化过程, 而光照后1:5 MnO_x/g-C₃N₄为光热协同催化NO的过程. 具体过程是g-C₃N₄的光生电子(e⁻)转移到MnO_x上参与光热协同的还原循环(Mn⁴⁺→Mn³⁺→Mn²⁺), 且低价Mn离子易给出电子(e⁻)与光生空穴(h⁺)相结合而诱导逆向的循环(Mn²⁺→Mn³⁺→Mn⁴⁺)使活性氧空位再生. 通过MnO_x(Mn⁴⁺/Mn³⁺/Mn²⁺)变价而产生的活性氧(O⁻)可将中间产物(NOH和N₂O₂⁻)氧化为终产物(NO₂⁻和NO₃⁻).

关键词: MnO_x; g-C₃N₄; 协同催化; 光热协同; 原位红外光谱; NO氧化

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*通讯联系人. 电话/传真: (023)62769785; 电子信箱: dfctbu@126.com

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