

Article

Oxygen Vacancy-Driven Improvement of NH₃-SCR Performance over α -MnO₂: Mechanistic Insights

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Abstract

Nitrogen oxides (NO_x), harmful pollutants primarily from fossil fuel combustion, pose significant environmental and health risks. Among mitigation technologies, NH₃-SCR is widely adopted due to its high efficiency and industrial viability. MnO₂-based catalysts, particularly α -MnO₂, have gained attention for low-temperature NH₃-SCR owing to their redox properties, low-temperature activity, and environmental compatibility. In this study, α -MnO₂ catalysts with tunable oxygen vacancy concentrations were synthesized by varying calcination atmospheres. Compared to α -MnO₂-Air, the oxygen vacancy-rich α -MnO₂-N₂ exhibited stronger acidity, enhanced redox properties, and superior NH₃/NO adsorption and activation, achieving 98% NO conversion at 125–250 °C. Oxygen vacancies promoted NH₃ adsorption on Lewis/Brønsted acid sites, facilitating -NH₂ intermediate formation, while enhancing NO oxidation to reactive nitrates. In situ DRIFTS revealed a dual E-R and L-H reaction pathway, with oxygen vacancies crucial for NO activation, intermediate formation, and N₂ generation. These findings underscore the importance of oxygen vacancy engineering in optimizing Mn-based SCR catalysts.

Keywords: oxygen vacancy; α -MnO₂; NH₃-SCR; reaction mechanism



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1. Introduction

Nitrogen oxides (NO_x), primarily emitted from fossil fuel combustion in power plants, industrial operations, and motor vehicles, are among the most deleterious atmospheric pollutants [1,2]. Their presence contributes significantly to photo-chemical smog, acid rain, and fine particulate matter formation, posing severe risks to human health and the ecological environment. Among the various technologies developed for NO_x mitigation, the selective catalytic reduction of NO_x with ammonia (NH₃-SCR) stands out as one of the most efficient and widely implemented methods due to its high denitrification efficiency and industrial feasibility [3,4].

Currently, V₂O₅-WO₃(MoO₃)/TiO₂ catalysts dominate commercial NH₃-SCR applications owing to their excellent catalytic activity and durability in the 300–400 °C temperature range [5]. However, these catalysts suffer from several critical drawbacks, including a narrow operational temperature window, poor low-temperature activity, vanadium toxicity, and susceptibility to deactivation by SO₂ and H₂O [6]. These limitations have driven the search for alternative catalysts that are environmentally benign, highly active at low temperatures (<250 °C), and resistant to poisoning and deactivation.

Manganese-based catalysts, particularly α -MnO₂, have attracted significant attention as promising candidates for low-temperature SCR due to their multiple valence states (Mn²⁺/Mn³⁺/Mn⁴⁺) and superior redox properties [7,8]. These intrinsic characteristics facilitate the redox cycle and enhance the activation of reactant molecules. However, MnO₂ suffers from drawbacks such as poor thermal stability and low N₂ selectivity [9,10]. To address these limitations, defect engineering, specifically the introduction of oxygen vacancies (Vo), has emerged as a powerful strategy for tuning the surface and electronic properties of MnO₂-based catalysts. Recent studies have revealed that oxygen vacancies can significantly improve NH₃-SCR performance by enhancing the adsorption and activation of reactants, promoting the formation of reactive oxygen species, and modulating the electronic environment around active sites [11,12]. For instance, Cong et al. [13] developed a novel N-doped CeO₂ catalyst with abundant oxygen vacancies, which exhibited superior NO_x removal efficiency over a wide temperature range owing to N-doping-induced defect structures. Beyond SCR catalysis, oxygen vacancy engineering has emerged as a powerful and universal strategy in fields such as photocatalysis and electrocatalysis [14]. For instance, Wang et al. [15] demonstrated that introducing oxygen vacancies into ZnO greatly enhanced visible-light-driven photocatalytic degradation of pollutants by modulating band structure and charge carrier dynamics. In the field of electrocatalysis, Liu et al. [16] reported that oxygen-deficient NiFe layered double hydroxides (LDHs) showed improved OER activity due to increased active sites and modified electronic structure. These studies collectively illustrate the wide applicability and effectiveness of oxygen vacancy modulation as a surface and electronic structure engineering tool.

In the field of MnO₂ catalysts, Wu et al. [17] discovered that oxygen vacancies not only possess strong oxygen affinity but also promote electron transfer, serving as the main active sites in the α -MnO_{2-x}/O₃ system and thereby accelerating organic pollutant degradation. Yang et al. [18] further demonstrated that β -MnO₂ nanosheets and nanorods rich in oxygen vacancies—obtained via phase transformation roasting of γ -MnO₂—showed significantly enhanced activity, with nanosheets achieving up to 90% conversion rates due to their higher oxygen vacancy content. Despite these advances, the specific regulatory mechanism by which oxygen vacancies influence the denitrification performance of α -MnO₂ catalysts remains unclear.

Density functional theory (DFT) is widely used to explore the electronic structure of catalytic materials. It is typically employed to calculate the oxygen vacancy formation energy and the adsorption behavior of reactants on the catalyst surface. These theoretical analyses are helpful for verifying the experimental results and clarifying the role of Vo in enhancing the adsorption of reactants and promoting the formation of -NH₂ and nitrate species [19–21]. Xie et al. [21] found using DFT calculations that oxygen vacancies significantly enhanced the molecular adsorption and oxidation on the surface of Fe-based catalysts and played a key role in the de-NO_x reaction.

Therefore, this study systematically investigates the role of oxygen vacancies in enhancing the NH₃-SCR performance of defective α -MnO₂ catalysts. By employing controlled synthesis strategies, we modulate the defect concentration to elucidate the relationship between oxygen vacancy density and catalytic activity. Through a combination of comprehensive physicochemical characterization, in situ DRIFTS analysis, and DFT calculations, we uncover how oxygen vacancies influence redox behavior, surface acidity, and the activation of NH₃ and NO. Particular attention is given to their role in regulating the E-R and L-H mechanisms. The combined experimental and theoretical approach aims to establish a comprehensive mechanistic model for the function of oxygen vacancies in α -MnO₂ catalysts and guide the rational design of highly efficient SCR materials.

2. Results and Discussion

2.1. Phase and Oxygen Vacancy Analysis

The crystal structure of the synthesized α -MnO₂ catalysts was analyzed using XRD, and the results are shown in Figure 1. Within the 2θ characteristic diffraction peaks were observed at 12.8°, 18.1°, 28.8°, 37.5°, 42.0°, 49.9°, 56.4°, 60.3°, and 69.7°, which are consistent with the standard JCPDS card PDF#44-014. These peaks confirm the formation of α -type MnO₂ with a tetragonal structure belonging to the I4/m(87) space group. The XRD patterns of samples synthesized under different calcination temperatures and atmospheres exhibit nearly identical peak positions, indicating that the variation in synthesis conditions did not significantly alter the phase structure.

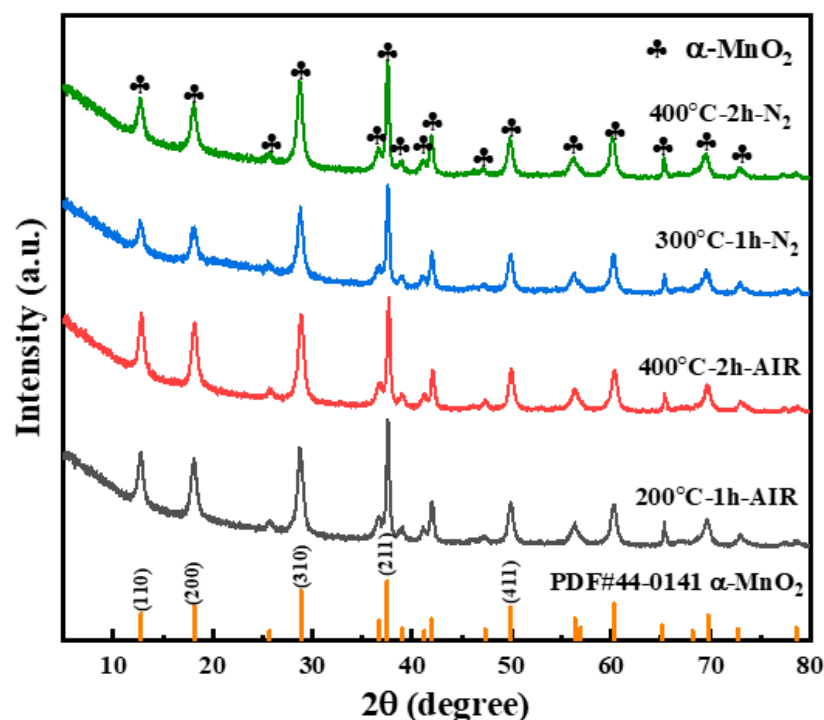


Figure 1. XRD patterns of α -MnO₂ catalysts.

The oxygen vacancy defects in α -MnO₂ catalysts prepared under different atmospheres were characterized using EPR, as shown in Figure 2. A comparison of spectral intensities between α -MnO₂-400 °C-2 h-N₂ and α -MnO₂-400 °C-2 h-AIR reveals that the catalyst treated under an N₂ atmosphere exhibits a significantly stronger and more symmetric EPR signal, indicating a higher concentration of oxygen vacancies. The signal observed at $g = 2.001$ is characteristic of unpaired electrons trapped in oxygen vacancy sites, consistent with the literature reports that associate g values around 2.002–2.003 with such defects [13]. For example, Zhao et al. [22] reported an EPR signal at $g = 2.002$ for Vo/Ti catalysts with varying Ti doping levels, attributing it to electrons trapped in oxygen vacancies. Similarly, Zhang et al. [23] observed a peak at $g = 2.002$ in Mo-doped TiO₂, confirming the presence of singly occupied oxygen vacancies. The results of this study, with a strong EPR signal at $g = 2.001$, further confirm that thermal treatment in an inert atmosphere effectively promotes the formation of oxygen vacancies in α -MnO₂.

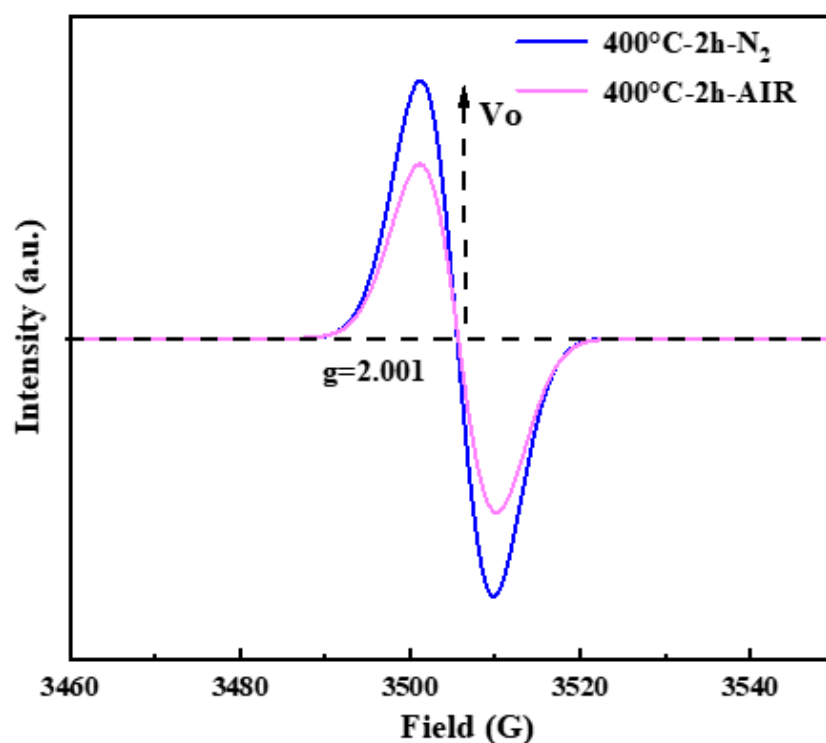


Figure 2. EPR patterns of α -MnO₂-N₂ and α -MnO₂-AIR catalysts.

2.2. Catalytic Performance Evaluation

Figure 3a,b show the NO_x conversion and N₂ selectivity of α -MnO₂ catalysts with different oxygen vacancy concentrations across a temperature range of 100 to 300 °C. As illustrated in Figure 3a, the denitrification activity of the catalysts is significantly influenced by the concentration of oxygen vacancies, particularly under low-temperature conditions. Notably, the α -MnO₂-400 °C-2 h-N₂ catalyst (hereafter referred to as α -MnO₂-N₂) exhibits superior catalytic activity and a wider active temperature window, achieving nearly 100% NO conversion within the 125–250 °C range. Similarly, the α -MnO₂-300 °C-1 h-N₂ sample also reaches nearly complete NO conversion in the same temperature range; however, its performance at 100 °C is reduced, with a conversion rate of only 78%. In contrast, catalysts prepared under an air atmosphere with lower oxygen vacancy concentrations, such as α -MnO₂-400 °C-2 h-AIR (hereafter referred to as α -MnO₂-AIR) and α -MnO₂-300 °C-1 h-AIR, demonstrate markedly lower NO removal efficiency at low temperatures. Specifically, α -MnO₂-300 °C-1 h-AIR achieves only 47.5% NO conversion at 100 °C, though performance improves with increasing temperature. Overall, α -MnO₂ catalysts synthesized under a nitrogen atmosphere consistently show enhanced NO removal performance compared to those synthesized in air, owing to the higher concentration of oxygen vacancies.

As shown in Figure 3b, the N₂ selectivity within the effective reaction window (150–250 °C) follows a similar trend: α -MnO₂-N₂ catalysts maintain higher N₂ selectivity than their AIR-treated counterparts. To further elucidate the role of oxygen vacancies in denitrification performance, subsequent characterization and analysis focused on α -MnO₂-N₂ and α -MnO₂-AIR catalysts.

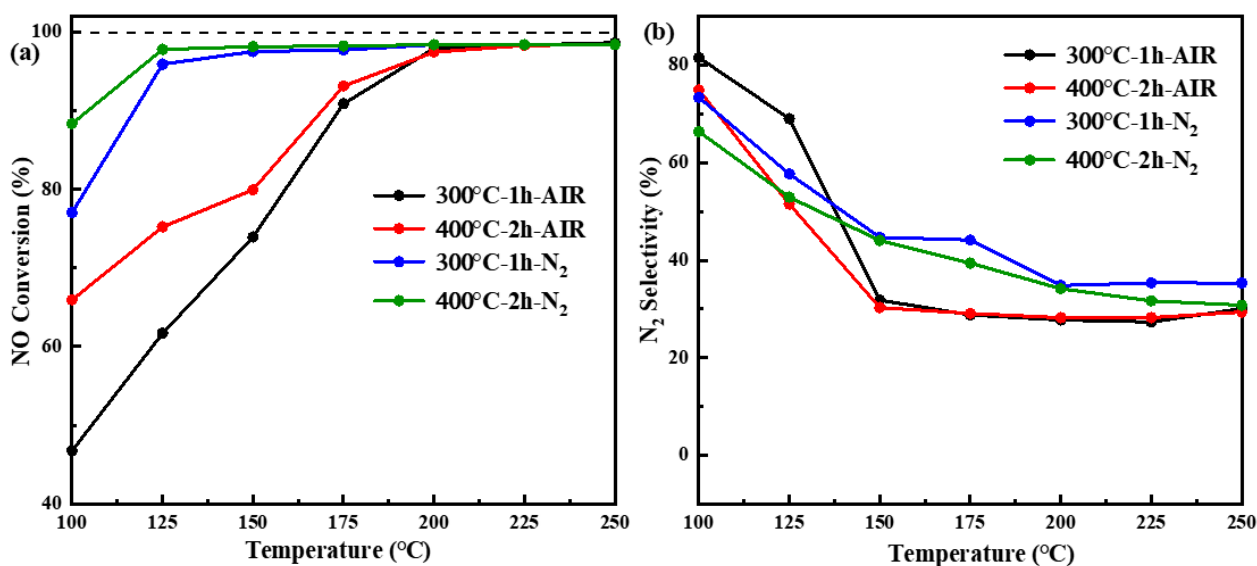


Figure 3. α -MnO₂ catalyst with (a) NO conversion and (b) N₂ selectivity. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol%, [N₂] equilibrium gas, total gas flow rate of 300 mL/min, GHSV = 30,000 h^{−1}.

2.3. Surface Physical and Chemical Properties Analysis

The morphologies and microstructural characteristics of α -MnO₂-N₂ and α -MnO₂-AIR catalysts were examined using SEM and TEM. As shown in Figure 4a,c, the α -MnO₂-N₂ catalyst exhibits a characteristic rod-like morphology, with numerous rod-shaped structures interlaced and densely stacked on the surface, forming tightly packed aggregates. Although the α -MnO₂-AIR catalyst, which possesses a lower concentration of oxygen vacancy defects, also retains a similar rod-like structure (Figure 4b,d), a more detailed inspection reveals subtle distinctions in the surface features.

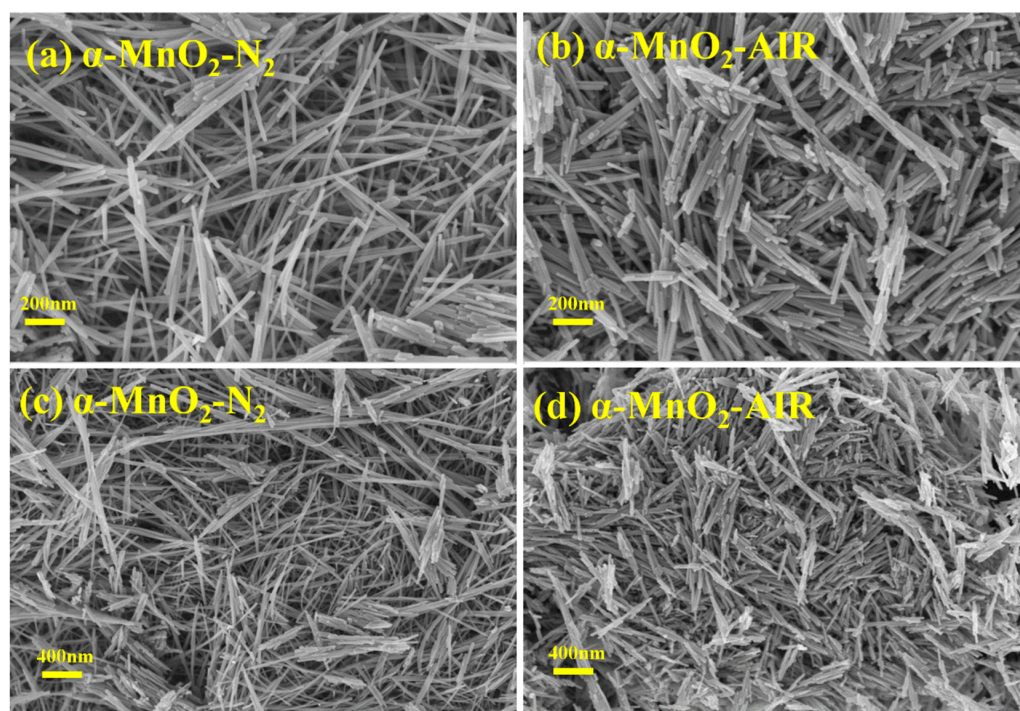


Figure 4. SEM images with different magnifications. (a,c) α -MnO₂-N₂ catalyst, (b,d) α -MnO₂-AIR catalyst.

Figure 5 presents TEM images of α -MnO₂ catalysts with different oxygen vacancy concentrations. As seen in Figure 5a,b, the α -MnO₂-N₂ catalyst maintains a distinct rod-like morphology at high resolution, with clearly discernible and well-ordered lattice fringes. The measured interplanar spacing of 0.69 nm corresponds to the (110) crystal plane of α -MnO₂. Similarly, TEM images of the α -MnO₂-AIR catalyst (Figure 5c,d) also show a rod-like structure, with the (110) plane being the predominant exposed surface. These observations confirm that both α -MnO₂-N₂ and α -MnO₂-AIR catalysts share the same dominant crystal orientation, suggesting that differences in catalytic performance are not due to changes in the crystal phase, but are more likely attributed to variations in surface defect concentrations, such as oxygen vacancies.

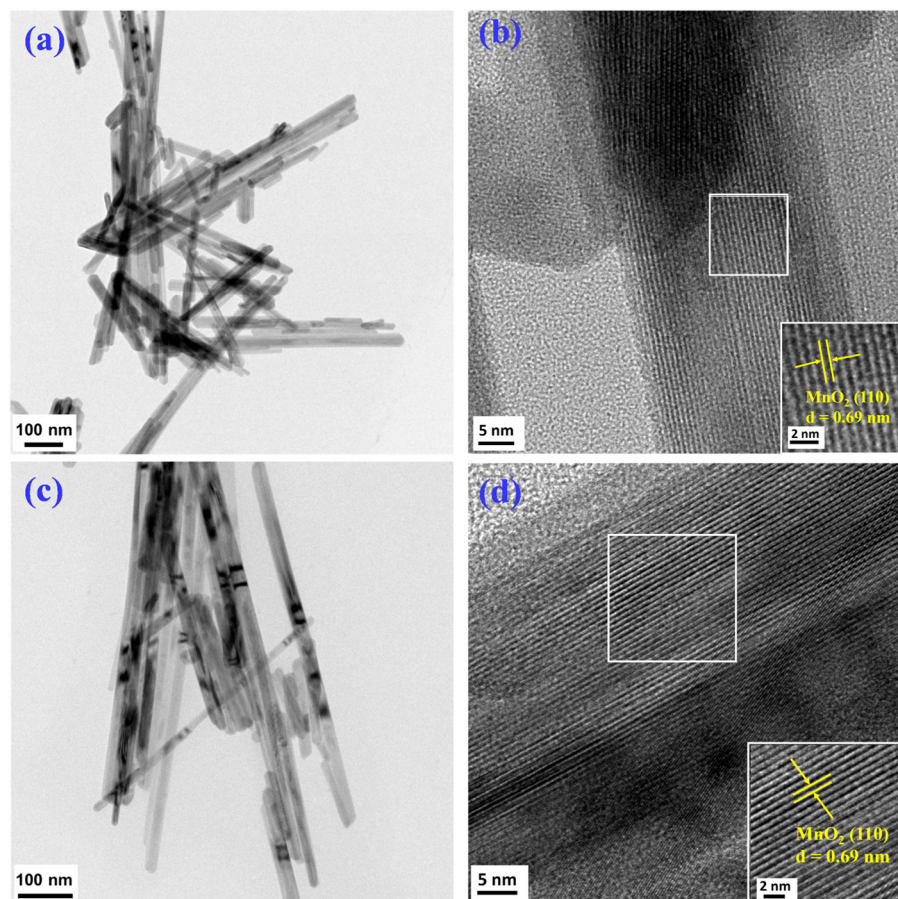


Figure 5. SEM images with different magnifications. (a,b) α -MnO₂-N₂ catalyst, (c,d) α -MnO₂-AIR catalyst.

Figure 6a,b show the N₂ adsorption–desorption isotherms and pore size distributions of the α -MnO₂-N₂ and α -MnO₂-AIR catalysts, respectively. Both catalysts exhibit type IV isotherms with H3 hysteresis loops, indicative of mesoporous structures [24]. The BET specific surface areas of α -MnO₂-N₂ and α -MnO₂-AIR are 50.01 m²/g and 46.69 m²/g, respectively. As shown in Figure 6b, the pore size distributions of both catalysts are concentrated within the range of 2–10 nm, demonstrating the characteristics of mesoporous materials [25]. The pore volume of α -MnO₂-N₂ within the pore size range of 2–5 nm is slightly larger than that of α -MnO₂-AIR. This indicates that the α -MnO₂-N₂ catalyst has a higher pore volume, which is conducive to the adsorption and diffusion of the reactant gas. The pore structure parameters of the α -MnO₂-N₂ and α -MnO₂-AIR catalysts are presented in Table 1.

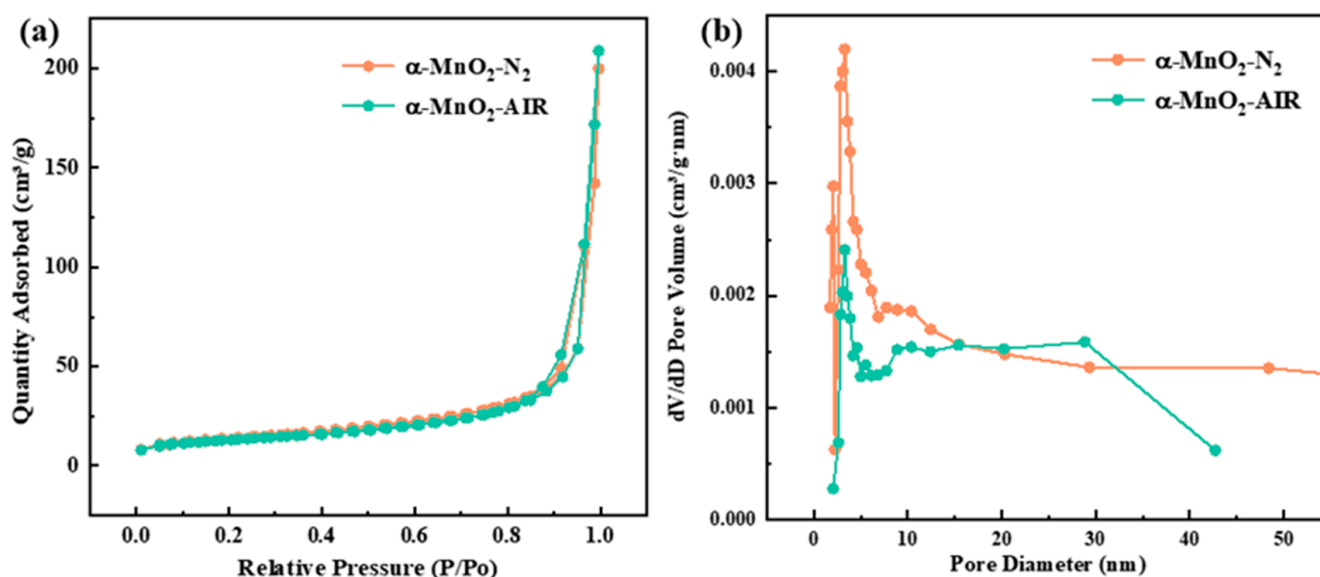


Figure 6. Temperature isotherm of (a) N₂ adsorption–desorption and (b) BJH pore size distribution for α-MnO₂-N₂ and α-MnO₂-AIR catalysts.

Table 1. Pore structure parameters of α-MnO₂-N₂ and α-MnO₂-AIR catalysts.

Catalyst	Surface Area(m ² /g)	Pore Volume (cm ³ /g)	Average Pore (nm)
α-MnO ₂ -N ₂	50.01	0.31	27.68
α-MnO ₂ -AIR	46.69	0.32	32.24

Figure 7a–d present the XPS results of the α-MnO₂ catalysts, including the survey spectra, Mn 3s, Mn 2p, and O 1s catalysts, respectively. In Figure 7a, the survey spectra confirm the presence of Mn, O, and C (contamination) elements in all samples. The high-resolution Mn 2p spectra in Figure 7b exhibit two distinct peaks located at 640.1–642.3 eV and 653.9–654.2 eV, corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively. Deconvolution of the Mn 2p_{3/2} peak reveals three components centered at 640.1–641.2 eV, 641.9–642.2 eV, and 642.7–643.5 eV, which can be attributed to Mn²⁺, Mn³⁺, and Mn⁴⁺ species, respectively [26]. As the valence state of high-valent Mn⁴⁺ decreases to achieve charge balance, oxygen defects may occur. Therefore, the low-valent state of Mn³⁺ is an indicator of oxygen defects [27,28]. The relative content of Mn²⁺, Mn³⁺, and Mn⁴⁺ ions on α-MnO₂ catalysts can be determined by analyzing the integral areas of these peaks, as shown in Table 2. Quantitative analysis indicates that the Mn³⁺ content on the catalyst surface exhibits the trend of α-MnO₂-N₂ (59.70%) > α-MnO₂-AIR (51.38%), suggesting a higher concentration of oxygen vacancies in the former.

Further validation is provided by the Mn 3s XPS spectra shown in Figure 7c. The average oxidation state (AOS) of Mn was calculated using the equation $AOS = 8.956 - 1.126 \times \Delta E$, where ΔE denotes the peak splitting width in the Mn 3s region [29,30]. The measured ΔE values for α-MnO₂-N₂ and α-MnO₂-AIR are 4.99 eV and 4.83 eV, corresponding to AOS values of 3.34 and 3.52, respectively. The lower AOS of α-MnO₂-N₂ confirms the higher Mn³⁺ content, in agreement with the Mn 2p_{3/2} spectral fitting results.

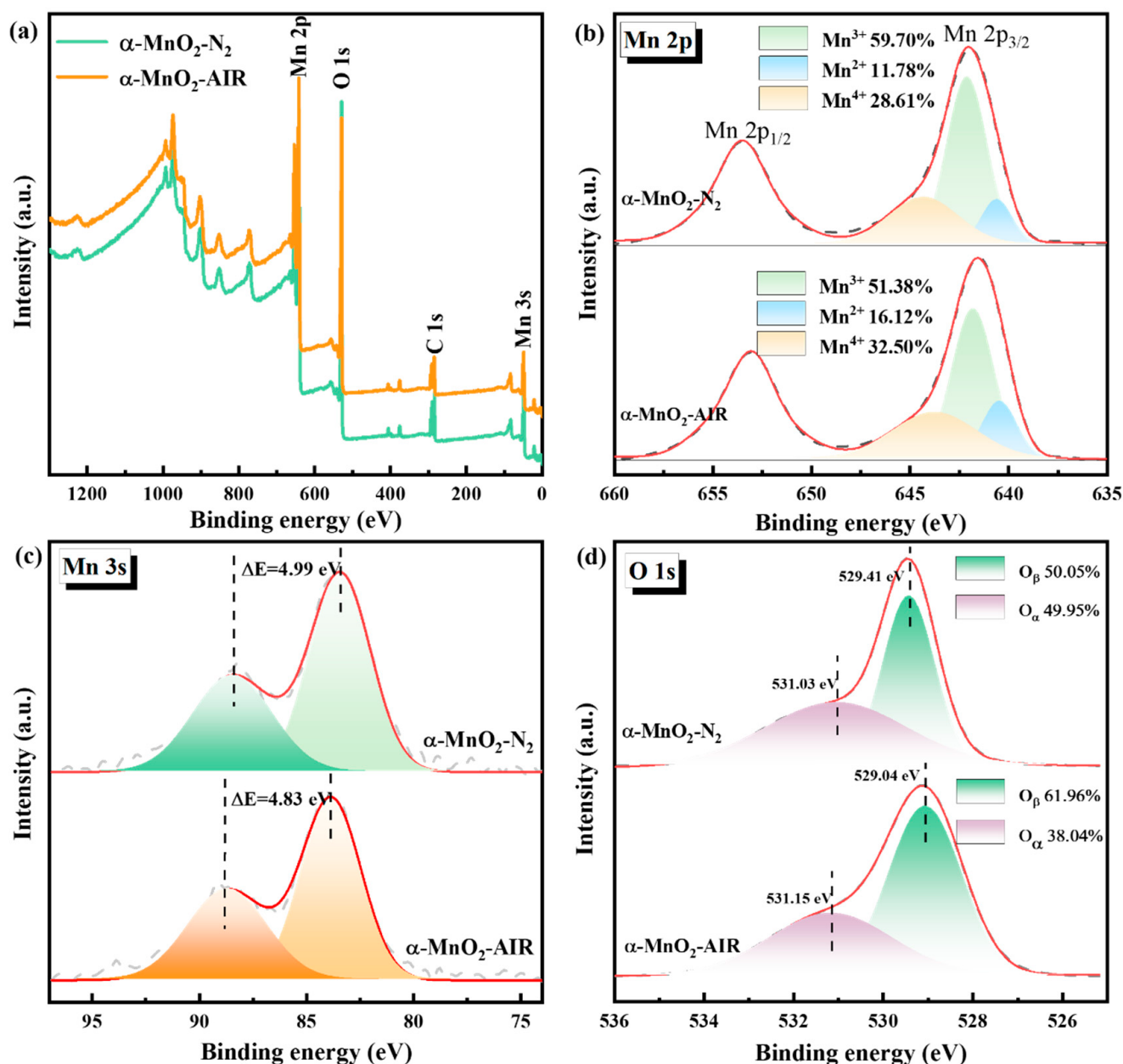


Figure 7. XPS spectra of α -MnO₂-N₂ and α -MnO₂-AIR catalysts: (a) survey spectra, (b) Mn 3s, (c) Mn 2p, (d) O 1s.

Table 2. The surface atomic concentrations of α -MnO₂-N₂ and α -MnO₂-AIR catalysts.

Sample	Relative Content (%)				
	O _α	O _β	Mn ²⁺	Mn ³⁺	Mn ⁴⁺
α -MnO ₂ -N ₂	49.95	50.05	11.78	59.70	28.61
α -MnO ₂ -AIR	38.04	61.96	16.12	51.38	32.50

In addition, oxygen vacancy defects can be used as an active site to promote oxygen adsorption and activation, so surface adsorbed oxygen is another indicator of oxygen defects. In Figure 7d, the O 1s XPS spectrum of each α -MnO₂ can be decomposed into two components. The main peak of binding energy 529.5–530.0 eV is attributed to lattice oxygen (O_β) and the peak of the binding energy of 531.4–531.8 eV refers to the surface adsorbed oxygen (O_α) [31,32]. The surface adsorbed oxygen concentration follows the order of α -MnO₂-N₂ > α -MnO₂-AIR, which is consistent with the order of Mn³⁺ on the

surface. Higher concentrations of Mn^{3+} and adsorbed oxygen on the surface of $\alpha\text{-MnO}_2\text{-N}_2$ catalysts indicate that they have more abundant oxygen defects, indicating that $\alpha\text{-MnO}_2\text{-N}_2$ has stronger electron affinity and electronegativity [33]. This property is conducive to accelerating the breaking of N-H bonds in adsorbed NH_3 molecules, promoting the formation of reaction intermediates -NH_2 , thereby improving catalytic activity.

Figure 8a and Table 3 show the NH_3 -TPD profiles and quantitative calculations for NH_3 -TPD data of each catalyst, respectively. Both catalysts exhibited multiple desorption peaks, corresponding to NH_3 desorption from weak, medium, and strong acid sites [34,35]. Compared to $\alpha\text{-MnO}_2\text{-AIR}$, the $\alpha\text{-MnO}_2\text{-N}_2$ catalyst displayed desorption peaks at higher temperatures, indicating the presence of stronger acid sites. Furthermore, the total desorption capacity of NH_3 by $\alpha\text{-MnO}_2\text{-N}_2$ is higher than that of $\alpha\text{-MnO}_2\text{-AIR}$, indicating that oxygen vacancies enhance the strength and density of acid sites, thereby improving the adsorption and activation capacity of the catalyst for NH_3 .

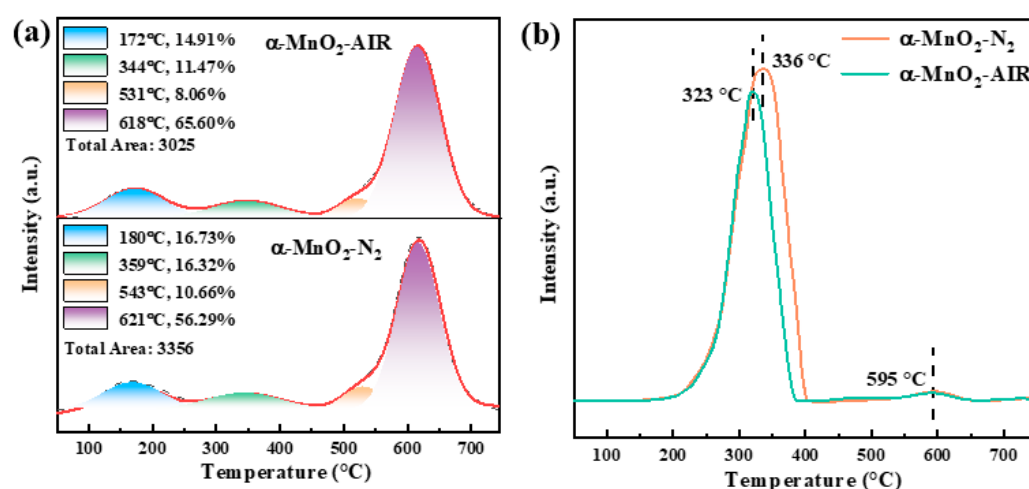


Figure 8. $\alpha\text{-MnO}_2\text{-AIR}$ and $\alpha\text{-MnO}_2\text{-N}_2$ catalysts: (a) NH_3 -TPD results and (b) H_2 -TPR results.

Table 3. Quantitative data of NH_3 -TPD on $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$ catalysts.

Sample	Weak Acid Area (a.u.)	Medium Acid Area (a.u.)	Strong Acid Area (a.u.)	Total Acid Area (a.u.)
$\alpha\text{-MnO}_2\text{-N}_2$	561.46	547.70	2246.84	3356
$\alpha\text{-MnO}_2\text{-AIR}$	451.03	346.70	2228.22	3025

The redox properties of the catalysts are important factors affecting the NH_3 -SCR reaction and were characterized in this study using H_2 -TPR. As can be seen in Figure 8b, the H_2 -TPR profiles of $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$ catalysts exhibit two similar reduction bands. For $\alpha\text{-MnO}_2\text{-N}_2$, the peaks are centered at 336 $^{\circ}\text{C}$ and 595 $^{\circ}\text{C}$, corresponding to the stepwise reduction of MnO_2 to Mn_2O_3 and further to MnO , respectively [36,37]. The $\alpha\text{-MnO}_2\text{-AIR}$ catalyst showed similar reduction features, with peak centers at 323 $^{\circ}\text{C}$ and 595 $^{\circ}\text{C}$; however, the narrower peak width indicates slightly lower reducibility. Quantitative H_2 consumption analysis revealed that $\alpha\text{-MnO}_2\text{-N}_2$ consumed 11,236.98 $\mu\text{mol/g}$ of H_2 , significantly higher than the 8643.16 $\mu\text{mol/g}$ consumed by $\alpha\text{-MnO}_2\text{-AIR}$, confirming that the catalyst with a higher oxygen vacancy concentration exhibits enhanced redox capacity. These results suggest that the superior redox properties of $\alpha\text{-MnO}_2\text{-N}_2$ contribute to its improved SCR activity and highlight the critical role of oxygen vacancies in tuning catalytic performance.

2.4. Oxygen Vacancy Formation Energy and Adsorption Energy Calculation

In this study, a tetragonal α - MnO_2 model, belonging to the $I4/m$ (87) space group, was employed for DFT calculations. The α - MnO_2 crystal structure was obtained from the Materials Project database, as shown in Figure 9a. The lattice parameters of the model are as follows: $a = 9.72 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 2.85 \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, and $\gamma = 90.00^\circ$. These parameters are in agreement with the values from the XRD reference card (PDF #44-0141): $a = 9.7847 \text{ \AA}$, $b = 9.7847 \text{ \AA}$, $c = 2.863 \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, and $\gamma = 90.00^\circ$.

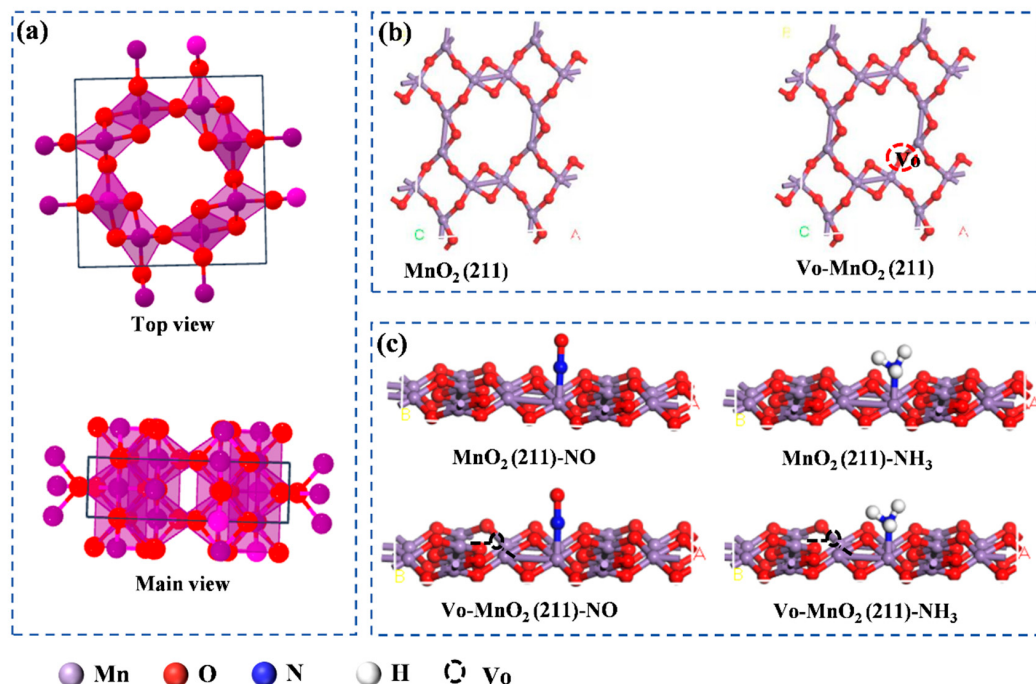


Figure 9. (a) Ideal model of α - MnO_2 , (b) MnO_2 (211) crystal face oxygen vacancy defect formation energy model, and (c) calculation structure model of adsorption energy of MnO_2 (211).

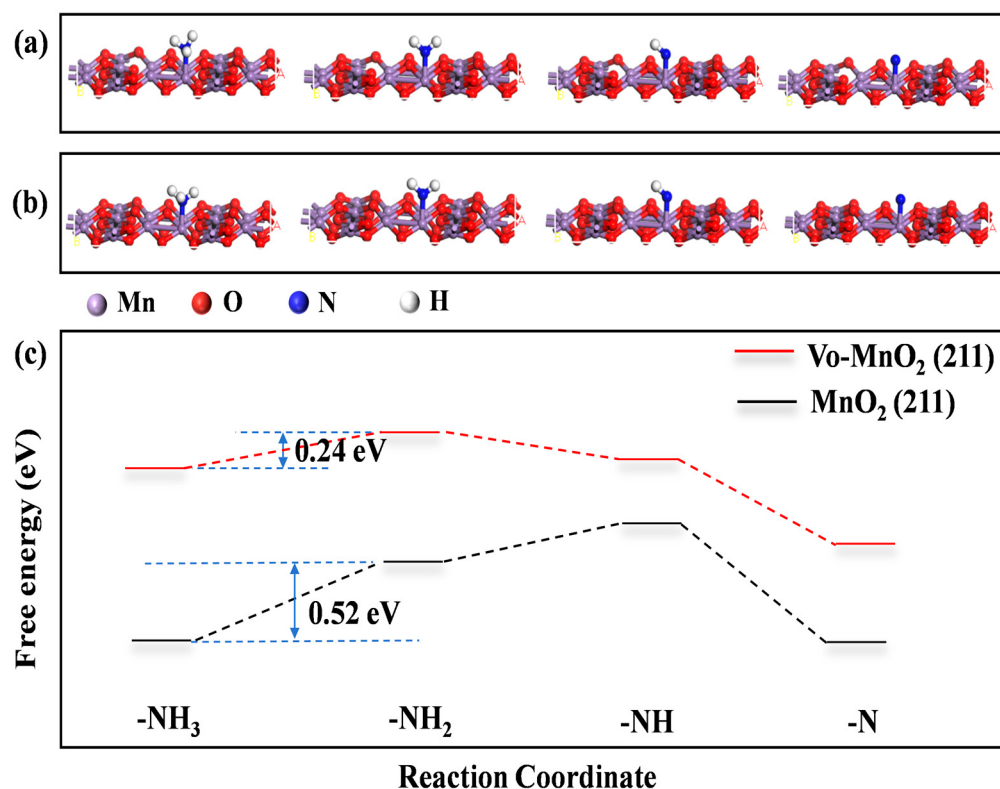
As shown in Figure 9b, the oxygen vacancy defect model was constructed by removing one surface oxygen atom from the perfect crystal surface. The formation energy of the oxygen vacancy (E_f), as defined using Equation (3), was calculated to assess the ease of vacancy formation. A lower E_f value indicates a greater tendency for oxygen vacancy formation. The E_f of the surface of MnO_2 (211) was calculated to be 1.62 eV, indicating that MnO_2 (211) is prone to generating oxygen vacancy defects.

Additionally, DFT calculations were performed to investigate the adsorption behavior of NH_3 and NO molecules on MnO_2 surfaces. The adsorption configurations were modeled by connecting the nitrogen atoms of NH_3 and NO to the Mn atoms on the catalyst surface [38], as shown in Figure 9c. First, the MnO_2 (211) surface was geometrically optimized to obtain a stable structure, followed by the placement and optimization of NH_3 or NO molecules on the surface. Similarly, the oxygen-defective surface, Vo-MnO_2 (211), was also optimized prior to the adsorption calculations. The adsorption models for both MnO_2 (211) and Vo-MnO_2 (211) are presented in Figure 9c, with the corresponding adsorption energies listed in Table 4. The results indicate that the presence of oxygen vacancies significantly enhances the adsorption capacity of MnO_2 for both NH_3 and NO . This suggests that, during the NH_3 -SCR process, NO and NH_3 molecules are more likely to adsorb on the oxygen-deficient MnO_2 surface, thereby promoting their activation and subsequent reaction.

Table 4. Formation energy of oxygen vacancies and adsorption energy of NO and NH₃ on MnO₂ (211) and Vo-MnO₂ (211) surfaces.

Model	Vo Formation Energy/eV	NO Adsorption Energy/eV	NH ₃ Adsorption Energy/eV
MnO ₂ (211)	-	−1.52	−107.92
Vo-MnO ₂ (211)	1.62	−1.65	−109.85

Figure 10 presents the calculated adsorption and dissociation behaviors of NH₃ on the MnO₂ (211) and Vo-MnO₂ (211) surfaces with oxygen vacancies. Figure 10a,b show the optimal adsorption configurations of NH₃ on the defect and perfect surfaces, while Figure 10c illustrates the free energy changes, revealing the stability and energy barriers of each intermediate species (-NH_3 , -NH_2 , -NH , -N). The energy curve indicates that the initial dissociation step ($\text{-NH}_3 \rightarrow \text{-NH}_2$) is endothermic on both surfaces. However, the dissociation barrier on the Vo-MnO₂ (211) surface is reduced to 0.24 eV, 0.28 eV lower than the 0.52 eV barrier on the perfect MnO₂ (211) surface. This suggests that oxygen vacancies weaken the N-H bond, enhancing the initial activation of NH₃. Further analysis shows that the $\text{-NH}_2 \rightarrow \text{-NH}$ process is endothermic on MnO₂ (211), but exothermic on Vo-MnO₂ (211). The overall energy distribution demonstrates a lower dissociation barrier for NH₃, indicating that the Vo-MnO₂ (211) surface can more easily dissociate NH₃ into -NH_2 , -NH , and -N species. Notably, in the NH₃-SCR process, -NH_2 is a key intermediate, but excessive dehydrogenation may increase N₂O by-products, reducing the catalyst's N₂ selectivity.

**Figure 10.** (a) Optimal adsorption configuration of NH₃ dissociation on the Vo-MnO₂ (211) plane, (b) optimal adsorption configuration of NH₃ dissociation on the MnO₂ (211) plane, and (c) energy spectrum of NH₃ adsorption and dissociation.

2.5. Surface Reaction Pathways Analysis

To investigate the reaction pathways on the catalyst surface, in situ DRIFTS analysis was further employed to study the adsorption and conversion behavior of NH₃. The results,

shown in Figure 11, reveal that upon NH_3 adsorption, both the $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$ catalysts exhibited characteristic bands corresponding to L-NH_3 adsorption at Lewis acid sites (1650 cm^{-1}), B-NH_4^+ adsorption at Brønsted acid sites (1694 and 1741 cm^{-1}), and -NH_2 groups (1526 cm^{-1}) [39,40]. Although there were no significant differences in the types of acid sites between the two catalysts, the adsorption bands of $\alpha\text{-MnO}_2\text{-N}_2$ remained stronger throughout the process, suggesting a higher density of acid sites and a stronger interaction with NH_3 . In contrast, the weaker adsorption bands observed for $\alpha\text{-MnO}_2\text{-AIR}$ indicate fewer surface active sites and a reduced ability to adsorb and activate NH_3 . However, the NH_3 -TPD signals show that the influence of oxygen vacancies on the desorption behavior of NH_3 is relatively minor. The similar NH_3 -TPD spectra for both catalysts suggest that oxygen vacancies primarily affect the chemical state of the adsorbed species rather than significantly altering the amount of NH_3 desorbed.

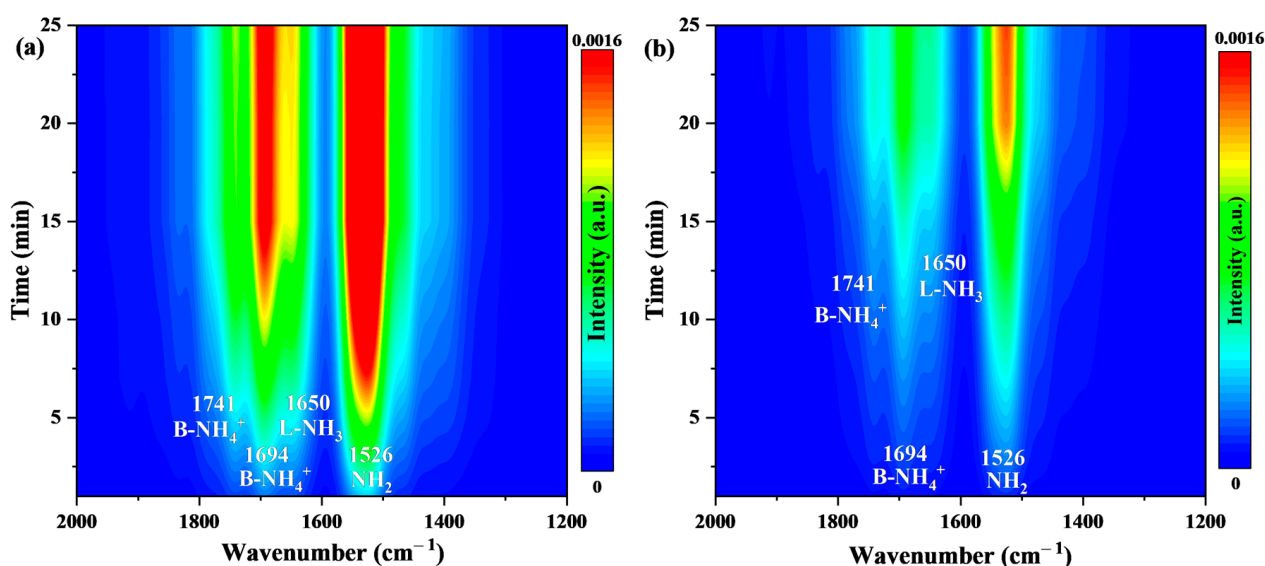


Figure 11. In situ infrared spectroscopy of NH_3 adsorption by (a) $\alpha\text{-MnO}_2\text{-N}_2$ and (b) $\alpha\text{-MnO}_2\text{-AIR}$ catalysts at $125\text{ }^\circ\text{C}$.

The in situ DRIFTS spectra of $\text{NO} + \text{O}_2$ adsorption on the $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$ catalysts are shown in Figure 12. As depicted in Figure 12a, with increasing adsorption time, various active nitrates and nitrites gradually form on the surface of $\alpha\text{-MnO}_2\text{-N}_2$, which contains oxygen vacancies. Specifically, the bands at 1257 and 1694 cm^{-1} correspond to bridging nitrates, the band at 1534 cm^{-1} corresponds to monodentate nitrates, and the band at 1390 cm^{-1} corresponds to adsorbed nitrate ions (NO_3^-) [41–43]. Similar characteristic spectral bands were observed on $\alpha\text{-MnO}_2\text{-AIR}$, including those for bridged nitrates (1257 and 1694 cm^{-1}), monodentate nitrates (1534 cm^{-1}), and nitrate ions (1395 cm^{-1}). However, the overall band intensity on $\alpha\text{-MnO}_2\text{-AIR}$ is significantly weaker than that on $\alpha\text{-MnO}_2\text{-N}_2$. These results indicate that the $\alpha\text{-MnO}_2\text{-AIR}$ catalyst, which has fewer oxygen vacancy defects, exhibits weaker adsorption and activation capabilities for NO . The presence of oxygen vacancies likely modulates the electronic structure of the catalyst surface, promoting the chemical adsorption and activation of NO molecules and facilitating the formation of reaction intermediates.

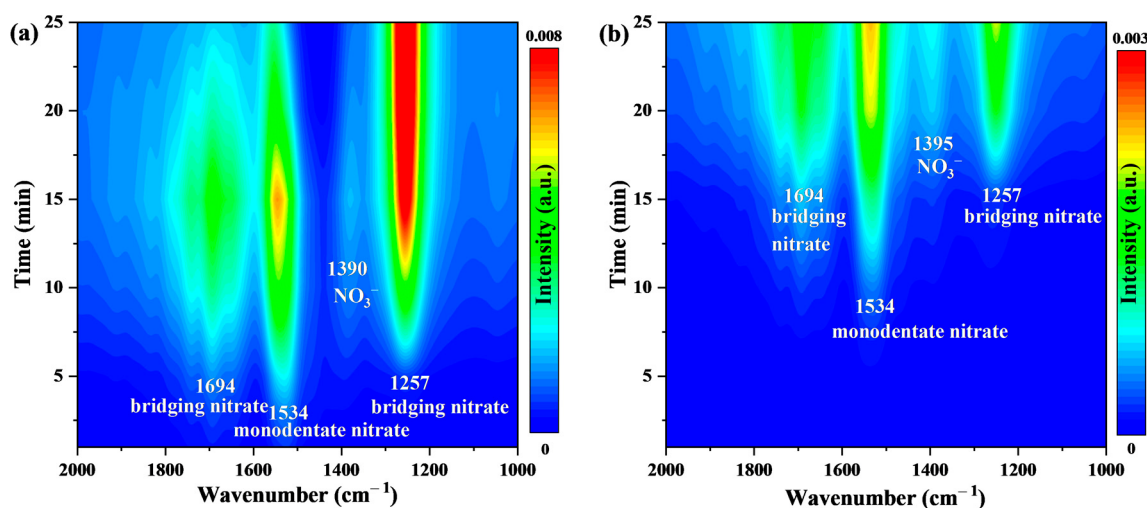


Figure 12. In situ infrared spectroscopy of NO + O₂ adsorption by (a) α -MnO₂-N₂ and (b) α -MnO₂-AIR catalysts at 125 °C.

To elucidate the influence of oxygen vacancy defects on the activation behavior of reactants over α -MnO₂ catalysts, in situ DRIFTS experiments were conducted on both α -MnO₂-N₂ and α -MnO₂-AIR. The reaction between pre-adsorbed NH₃ with NO + O₂ was examined at 125 °C, and the corresponding infrared spectra are presented in Figure 13a,b. As shown in Figure 13a, after 25 min of NH₃ adsorption on the α -MnO₂-N₂ catalyst, distinct absorption bands appeared at 1650 cm⁻¹ (L-NH₃), 1694 cm⁻¹ and 1741 cm⁻¹ (B-NH₄⁺), as well as 1526 cm⁻¹ (-NH₂), corresponding to various adsorbed NH₃ species. Upon switching to NO + O₂, the bands assigned to L-NH₃ (1650 cm⁻¹) and B-NH₄⁺ (1694 and 1741 cm⁻¹) rapidly disappeared, while the -NH₂ band (1526 cm⁻¹) diminished more gradually, suggesting that these NH₃ species actively participated in the NH₃-SCR reaction. With continued exposure to NO + O₂, new bands slowly emerged at 1702, 1550, and 1252 cm⁻¹, which are attributed to nitrate species. These observations indicate that both L-acid and B-acid site-bound NH₃ species are reactive intermediates in the SCR process.

Similar trends were observed for α -MnO₂-AIR after 30 min of NH₃ adsorption, with corresponding bands for -NH₂ (1526 cm⁻¹), L-NH₃ (1650 cm⁻¹), and B-NH₄⁺ (1694 and 1741 cm⁻¹). After switching to NO + O₂, the reaction pathway resembled that of α -MnO₂-N₂; however, the intensities of the nitrate species bands were significantly lower. Throughout the reaction, no adsorption bands of NO_x species were detected before the complete consumption of NH₃, suggesting that gaseous NO preferentially reacts with surface NH₃ species prior to being adsorbed and activated on the catalyst surface. These results indicate that the reaction follows an E-R mechanism.

Figure 13c,d show the spectra of NH₃ adsorption after the pre-adsorption of NO + O₂ for α -MnO₂-N₂ and α -MnO₂-AIR catalysts. As can be seen in Figure 13c, for the α -MnO₂-N₂ catalyst, bands at 1532, 1253, 1664, 1694, 1741, and 1390 cm⁻¹ are detected after pre-adsorption of NO + O₂. The bands at 1253, 1664, 1694, and 1741 cm⁻¹ correspond to bridging nitrates. In addition, the band at 1534 cm⁻¹ corresponds to monodentate nitrates, and the band at 1390 cm⁻¹ corresponds to adsorbed nitrate ions (NO₃⁻). Furthermore, the bands assigned to bridging nitrates (1664, 1694, and 1741 cm⁻¹) and nitrate ions (1390 cm⁻¹) rapidly disappeared after the introduction of NH₃. Meanwhile, the monodentate nitrate band at 1532 cm⁻¹ gradually shifted to 1564 cm⁻¹, and the bridging nitrate at 1253 cm⁻¹ decreased slowly. After 15 min of NH₃ exposure, new absorption bands appeared at 1536 cm⁻¹ and 1694 cm⁻¹, which are attributed to L-NH₃ species and B-NH₄⁺ species, respectively. It is worth noting that the peak at 1253 cm⁻¹ may correspond to unreacted bridging nitrates.

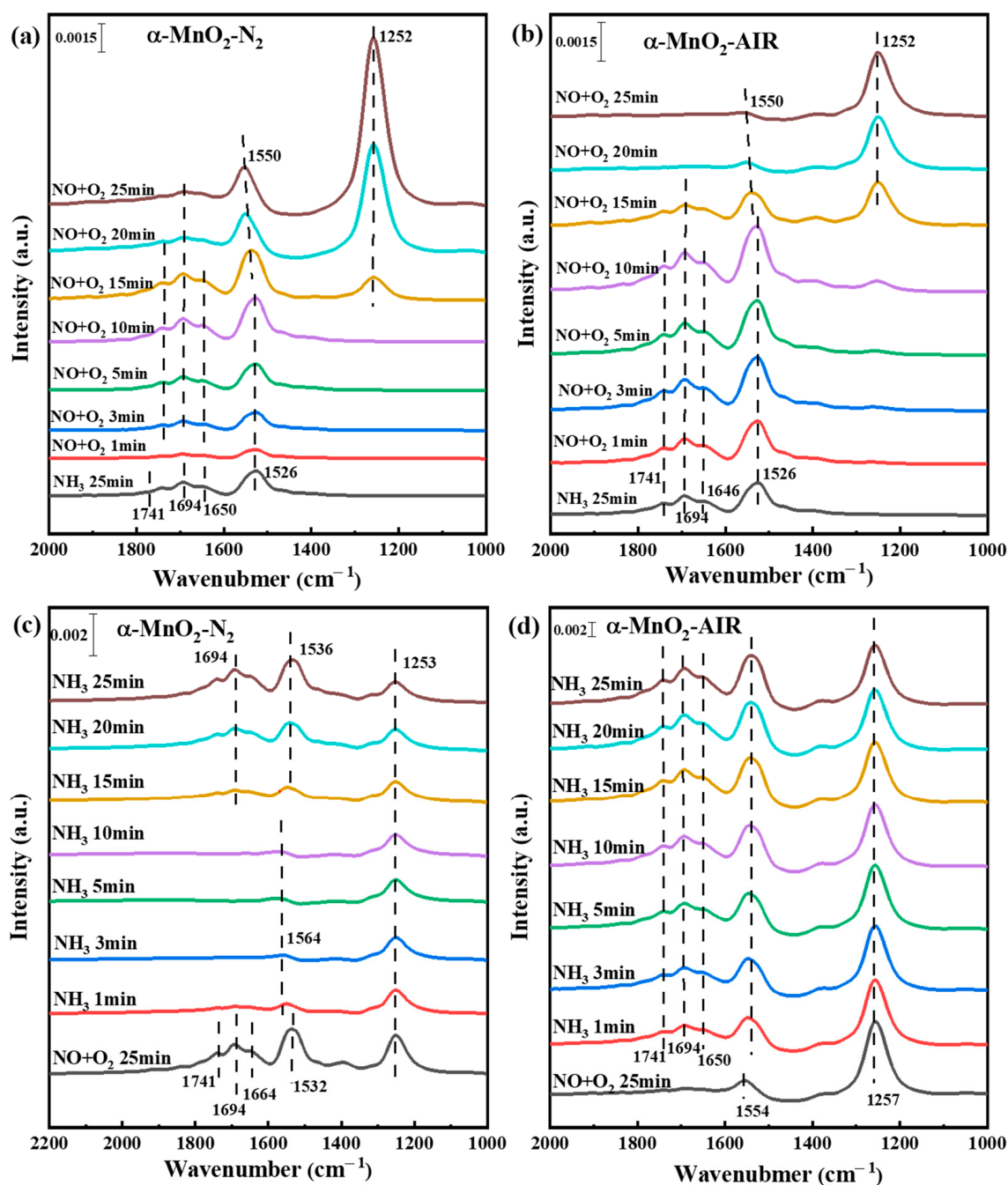


Figure 13. In situ infrared spectra of (a) $\alpha\text{-MnO}_2\text{-N}_2$ and (b) $\alpha\text{-MnO}_2\text{-AIR}$ catalysts for pre-adsorption of NH_3 and re-adsorption of $\text{NO} + \text{O}_2$ at 125°C . In situ infrared spectra of (c) $\alpha\text{-MnO}_2\text{-N}_2$ and (d) $\alpha\text{-MnO}_2\text{-AIR}$ catalysts for pre-adsorption of $\text{NO} + \text{O}_2$ and re-adsorption of NH_3 at 125°C .

As can be seen in Figure 13d, for the $\alpha\text{-MnO}_2\text{-AIR}$ catalyst, monodentate nitrates (1534 cm^{-1}), bridging nitrates (1257 , 1694 , and 1741 cm^{-1}), and nitrate ions (1397 cm^{-1}) were detected after pre-adsorbing $\text{NO} + \text{O}_2$. Upon the introduction of NH_3 , the intensities of the nitrate-related peaks at 1650 , 1694 , and 1741 cm^{-1} were enhanced within 1 min, which might be attributed to the formation of intermediate species during the reaction with NH_3 . Throughout the reaction, the band at 1257 cm^{-1} gradually decreased but remained present even after 25 min, indicating the relatively stable nature of these bridging nitrates. Both $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$ catalysts were able to adsorb and activate NO , forming nitrate species that subsequently reacted with adsorbed NH_3 . This reaction pathway follows the L-H mechanism.

During the $\text{NO} + \text{O}_2$ adsorption step, oxygen vacancy defects served as electron-rich centers, facilitating the chemisorption and oxidation of NO into nitrate and nitrate ion species. In contrast, due to the lower concentration of oxygen vacancies, the $\alpha\text{-MnO}_2\text{-AIR}$ catalyst had fewer and less active surface sites, which restricted NO adsorption and nitrate formation, thereby reducing the subsequent reactivity with NH_3 .

3. Experimental

3.1. Preparation of Catalyst

In a typical synthesis, 1.13 g of KMnO_4 and 0.47 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 72 mL of deionized water under magnetic stirring to form a homogeneous precursor solution for $\alpha\text{-MnO}_2$. After stirring for approximately 30 min, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave, sealed, and heated in an oven at 160°C for 12 h. Upon completion of the hydrothermal reaction, the autoclave was allowed to cool naturally to room temperature. The resulting precipitate was collected by filtration, thoroughly washed with deionized water and ethanol several times, and then dried at 80°C for 24 h.

Subsequently, the dried products were calcined for 1 h and 2 h in N_2/AIR atmospheres at different temperatures (300°C and 400°C) to introduce oxygen vacancies, thereby obtaining $\alpha\text{-MnO}_2$ catalysts with different oxygen vacancy concentrations, denoted as “ $\alpha\text{-MnO}_2\text{-}400^\circ\text{C-2 h-N}_2$ ”, “ $\alpha\text{-MnO}_2\text{-}400^\circ\text{C-2 h-AIR}$ ”, “ $\alpha\text{-MnO}_2\text{-}300^\circ\text{C-1 h-N}_2$ ” and “ $\alpha\text{-MnO}_2\text{-}300^\circ\text{C-1 h-AIR}$ ”. Preliminary $\text{NH}_3\text{-SCR}$ activity tests showed that variations in temperature and calcination time had relatively minor effects within the studied range, whereas the calcination atmosphere significantly influenced NO conversion performance. In particular, $\alpha\text{-MnO}_2\text{-}400^\circ\text{C-2 h-N}_2$ exhibited substantially higher catalytic activity than its air-calcined counterpart. Based on this result, $\alpha\text{-MnO}_2\text{-}400^\circ\text{C-2 h-N}_2$ and $\alpha\text{-MnO}_2\text{-}400^\circ\text{C-2 h-AIR}$ were selected for in-depth characterization and analysis of oxygen vacancy-related properties and are hereafter referred to as $\alpha\text{-MnO}_2\text{-N}_2$ and $\alpha\text{-MnO}_2\text{-AIR}$, respectively.

3.2. Catalyst Characterization

The crystal structure and phase composition of the synthesized catalysts were identified with X-ray diffraction (XRD) using a Bruker AXS D8 diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) (Bruker, Billerica, MA, USA). Measurements were conducted under an operating voltage of 40 kV and a tube current of 40 mA. The oxygen vacancy defects of the catalyst were detected using electron paramagnetic resonance (EPR). This detection was carried out on a continuous wave spectrometer at 9.4 GHz (X-band, Bruker ESP-300, EMX-10/12, Bruker, Billerica, MA, USA).

To examine the morphology and lattice structures, transmission electron microscopy (TEM) analysis was carried out on a JEOL JEM-2100F microscope (JEOL, Tokyo, Japan). Surface elemental distribution was investigated using scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS), performed on a ZEISS Gemini 300 (ZEISS, Jena, Germany). Prior to SEM observation, all samples were sputter-coated with a thin gold layer under vacuum to improve conductivity and image resolution. Textural properties, including specific surface area and pore volume, were determined with nitrogen adsorption–desorption isotherms using the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2460 system (Micromeritics, Norcross, GA, USA).

The surface chemical states and elemental composition were analyzed with X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha instrument (Thermo Fisher Scientific, Waltham, MA, USA). To probe surface acidity, temperature-programmed desorption of ammonia ($\text{NH}_3\text{-TPD}$) was conducted with a Thermo Fisher Scientific Antaris IGS gas analyzer (Thermo Fisher Scientific, Waltham, MA, USA). In each test, 0.1 g of

sample was saturated with NH_3 at 30 °C, followed by heating to 800 °C while monitoring the desorbed NH_3 signal. Hydrogen temperature-programmed reduction (H_2 -TPR) measurements were performed on a Chembet Pulsar TPR/TPD apparatus (Anton Paar, Graz, Austria). Each run used 0.1 g of catalyst placed in a U-shaped quartz reactor. Samples were first pretreated in an argon atmosphere at 300 °C for 1 h (flow rate: 50 mL/min), cooled to room temperature, and then heated to 800 °C under a reducing gas stream consisting of 10 vol% H_2 in Ar at the same flow rate.

In situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS) experiments were conducted using a Nicolet IS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), covering a spectral range of 650–4500 cm^{-1} . Catalysts were pretreated in flowing air at 400 °C for 30 min to remove surface impurities and moisture, followed by background collection under N_2 at 250 °C. Subsequently, spectra were recorded under NH_3/N_2 and $\text{NO} + \text{O}_2/\text{N}_2$ atmospheres to investigate surface intermediates and reaction mechanisms associated with the NH_3 -SCR process.

3.3. Catalyst Activity Tests

The catalytic performance for NH_3 -SCR of NO_x was evaluated using a fixed-bed quartz reactor. The reaction temperature varied between 100 °C and 300 °C, with the gas hourly space velocity (GHSV) maintained at 30,000 h^{-1} . The feed gas consisted of 500 ppm NH_3 , 500 ppm NO , and 5 vol% O_2 , balanced with nitrogen. The composition of the outlet gases was monitored using instruments from Thermo Fisher Scientific and the Antaris IGS system (Waltham, MA, USA). The NO conversion efficiency and N_2 selectivity were calculated using the following equations in terms of the Chinese standard (GB/T 38219–2019) [44]:

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

$$\text{N}_2 \text{ selectivity (\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% \quad (2)$$

Here, $[\text{NO}]_{\text{in}}$ and $[\text{NO}]_{\text{out}}$ represent the NO content of the gas introduced into the reactor and at the reactor outlet; $[\text{NH}_3]_{\text{in}}$ and $[\text{NH}_3]_{\text{out}}$ are the NH_3 contents introduced into the reactor and the tail gas at the reactor outlet, respectively; and $[\text{N}_2\text{O}]_{\text{out}}$ represents the N_2O content in the tail gas at the reactor outlet, with the unit being ppm.

3.4. Density Functional Theory (DFT) Calculations

All DFT calculations in this paper are performed using the Cambridge Sequential Total Energy Package (CASTEP) program of Materials Studio 8.0 software, which is a quantum mechanical program based on density functional theory. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) method is used to exchange correlation functional. The projector enhanced wave (PAW) method represents the interaction between the core and valence electrons. Cut-off energy is set at 400 eV. The $2 \times 2 \times 1$ Monkhorst Pack grid is used to precisely select the region integral. The self-consistent field (SCF) collection tolerance is set to 10^{-5} eV, and the maximum force tolerance for structural optimization is set to 0.05 eV/Å. The vacuum area is set to 15 Å to avoid interaction between periodic plates.

The oxygen vacancy calculation model is used to remove one oxygen atom from the complete surface structure, labeled Vo. The difficulty of oxygen vacancy formation is measured by oxygen vacancy formation energy, which is defined as follows [45]:

$$-E_f = E_{\text{surface}} - (E_{\text{defect}} + E_o) \quad (3)$$

$E_{surface}$ and E_{defect} represent the total energies of the complete and defective surfaces, respectively, and E_0 represents the atomic energy of an O_2 molecule.

In order to study the stability of NH_3 and NO on the catalyst surface, the adsorption strength of the catalyst during the adsorption process was calculated using the following formula [46]:

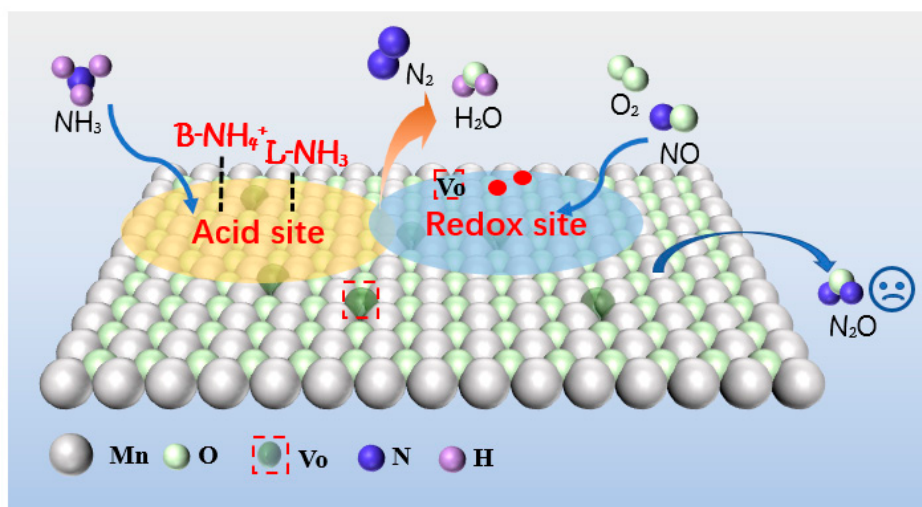
$$E_{ads} = E_{slab+molecule} - E_{slab} - E_{molecule} \quad (4)$$

where $E_{slab+molecule}$ is the total energy of the surface and adsorbent, and E_{slab} and $E_{molecule}$ are the energy of the surface and the energy of the adsorbent molecules, respectively.

4. Reaction Mechanism over Catalysts

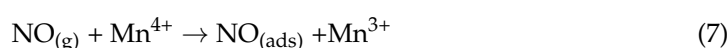
As mentioned earlier, oxygen vacancy defects play an important role in the apparent physicochemical properties of MnO_2 catalysts and the reaction mechanism of NH_3 -SCR. The abundant oxygen vacancies in α - MnO_2 - N_2 significantly enhance its redox properties and surface acidity, thereby improving the adsorption and activation of both NH_3 and NO . This leads to the formation of more reactive nitrate intermediates and ultimately results in superior catalytic performance, especially at low to medium temperatures.

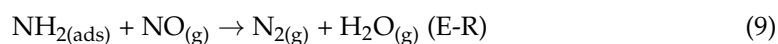
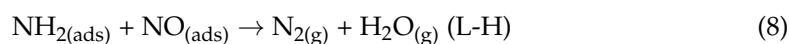
The proposed reaction mechanism is illustrated in Scheme 1. In the acid cycle, NH_3 adsorbs onto both Lewis and Brønsted acid sites. Oxygen vacancies facilitate this process by increasing the number of active adsorption sites and promoting the formation of $-NH_2$ intermediates via hydrogen abstraction. In the redox cycle, oxygen vacancies promote the adsorption and dissociation of O_2 , provide active surface oxygen (O_α), and facilitate the cycle process of Mn^{3+}/Mn^{4+} .



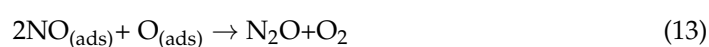
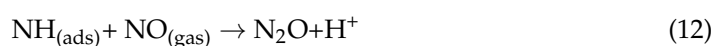
Scheme 1. Mechanism models for NH_3 -SCR reaction on MnO_2 catalysts.

In situ DRIFTS analysis reveals that surface reactions on both catalysts follow a combination of E-R and L-H mechanisms. NH_3 molecules are activated at oxygen vacancy sites through electron transfer, forming $-NH_2$ species and reducing Mn^{4+} to Mn^{3+} . These intermediates then react with NO (either gaseous or adsorbed), producing nitrates that decompose into N_2 and H_2O . Meanwhile, O_2 is dissociated at vacancy sites to regenerate Mn^{4+} and replenish surface oxygen. The main reaction equations are as follows:





MnO₂ catalysts exhibit excellent low-temperature activity in the NH₃-SCR reaction, and the strong oxidizing ability of Mn⁴⁺ species can easily trigger side reactions, leading to the formation of N₂O as a by-product. This phenomenon becomes more pronounced at medium to high temperatures or under excess O₂ conditions. Moreover, NO may also directly participate in the formation of N₂O under the influence of highly oxidized Mn species or surface-active oxygen species.



5. Conclusions

This study systematically investigated the influence of oxygen vacancy regulation on the low-temperature NH₃-SCR performance and reaction mechanism over α-MnO₂ catalysts. Through catalyst synthesis, characterization, performance evaluation, and DFT computational analysis, the following key conclusions can be drawn:

1. Oxygen vacancies play a crucial role in the surface properties and catalytic performance of α-MnO₂. Compared to the α-MnO₂-AIR catalyst, the oxygen vacancy-rich α-MnO₂-N₂ catalyst exhibits stronger acidity, enhanced redox properties, and significantly improved NH₃ and NO adsorption and activation capabilities. The presence of oxygen vacancies facilitates NH₃ adsorption on both Lewis and Brønsted acid sites and promotes the formation of -NH₂ intermediates via hydrogen abstraction. Additionally, oxygen vacancies enhance the adsorption and oxidation of NO, leading to the formation of nitrate intermediates that subsequently react with adsorbed NH₃ to yield N₂ and H₂O. These synergistic effects lead to a significant improvement in low- and medium-temperature NO_x conversion efficiency.
2. The NH₃-SCR reaction over α-MnO₂ follows a dual-pathway mechanism involving both E-R and L-H routes. In situ DRIFTS analyses revealed that the α-MnO₂-N₂ exhibits stronger and more sustained formation of key intermediates, including L-NH₃, B-NH₄⁺, and nitrate species, indicating a stronger ability to activate and convert reactants via both mechanisms. Notably, NO preferentially reacted with surface-adsorbed NH₃ species before being chemisorbed, following the E-R mechanism. Conversely, when NO was pre-adsorbed, its subsequent reaction with NH₃ followed a typical L-H pathway, in which bridging and monodentate nitrates played a key role. Oxygen vacancies were found to be essential in both cases for promoting NO oxidation, intermediate formation, and final N₂ generation.

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Conflicts of Interest: The authors declare no conflicts of interest.

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