

Study on low-temperature NH_3 -SCR denitration mechanism of biochar-supported Mn-Cu-Nb catalyst

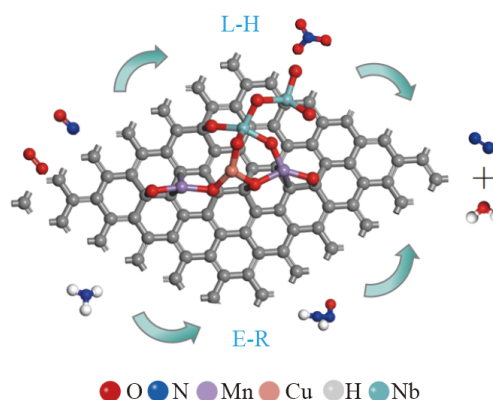
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Abstract: Under the context of global energy transition and carbon neutrality, controlling nitrogen oxide (NO_x) emissions from biomass combustion is of great significance, and the development of high-efficiency low-temperature catalysts has become a current research focus. In this study, Nb was used to dope and modify the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ catalyst to construct the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$ system. The doping amount was optimized through selective catalytic reduction (SCR) activity tests. The reaction mechanism was explored by combining *in situ* DRIFTS and density functional theory (DFT) simulations. Experimental findings revealed that the catalyst doped with 0.05% Nb achieved the optimal performance, sustaining a NO conversion efficiency of $\geq 94\%$ within the temperature window of 150–275 °C while demonstrating improved resistance to alkali metal K poisoning. Mechanistic analyses showed that at low temperatures, the catalyst facilitated the SCR reaction *via* both the Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) pathways, with the synergistic interaction between multiple active sites driving the efficient conversion of NH_3 and NO. DFT calculations further confirmed that both pathways had the characteristics of low reaction energy barriers and significant exothermicity, ensuring the high activity and feasibility of the low-temperature reaction. The findings provided foundational theoretical support for the design of Nb-doped Mn-Cu-supported catalysts and the exploration of the underlying working mechanisms.

Key words: low-temperature NH_3 -SCR catalyst; selective catalytic reduction; $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$; DFT calculation; reaction mechanism



The accelerated global industrialization has driven the growth of energy consumption. Under the dual pressures of addressing climate change and advancing energy transition, the efficient utilization of renewable energy has become a crucial breakthrough. As a carbon-neutral energy source, biomass energy has attracted considerable attention in recent years^[1–3]. However, the combustion of biomass is accompanied by a significant release of nitrogen oxides (NO_x), primarily due to the characteristics such as inherent nitrogen content (e.g. in proteins and amino acids) and high volatile matters. These emissions pose considerable risks of air pollution and ecological damage^[4–5]. Controlling NO_x emissions from biomass combustion holds significant practical importance. Among existing denitrification

technologies, NH_3 -SCR (NH_3 -selective catalytic reduction) has become the mainstream solution due to the high efficiency^[6–7]. Commercial vanadium-based catalysts dominate the major market by virtue of the excellent N_2 selectivity, thermal stability and sulfur resistance^[8–9], yet the application has obvious drawbacks including relatively narrow active temperature window, high light-off temperature and the potential biotoxicity of vanadium, which may cause secondary pollution^[10–11]. To address the low-temperature nature of biomass flue gas, the development of novel, high-performance and eco-friendly low-temperature SCR catalysts has emerged as a pivotal focus.

Over the past few years, biochar-based supports have

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emerged thanks to their significant cost advantages, environmentally friendly properties and potential for low-temperature denitrification^[12–13]. The performance advantages stem from a dual mechanism: (1) the well-developed hierarchical pore structure provides physical support for the uniform dispersion of active components and gas mass transfer; (2) carboxyl, phenolic hydroxyl and other surface functional groups endow intrinsic catalytic ability by providing active sites^[14]. However, the denitrification efficiency of pure biochar-based supports is relatively low, with NO conversion generally below 10%^[15]. A study by Liu et al.^[16] demonstrated that unmodified coconut shell activated carbon showed weak denitrification activity at the low temperature of 150 °C, where NO conversion was only 7.3%. Nevertheless, after loading active components such as transition metals, the activity was significantly enhanced. This was mainly attributed to the electron transfer effect between the carbon-based support and active components, as well as the synergistic catalytic system formed by metal-organic coordination.

Studies have shown that single-component biochar-supported catalysts have obvious limitations in denitrification applications, including poor low-temperature activity, inferior hydrothermal stability and insufficient tolerance to water and sulfur^[17]. To overcome these technical bottlenecks, researchers have focused on developing biochar-based catalysts with the synergistic effect of multi-component active species in recent years. Through the interaction between different elements, we can effectively regulate the material's microstructure and create more active sites, thereby significantly improving the catalytic performance.

Manganese (Mn) often serves as the main active component due to the special electronic structure and multivalent properties, which endow it excellent redox performance under low-temperature^[18–19]. Meanwhile, rare earth metal cerium (Ce) is frequently introduced as a high-efficiency promoter due to the unique dynamic oxygen storage capacity and reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple^[20]. Researches have demonstrated that biochar-based composite catalysts outperform single-component systems in terms of comprehensive performance. For example, the Mn-Ce/BC catalyst developed by Yang et al.^[21] achieved a NO removal efficiency of 99.2% at 175 °C, notably exceeding that of single-component catalysts. This was attributed to the efficient oxygen migration mechanism between Mn and Ce. Similarly, the Mn-Ce/BCN catalyst prepared by Jiang et al.^[22] exhibited stronger sulfur and water resistance. Under the same loading of 10%, the stability was significantly improved compared to the single-component Mn/BCN catalyst. Studies have revealed that other transition metal elements—beyond cerium (Ce)—can remarkably improve the denitrification performance of the Mn/BC catalyst. Our team fabricated the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ catalyst through ultrasonic-assisted impregnation method which exhibited over 85% NO conversion even at the temperature of 150 °C^[23]. However, in the practical biomass

flue gas treatment, the aforementioned catalysts still face notable difficulties, in particular, improving the tolerance to alkali metal (such as K, Na) poisoning.

Based on previous work of the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ catalyst, our group designed a novel ternary $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$ composite by introducing niobium (Nb) as structural and electronic regulator due to the ability to enhance redox behavior, strengthen surface acidity and improve resistance to alkali metals^[24]—all essential for low-temperature SCR under biomass flue gas conditions. This strategy aligned with recent advances in Nb-modified catalysts i.e. Li et al.^[25] demonstrated that Nb-induced Ce–O–Nb bonds in CeVO_4 increased the surface active oxygen and oxygen vacancies, synergistically boosting the acidity and oxidation ability to achieve over 90% NO conversion between 210–420 °C while suppressing the non-selective NH_3 oxidation. Similarly, Wang et al.^[26] observed that Nb doping in $\text{Zr}_5\text{W}_1\text{O}_x$ broadened the high-temperature activity window by ~30 °C *via* strengthening the medium-strong acid sites for improved NH_3 adsorption. Cao et al.^[27] replaced W with Nb to form VNbTi catalysts, which exhibited enhanced KCl tolerance due to electronic modulation that inhibited the stable nitrate/nitrite formation. These studies underscored the Nb's multifunctional role in promoting SCR performance under challenging conditions. However, the fundamental mechanisms governing its function in biochar-supported Mn-Cu systems remain unexplored. Specifically, the role of Nb in regulating reactant adsorption, intermediate evolution and reaction pathway within the unique low-temperature window of $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$ represents a critical knowledge gap. To address this, we employed an integrated multiscale approach combining *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with density functional theory (DFT) calculations which enabled real-time monitoring of surface intermediate dynamics while providing atomic-level insights into Nb-modulated NH_3/NO adsorption behavior and the formation/decomposition pathways of key species such as NH_2NO and nitrate adsorbates. By fundamentally understanding how Nb enhances both Eley-Rideal and Langmuir-Hinshelwood mechanisms through electronic and structural regulation, this work establishes new design principles for high-performance, alkali-resistant SCR catalysts for biomass flue gas treatment.

1 Experimental

1.1 Catalysts preparation

Support preparation: In this study, coconut shell biomass carbon (BC) served as the base material for the catalyst support. Firstly, raw coconut shells were crushed to a 20–40 mesh, rinsed repeatedly with deionized water to eliminate impurities and then dried in 80 °C. To enhance the support's surface properties, BC was modified with nitric acid

solution: pretreated BC was immersed in a 20% nitric acid solution and stirred continuously for 4 h in 80 °C. Once the reaction was finished, the mixture was filtrated. The obtained solid was rinsed repeatedly with deionized water till neutrality. Ultimately, the sample was dried at 105 °C for 12 h, yielding the modified biomass carbon support (BCN).

Fresh catalyst preparation: One-step impregnation method was employed to synthesize the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ and the Nb-doped catalysts ($\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$, where $x = 0.03\% \text{--} 0.20\%$). For $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ preparation: $\text{Mn}(\text{NO}_3)_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in deionized water with a stoichiometric ratio of Mn to Cu of 7:3, ensuring a total active component loading of 10%. Then, the pretreated BCN support (specific surface area of 799.1 m^2/g) was introduced into the solution. After ultrasonically dispersing the mixture for 30 min at ambient temperature, it was transferred to an oil bath at 80 °C and stirred magnetically for 4 h. The produced sample underwent a drying process at 105 °C for 12 h and subsequently calcination at 400 °C for 4 h in nitrogen environment. For the Nb-doped samples, a stoichiometric amount of NbCl_5 ($x = 0.03\%, 0.05\%, 0.07\%, 0.1\%$ and 0.2%) was added simultaneously when preparing the impregnation solution. The rest of the preparation process remained unchanged. All catalysts were prepared using BCN supports from the same batch to ensure the consistency in specific surface area.

K-poisoned catalysts preparation: To evaluate the alkali metal (K) resistance of the catalysts, K-poisoned catalysts were prepared *via* wet impregnation using KNO_3 as precursor for alkali metal oxide (K_2O): firstly, quantitative amount of KNO_3 was fully dissolved in deionized water to form solution. The mass of KNO_3 was based on the 2% K_2O loading. Then, calculated amounts of fresh $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ and $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalysts were added. The mixture was placed in an ultrasonic disperser for 30 min. The mixture was thus stirred at ambient temperature for 4 h to form a “paste-like slurry,” which was then dried at 105 °C for 12 h. Finally, the samples were calcined at 400 °C for 4 h under nitrogen atmosphere, yielding the K-poisoned catalysts which designated as $\text{Mn}_7\text{-Cu}_3/\text{BCN-K}$ and $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN-K}$, respectively.

1.2 Evaluation of catalyst denitrification performance

A fixed-bed reactor was used to evaluate the catalysts' denitrification performance (Figure 1). The system comprised three modules: gas supply, catalytic reaction and flue gas analysis module. Simulated flue gas was configured as follows: 5.0×10^{-4} of NO, 3% of O_2 and N_2 as the balance gas, with a total flow rate of 1 L/min. The simulated flue gas and reduction agent (5.0×10^{-4} of NH_3) were co-introduced into the reactor (loaded with a specified amount of catalyst) to initiate the reaction. An intelligent temperature control system was used to regulate the reaction temperature with 9 gradients (25 °C intervals) spanning

75–275 °C. Flue gas was analyzed in real time on Testo 350. All experimental data were the average values of three independent repeated experiments to ensure the reliability. A device was installed at the outlet to treat the unreacted NO and NH_3 , minimizing environmental pollution.

In the process of catalyst denitration activity test, NO conversion was calculated by Equation (1):

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

In the formula, “in” and “out” stand for the inlet and outlet gas concentrations under steady-state conditions, respectively.

1.3 Catalysts characterization and DFT calculation

In situ DRIFTS Analysis: The analysis was conducted using a Bruker 80 V Fourier transform infrared (FT-IR) spectrometer equipped with N_2 -cooled mercury-cadmium-telluride (MCT) detector, temperature-controlled *in situ* reaction cell and appropriate diffuse reflectance elements. Before tests, specific quantity of catalyst powder was placed in the reaction cell and heated to 300 °C to eliminate any impurities. N_2 was subsequently introduced to cool the reaction chamber. Then, the target gases were injected, where real-time spectra were collected with a total of 32 scans and a 4 cm^{-1} resolution.

Density Functional Theory (DFT): Using Materials Studio's Dmol 3 module^[28], the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ microstructural model was constructed and geometrically optimized to a stable state. In calculations, the Local Density Approximation (LDA) addressed electron correlation energy, while the Double Numerical Plus Polarization (DNP) basis set described valence electrons. Geometric optimization convergence criteria were defined as: electron density difference $< 1 \times 10^{-5}$ Hartree/ $\text{\AA}^3$, maximum nuclear force $< 1 \times 10^{-3}$ Hartree/ $\text{\AA}$ and maximum nuclear displacement $< 1 \times 10^{-3}$ $\text{\AA}$.

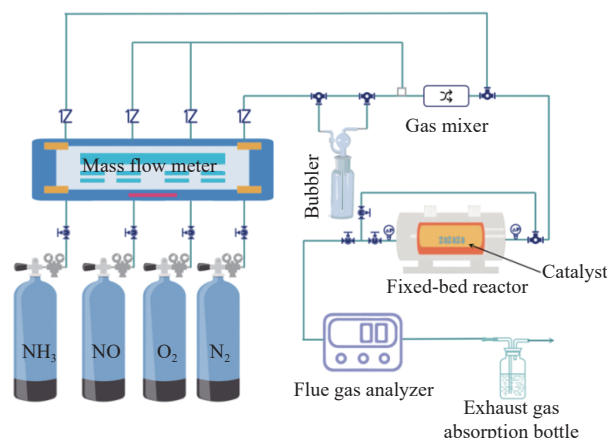


Fig. 1 Schematic diagram of the catalyst performance evaluation device

The denitrification reaction involved three key energy-related parameters to quantify critical reaction characteristics: adsorption stability, reaction initiation difficulty and energy change before and after the reaction. These parameters were calculated *via* specific formulas as shown in Equations (2), (3) and (4), respectively:

$$E_{\text{ad}} = E_{\text{slab+molecule}} - E_{\text{slab}} - E_{\text{molecule}} \quad (2)$$

in which E_{ad} represented the adsorption energy; $E_{\text{slab+molecule}}$ denoted the total energy of the molecule and the catalyst after adsorption; E_{slab} stand for the energy of the catalyst support before adsorption.

$$E_{\text{a}} = E_{\text{TS}} - E_{\text{IM}} \quad (3)$$

In the formula, E_{a} referred to the energy barrier; E_{TS} denoted the transition state energy; E_{IM} stand for the energy of the reactants' initial state.

$$E_{\text{r}} = E_{\text{products}} - E_{\text{reactants}} \quad (4)$$

in which E_{r} referred to the reaction energy; E_{products} denoted the total energy of all product species after the elementary reaction; $E_{\text{reactants}}$ stand for the total energy of all reactant species before elementary reaction.

2 Results and discussion

2.1 Analysis of catalyst active component content

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the loadings of Mn, Cu and Nb in the catalysts with different Nb dopings (Table 1). The total contents of Mn and Cu in all samples were maintained at 10% (Mn:Cu = 7:3), while the Nb doping amounts were within the target range (0.03%–0.20%). The deviation between the actual and the theoretical values was less than 5%, suggesting that the introduction of Nb had no significant impact on the loading efficiency of the Mn and Cu active components. This ruled out the interference of variations in total active component content on catalytic performance, thereby effectively confirming that differences in catalytic performance were primarily driven by Nb doping.

Table 1 Contents of active components in the catalysts with different amounts of Nb

Catalyst	w/%		
	Mn	Cu	Nb
Mn ₇ -Cu ₃ /BCN	7.01	2.98	—
Mn ₇ -Cu ₃ -Nb _{0.03} /BCN	7.02	2.97	0.031
Mn ₇ -Cu ₃ -Nb _{0.05} /BCN	6.99	2.99	0.052
Mn ₇ -Cu ₃ -Nb _{0.07} /BCN	6.98	3.01	0.071
Mn ₇ -Cu ₃ -Nb _{0.1} /BCN	7.01	2.99	0.103
Mn ₇ -Cu ₃ -Nb _{0.2} /BCN	6.99	2.98	0.203
Theoretical value	7.00	3.0	0.03–0.20

2.2 Evaluation of catalyst performance

Mn₇-Cu₃/BCN was used as reference to examine the influence of Nb amounts on the denitrification performance (Figure 2). The results indicated that the pure Nb sample (10%) had poor catalytic activity, with NO conversion below 30% across all tested temperatures. When Nb doping was 0.03%, Mn₇-Cu₃-Nb_{0.03}/BCN exhibited a 0.4%–2.2% higher NO conversion at the temperatures ≤ 125 °C, but a lower value at the temperatures > 125 °C. Importantly, the catalyst showed optimal wide-temperature activity when Nb doping was 0.05%, with NO conversion of 94.2% at 150 °C. However, the activity declined when Nb doping exceeded 0.05%. Specifically, at 0.07% Nb, the activity in the range of 75–275 °C was lower than that of the Nb-free sample, likely because excessive Nb covered the active sites. As Nb doping further increased to 0.1%–0.2%, the activity continued to decrease, with a more significant drop at the temperatures below 175 °C.

Figure 3 presented a comparison of NO conversion between two K-poisoned catalysts: Mn₇-Cu₃/BCN-K and Mn₇-Cu₃-Nb_{0.05}/BCN-K. The findings showed that after K poisoning, the activity of Mn₇-Cu₃/BCN decreased to varying degrees across all tested temperatures. Notably, in the range of 75–175 °C, the NO conversion fell by more than 10%, with the sharpest decline at 125 °C (a 21.2% drop). The results demonstrated that K poisoning significantly suppressed the denitrification performance of Mn₇-Cu₃/BCN which was more pronounced in the low-temperature region (<175 °C). This could be explained by K species preferentially interacting with Mn active sites—given that Mn sites usually had superior catalytic activity under low-temperature. On the other hand, while the Mn₇-Cu₃-Nb_{0.05}/BCN catalyst also lost activity after K poisoning, the deactivation was primarily in temperatures below 150 °C, and the activity attenuation was milder under identical poisoning conditions.

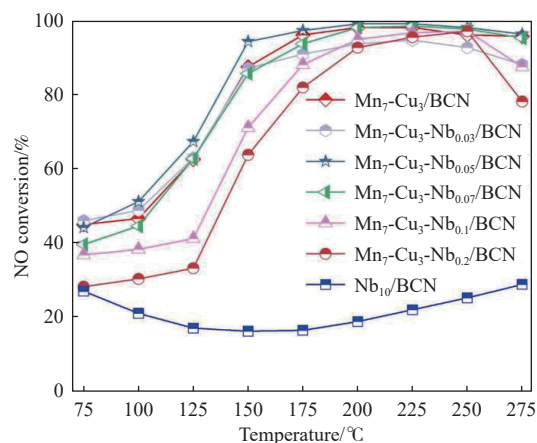


Fig. 2 Influence of Nb amounts on the NO conversion of Mn₇-Cu₃-Nb_x/BCN catalysts

Note: The pure Nb sample (10%) served as control for the maximum concentration of Nb alone to assess the intrinsic activity of elemental Nb, not the actual doping ratio.

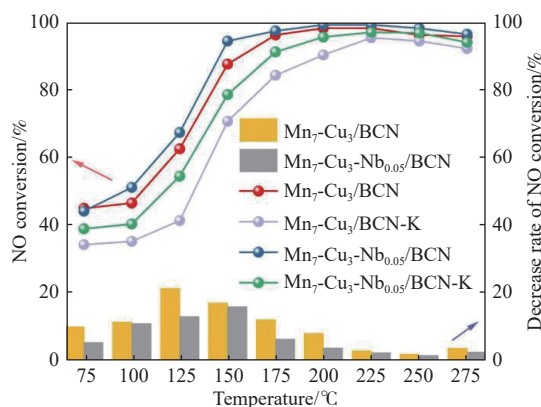


Fig. 3 K poisoning resistance of $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ and $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$

This comparison clearly verified that Nb doping could effectively improve the K poisoning resistance of $\text{Mn}_7\text{-Cu}_3/\text{BCN}$, offering key support for its practical use in alkali metal-containing flue gas environments. It was worth noting that the K-poisoning mechanism (including BET surface area and NH_3 -TPD analysis of surface acidity) had been investigated in our previous work^[29]. These results confirmed that the deactivation of $\text{Mn}_7\text{-Cu}_3/\text{BCN-K}$ primarily stemmed from the chemical neutralization of acid sites associated with Mn species and physical pore blockage—further validating that Nb doping mitigated K-induced damage by protecting Mn-related acid sites and active centers.

Comprehensive analysis indicated that doping the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ catalyst with appropriate amount of Nb (0.05%) could boost both denitrification performance and resistance to K poisoning. The K-poisoning activity test here primarily served to highlight the performance robustness of the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst, thereby justifying its selection as the optimal catalyst in this study and laying a foundational basis for the subsequent investigation into the intrinsic low-temperature NH_3 -SCR denitration mechanism.

2.3 In situ infrared spectroscopy characterization

2.3.1 Transient reaction between $\text{NO}+\text{O}_2$ and preadsorbed NH_3

According to the denitrification activity test results, the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst exhibited the highest NO conversion efficiency at 225 °C. So, this temperature was chosen for mechanism study. The catalyst pretreatment procedure was as follows: 50 mg of the sample was placed in the *in situ* cell, heated to 300 °C at 10 °C/min under N_2 (flow rate of 100 mL/min) and subjected to purging for 1 h. Subsequently, the temperature was reduced to 225 °C. N_2 purging was maintained for 30 min to eliminate impurities, during which the background spectrum was recorded.

Once the system was stabilized, a 1.0×10^{-3} NH_3/N_2 gas mixture (flow rate: 100 mL/min) was switched and

saturated adsorption was performed at 225 °C for 60 min. The spectra with background subtraction were presented in Figure 4. After NH_3 was introduced for 2 min, a weakly adsorption peak firstly appeared at 1344 cm^{-1} . The peak, corresponding to the characteristic absorption of $-\text{NH}_2$ species formed on Lewis acid sites^[30], maintained stable throughout the adsorption process. As demonstrated in previous studies, NH_3 activation was the rate-limiting step in the NH_3 -SCR reaction. The rapid formation of $-\text{NH}_2$ on the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst indicated that NH_3 was more easily activated, which was conducive to enhance the reaction rate. Furthermore, the existence of the active intermediate $-\text{NH}_2$ provided effective evidence that NH_3 adsorption and activation proceeded in tandem. After NH_3 was introduced for 5 min, distinct characteristic peaks of NH_4^+ species became visible at 1740 and 1415 cm^{-1} . These peaks were associated with the symmetric and asymmetric bending modes of NH_4^+ bound to Brønsted acid sites^[31–32]. As NH_3 flow continued, additional peaks emerged at 3333 and 1625 cm^{-1} at time of 15 min. The peak at 3333 cm^{-1} was attributed to the N–H vibrational mode of coordinated NH_3 molecules^[33], whereas the band at 1625 cm^{-1} corresponded to the combined symmetric and asymmetric bending vibrations of ammonia coordinated to Lewis acid sites^[34]. The intensities of the above mentioned peaks increased as adsorption time extended, and all peak intensities stabilized after 50 min—an indication that the system had reached adsorption saturation. In summary, NH_3 existed primarily as coordinated NH_3 and NH_4^+ on the surface of the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst. This observation confirmed the Lewis and Brønsted acid sites on the catalyst surface. Meanwhile, the rapid generation of the active intermediate $-\text{NH}_2$ significantly promoted the NH_3 activation efficiency, laying a foundation for the efficient advancement of the NH_3 -SCR reaction.

Figure 5 illustrated the spectra of the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst during the reaction of pre-adsorbed NH_3 with $\text{NO} + \text{O}_2$. The results demonstrated that after saturated NH_3 pre-adsorption, the adsorbed species did not completely disappear following N_2 purging—only a slight reduction in peak intensity was observed.

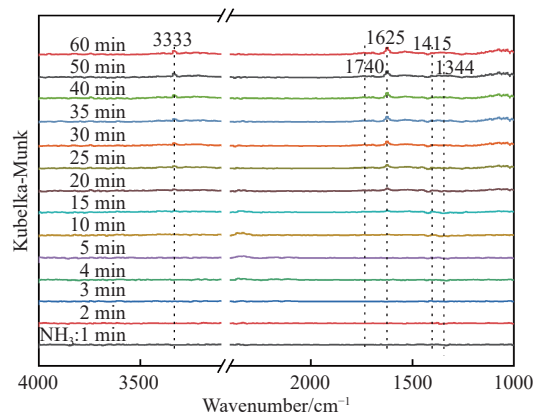


Fig. 4 *In situ* DRIFT spectra of $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst pre-adsorbed with NH_3 at 225 °C

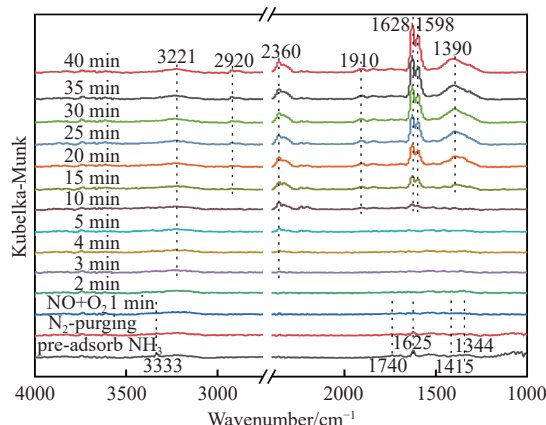
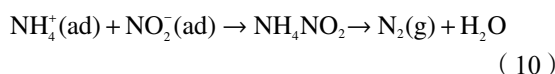
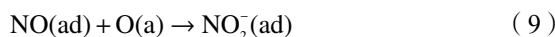
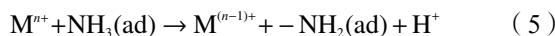


Fig. 5 *In situ* DRIFT spectra of the transient reaction of NO+O₂ with pre-adsorbed NH₃ at 225 °C

When a gas mixture of 1.0×10^{-3} NO + 3% O₂ was introduced for 1 min, the peaks initially located at 1740, 1415 and 1344 cm⁻¹ completely vanished. This indicated that the NH₄⁺ species and the active intermediate (-NH₂) exhibited high reactivity, which enabled rapid reaction with NO and thereby effectively enhanced the Eley-Rideal (E-R) mechanism. By the second minute of the reaction, the N-H vibrational peaks at 3333 and 1361 cm⁻¹ (assigned to NH₃ coordinated with Lewis acid sites) were fully exhausted. As the reaction continued, the peak at 1625 cm⁻¹ gradually shifted to 1628 cm⁻¹, which implied that once the coordinated NH₃ on Lewis acid sites was consumed, NO began to adsorb at these sites. Meanwhile, at time of 3 min, vibration peaks corresponding to NO-adsorbed species appeared at 3221 and 2360 cm⁻¹, confirming the initiation of NO adsorption. When the NO + O₂ mixture was continuously fed until 10 min, additional vibration peaks emerged at 1910, 1598, 1390 and 2920 cm⁻¹ and gradually increased in intensity, indicating the continuous accumulation of NO adsorption products on the catalyst surface. Collectively, these results verified that the Mn₇-Cu₃-Nb_{0.05}/BCN catalyst followed the Eley-Rideal (E-R) pathway at 225 °C. The specific reaction pathway was as follows:



2.3.2 Transient reaction between NH₃ and preabsorbed NO+O₂

In order to investigate whether the Langmuir-Hinshelwood (L-H) model dictated the NH₃-SCR process

on Mn₇-Cu₃-Nb_{0.05}/BCN catalyst, another *in situ* experiment was conducted at 225 °C with a reversed sequence of gas supply: pre-adsorption of NO + O₂ followed by the introduction of NH₃. Before the experiment, the catalyst was pretreated according to the process described in Section 2.3.1. Figure 6 displayed the *in situ* DRIFT spectra of the catalyst while pre-adsorbing NO + O₂ at 225 °C. Upon the introduction of NO + O₂ for 1 min, a faint adsorption peak was observed at 1910 cm⁻¹, maintaining a stable intensity. This peak was attributed to the vibration of NO molecules bound to Cu²⁺ sites^[35]. After feeding NO + O₂ for 2 min, a stretching vibration peak corresponding to C≡N coordinated with NO appeared at 2360 cm⁻¹. This vibration peak gradually increased as NO + O₂ supply continued which reached maximum at 10 min. Meanwhile, at 3 min, vibration peaks associated with bridged nitrate and bidentate nitrate species were observed at 1628 and 1598 cm⁻¹, respectively. This phenomenon indicated that part of the unstable NO species gradually converted into more stable forms. At 10 min, vibration peaks of nitrate species in different oxidation states appeared at 2917, 1361 and 1755 cm⁻¹, which were attributed to saturated alkyl groups, *cis*-N₂O₂²⁻^[38] and N₂O₄^[39], respectively. When the NO + O₂ adsorption time reached 50 min, the intensities of all adsorption peaks tended to stabilize, suggesting that the catalyst achieved saturated adsorption of NO. Notably, the bridged nitrate species (at 1628 cm⁻¹) exhibited significantly superior performance in both adsorption rate and peak intensity compared to other nitrate species. This result revealed that bridged nitrate formed more easily on the catalyst surface, with the main reason being the synergistic effect of Mn-Cu bimetallic sites. This cooperative effect significantly reduced the activation energy required for the bridged adsorption of NO molecules.

A comparative analysis of the adsorption behaviors of NO and NH₃ showed that NO adsorbed more rapidly, enabling it to occupy the active sites in a shorter time. In addition, NO facilitated the formation of a wider range of nitrate species on the catalyst surface, thereby diversifying the surface reaction routes and intermediates.

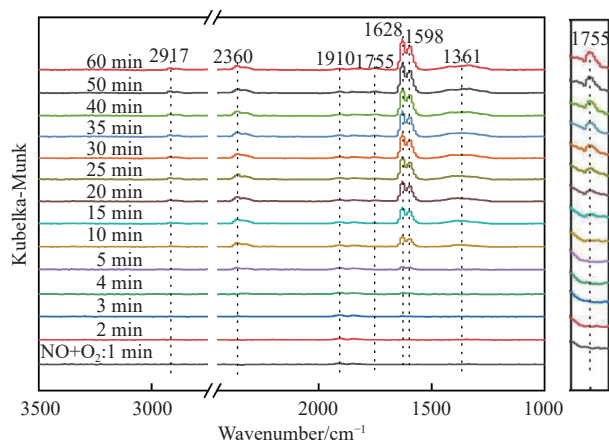


Fig. 6 *In situ* DRIFT spectra of Mn₇-Cu₃-Nb_{0.05}/BCN catalyst pre-adsorbed with NO+O₂ at 225 °C

The characteristic peak intensities associated with NO were also notably stronger than those of NH₃, suggesting that the catalyst possessed superior ability to activate NO molecules. This enhanced activation further promoted the reactivity of nitrate intermediates in the NH₃-SCR process. In summary, NO exhibited stronger coordination and oxidation capabilities on the catalyst surface. This was reflected not only in the rapid adsorption and the generation of diverse species but also in the role in optimizing the reaction pathway and improving reaction efficiency.

Figure 7 presented the spectra of the Mn₇-Cu₃-Nb_{0.05}/BCN catalyst's transient reaction with NH₃ after pre-adsorption of NO+O₂. After 30 min of N₂ purging following saturation with NO+O₂ adsorption, only the N₂O₄ species (1755 cm⁻¹) completely disappeared, while vibration peaks of other nitrate species showed varying degrees of weakening. When NH₃ was introduced for 1 min, the peaks at 2917, 2360, 1910, 1628 and 1598 cm⁻¹ all disappeared, indicating that these species were highly reactivity with NH₃. As the reaction proceeded, NH₃ adsorbed on the surface underwent reactions with specific nitrate intermediates, leading to the formation of NH₄NO₃ which either decomposed into N₂O or participated in subsequent reactions with NO to yield N₂, NO₂ and H₂O, thereby enhancing the "Fast-SCR" pathway. At 5 min, the *cis*-N₂O₂²⁻ species at 1361 cm⁻¹ was completely consumed. Notably, at time of 2 and 3 min after NH₃ introduction, *cis*-N₂O₂²⁻ species remained incompletely reacted, whereas vibration peaks emerged at 1625 cm⁻¹ (NH₃ coordinated to Lewis acid sites) and 1414 cm⁻¹ (NH₄⁺ formed by NH₃ on Brønsted acid sites). However, the peaks of these two newly emerged species showed no significant change in intensity within the first 10 min, remaining at relatively low levels. This phenomenon might stem from the transient reaction between NH₃ adsorbed species and *cis*-N₂O₂²⁻ species that occurred immediately after formed on the catalyst surface. This reaction resulted in the mutual consumption, thereby precluding any significant increase in the intensity of vibrational peaks. After 10 min reaction, characteristic peaks associated with NH₃ adsorbent species (3333, 3215, 1773 and 1342 cm⁻¹) gradually emerged and intensified over time, indicating the accumulation of NH₃ adsorbent species at the acidic sites. Based on these observations, it could be confirmed that the Mn₇-Cu₃-Nb_{0.05}/BCN catalyst simultaneously followed the Langmuir-Hinshelwood (L-H) mechanism under 225 °C. The detailed reaction pathway was described as below:

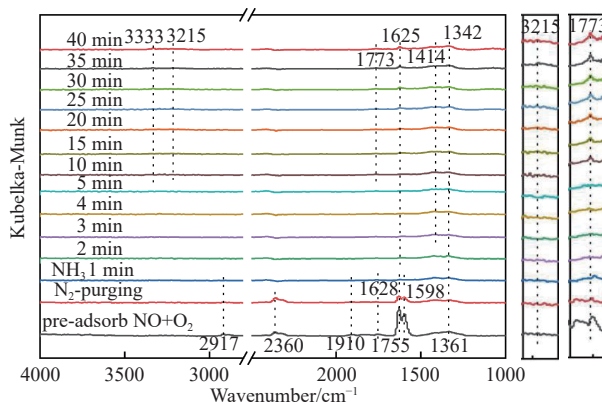
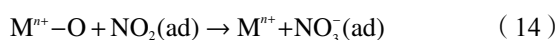
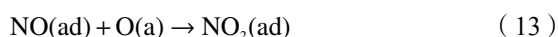
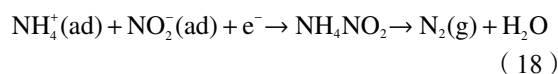
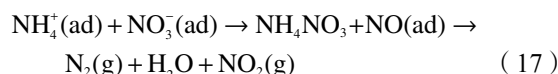
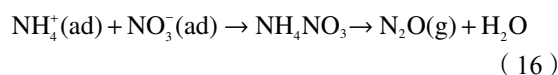


Fig. 7 *In situ* DRIFT spectra of the transient reaction of NH₃ with pre-adsorbed NO+O₂ at 225 °C



In summary, at the low temperature of 225 °C, the Mn₇-Cu₃-Nb_{0.05}/BCN catalyst operated via a E-R and L-H dual-mechanism model. This bifunctional capability enabled a synergistic conversion of NH₃ and NO, underscoring the cooperative function of multiple active sites in low-temperature SCR catalysis. Such multi-site synergy not only diversified the catalytic routes but also laid the groundwork for kinetic optimization, accentuating the catalyst's high efficiency and practical adaptability.

2.4 DFT simulation

While *in situ* DRIFT spectra significantly advanced the understanding of denitration mechanisms over carbon-supported catalysts, key nuances regarding the mechanistic details remain unresolved. These included how active components form functional sites on the support, the preferential configuration and site selection of adsorbing reactant molecules as well as the surface migration of adsorbed intermediates. To bridge the knowledge gap, density functional theory (DFT) calculations was employed to systematically examine the adsorption of NH₃ and NO on the catalyst surfaces. Furthermore, the individual elementary steps of the NH₃-SCR reaction were analyzed to offer atomic-level insight into the microscopic mechanism.

2.4.1 Catalyst model construction

To balance the computational accuracy and efficiency, a carbon-based support model consisting of six aromatic rings was employed in this study. Previous studies consistently identified Mn⁴⁺, Mn³⁺ and Cu²⁺ as the key catalytic centers

in Mn-Cu-based systems, dictating the pathway and efficiency of the NH_3 -SCR denitration reaction. Therefore, two types of basic models, namely MnO_2 -CuO/BCN and Mn_2O_3 -CuO/BCN, were constructed. To ensure the comparability of the models, the number of active sites was fixed in both configurations. Specifically, two MnO_2 molecules (or Mn_2O_3 molecules) and one CuO molecule were closely arranged on the surface of the carbon-based support (BCN). In constructing the MnO_2 -CuO-Nb/BCN and Mn_2O_3 -CuO-Nb/BCN models, two Nb atoms were introduced on the surface to mimic the reality, as Nb in the calcined catalyst existed mainly in the form of Nb_2O_5 . The optimized stable configurations were presented in Figures 8 and 9 which were labeled as MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN and Mn_2O_3 -CuO-Nb $_2\text{O}_5$ /BCN, respectively.

The metal sites in both stable configurations exhibited excellent surface exposure properties, which provided an ideal structural foundation for the activity in the SCR reaction. In the MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN configuration, the surface was distributed with two manganese sites (Mn-1 and Mn-2), one copper site (Cu-1) and two niobium sites (Nb-1 and Nb-2). The connection mode was as follows: Cu-1 coordinated with Mn-1 and Mn-2 through double oxygen bridge bonds, forming Mn-O-Cu catalytic units. Meanwhile, Nb-1 acted as a “structural anchor” and bridged Cu-1, Mn-2 and Nb-2 *via* oxygen atoms, enabling the firm combination of active components with the BCN support. For the Mn_2O_3 -CuO-Nb $_2\text{O}_5$ /BCN configuration, the surface of the carbon-based support also contained two manganese sites (Mn-1' and Mn-2'), one copper site (Cu-1') and two niobium sites (Nb-1' and Nb-2'). The connection mode was similar to that of MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN. However, the interaction sites between oxygen atoms and the support were significantly reduced. Theoretical calculation results showed that the adsorption energies between the active components and the carbon-based support in both configurations exceeded 50 kJ/mol, confirming that the metal species were stably anchored on the support surface through chemisorption^[40]. This property not only ensured the stability of the catalyst but also provided a guarantee for maintaining high activity during the reaction.

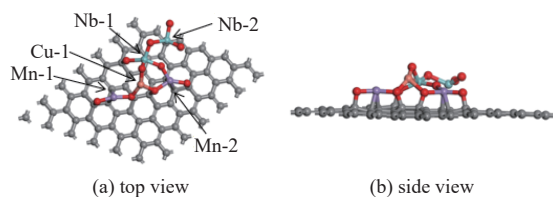


Fig. 8 MnO_2 -CuO-Nb $_2\text{O}_5$ configurations

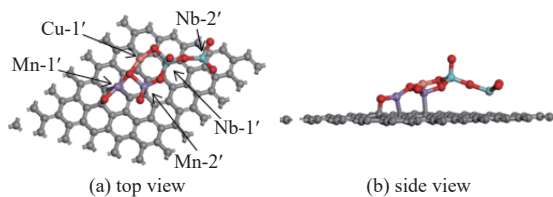


Fig. 9 Mn_2O_3 -CuO-Nb $_2\text{O}_5$ configurations

2.4.2 Adsorption of reaction gas on catalyst surface

As the initial stage of NH_3 -SCR, gas adsorption on the catalyst surface set the trajectory for all subsequent steps. It was known that NH_3 and NO adsorbed differently at various active sites, directly influencing the reaction pathway and efficiency. Through the construction of multiple configurations and energy comparisons, selective adsorption patterns on different sites were identified. With Nb species exhibiting minor activity, the analysis concentrated on Mn and Cu as the key active centers responsible for molecular adsorption and activation.

2.4.2.1 NH_3 adsorption

The multiple adsorption configurations of NH_3 on the MnO_x and CuO surfaces arised from the variability in spatial orientation of the N and H atoms relative to the active sites on the carbon-based support. Figure 10 presented the computationally optimized stable configurations. The results indicated that the adsorption energies of NH_3 on both MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN and Mn_2O_3 -CuO-Nb $_2\text{O}_5$ /BCN were negative, which confirmed that the adsorption process was exothermic. Additionally, the absolute values of all adsorption energies exceeded 50 kJ/mol, demonstrating that NH_3 molecules were stably adsorbed on the two configurations through chemisorption^[41].

DFT calculations identified three distinct stable adsorption configurations for NH_3 on the MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN surface, wherein the N atom directly coordinated with the Mn-1, Mn-2 and Cu-1 sites. The adsorption energies were quantified as -241.1, -299.1 and -234.3 kJ/mol for Mn-1, Mn-2 and Cu-1, respectively. The markedly stronger adsorption at the Mn-2 site established it as the principal active center for NH_3 activation. Similarly, in the Mn_2O_3 -CuO-Nb $_2\text{O}_5$ /BCN system, NH_3 molecules also achieved stable adsorption through N-Mn/Cu bonding.

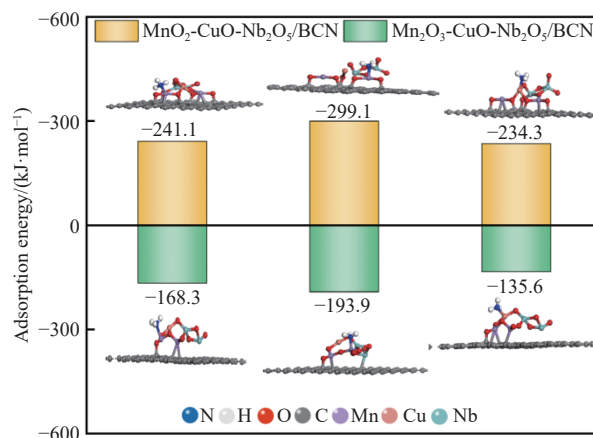


Fig. 10 Adsorption configurations of NH_3 on the surfaces of MnO_2 -CuO-Nb $_2\text{O}_5$ /BCN and Mn_2O_3 -CuO-Nb $_2\text{O}_5$ /BCN

However, the adsorption energies of all active sites (Mn-2': -193.9 kJ/mol; Mn-1': -168.3 kJ/mol; Cu-1': -135.6 kJ/mol) were lower than those in the MnO₂-CuO-Nb₂O₅/BCN catalyst, confirming that the oxidation state of Mn exerted a significant influence on NH₃ adsorption performance. Notably, the Mn-2/Mn-2' sites in both catalytic systems demonstrated optimal NH₃ adsorption performance. This could be primarily ascribed to the structural modulation induced by Nb species. Specifically, the introduced Nb⁵⁺ ions preferentially formed oxygen-bridged coordination bonds with the Mn-2/Mn-2' sites. Concurrently, the intrinsic acidity of Nb significantly enhanced the local acid strength, creating a synergistic effect that substantially promoted the capture of NH₃ molecules.

2.4.2.2 NO adsorption

Figure 11 illustrated the NO adsorption configurations on MnO₂-CuO-Nb₂O₅/BCN and Mn₂O₃-CuO-Nb₂O₅/BCN surfaces. For the MnO₂-CuO-Nb₂O₅/BCN catalyst, three stable NO adsorption modes were observed: (1) N atom coordination with the Mn-1 site, (2) N atom coordination with the Mn-2 site and (3) N atom coordination with the Cu-1 site. The respective adsorption energies were -269.8, -257.7 and -219.0 kJ/mol, respectively, confirming Mn-1 as the primary active site for NO adsorption. In contrast, the Mn₂O₃-CuO-Nb₂O₅/BCN catalyst also displayed three NO adsorption configurations: (1) N atom coordination with the Mn-1' site; (2) bidentate coordination, with N and O atoms binding to Mn-2' and Nb-1' sites, respectively; and (3) N atom coordination with the Cu-1' site. These exhibited sequential adsorption energies of -231.5, -214.4 and -166.9 kJ/mol, respectively. The MnO₂-CuO-Nb₂O₅/BCN configuration had significantly superior NO adsorption capacity than the Mn₂O₃-CuO-Nb₂O₅/BCN configuration, which was mainly attributed to the stronger NO affinity of the MnO₂ crystal phase.

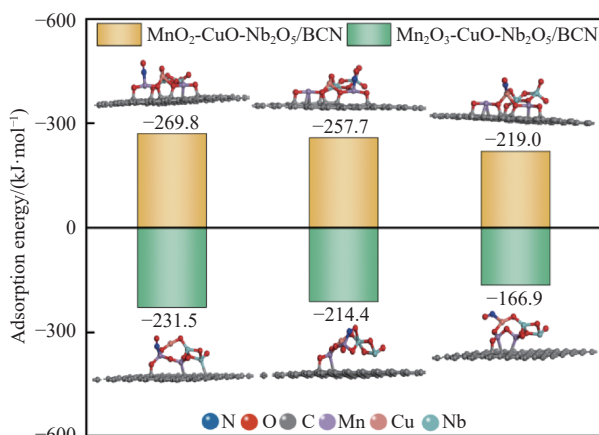


Fig. 11 Adsorption configurations of NO on the surfaces of MnO₂-CuO-Nb₂O₅/BCN and Mn₂O₃-CuO-Nb₂O₅/BCN

Notably, the Cu sites in both catalysts exhibited the least adsorption energies, indicating the comparatively weak interaction with NO molecules. This observation not only underscored the subordinate role of Cu species in the direct adsorption of NO, but also reinforced the predominant function of Mn active sites in driving the SCR reaction, a conclusion that aligns with our previous findings.

2.4.3 NH₃-SCR denitration reaction pathway

Adsorbed NH₃ and NO on the catalyst surface could further transform into N₂ and H₂O through E-R and/or L-H mechanisms. To elucidate the microscale mechanism of Mn₇-Cu₃-Nb_{0.05}/BCN catalysts, both reaction pathways were computed. The results suggested that in the MnO₂-CuO-Nb₂O₅/BCN configuration, Mn-2 and Mn-1 sites dominated the E-R and L-H pathways respectively. Whereas in the Mn₂O₃-CuO-Nb₂O₅/BCN configuration, the corresponding active sites were Mn-2' and Mn-1'. Given that the MnO₂-CuO-Nb₂O₅/BCN configuration exhibited superior gas adsorption performance, it was selected as a representative model for detailed analysis of the NH₃-SCR reaction pathway.

2.4.3.1 E-R reaction mechanism pathway

The Mn₇-Cu₃-Nb_{0.05}/BCN catalyst underwent the processes including NH₃ adsorption and activation, formation of transition intermediates and decomposition during E-R mechanism. NH₃ dehydrogenation served as the pivotal step in efficient NH₃-SCR (E-R mechanism), which was a multi-stage, continuous hydrogen release process consisting of three core steps: NH₃ → -NH₂ + -H, -NH₂ → -NH + -H and -NH → -N + -H. Given that *in situ* redox characterization detected the presence of the key intermediate -NH₂ (confirmed as the most crucial species in SCR reactions), this study focused on investigating the reaction mechanism of the initial dehydrogenation step (NH₃ → -NH₂ + -H) as shown in Figure 12. Theoretical calculations results revealed that NH₃ preferentially adsorbed at the Mn-2 active site, where N-H bond cleavage occurred under the influence of neighboring surface-active atoms (O).

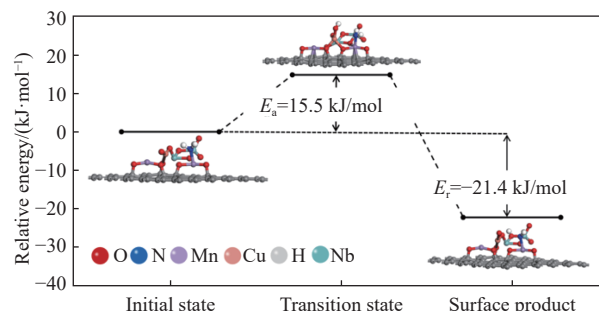


Fig. 12 NH₃ adsorption and dehydrogenation processes on the surface of the MnO₂-CuO-Nb₂O₅/BCN configuration

During the reaction, dissociated $-\text{NH}_2$ stayed in coordination with the Mn-2 site, with the $-\text{H}$ atom combining with O to form hydroxyl groups ($\text{OH}^\cdot$). This step demonstrated low energy barriers ($E_a = 15.5 \text{ kJ/mol}$) and significant exothermic characteristics ($E_r = -21.4 \text{ kJ/mol}$), confirming the thermodynamic spontaneity and kinetic feasibility.

The generated $-\text{NH}_2$ proceeded along two reaction routes: in one direction, it interacted with adsorbed NO in neighboring areas to form NH_2NO . Conversely, it experienced additional oxidative dehydrogenation in the presence of oxygen species on the catalyst surface, resulting in the formation of $-\text{NH}$ and $-\text{N}_2$. Figure 13 illustrated the complete sequence of the NH_2NO synthesis and breaking processes. During the formation of NH_2NO , the N atom in the $-\text{NH}_2$ radical firstly bonded to the Mn ions. Subsequently, the adsorbed NO molecule further formed an N–N bond *via* the bonding between its N atom and the N atom in $-\text{NH}_2$, ultimately resulting in the formation of NH_2NO . The calculated reaction heat for the step was -11.8 kJ/mol , confirming its exothermic character which was consistent with the stability of the N–N bond. The step also presented a low energy barrier of 5.8 kJ/mol , mainly attributable to the energy cost that had been incurred during the prior generation of the $-\text{NH}_2$ group.

Since NH_2NO was an unstable intermediates, it decomposed rapidly into H_2O and N_2 after being formed^[42]. The NH_2NO decomposition could be fully achieved through only one transition state structure as follows: firstly, the N–O and N–H bond underwent simultaneous cleavage. Then, the involved atoms fused to create free-OH and attached N_2 . Ultimately, the free-OH interacted with H atoms adsorbed by the catalyst, leading to the formation of H_2O . This process had an energy barrier of 22.5 kJ/mol and released 40.6 kJ/mol of heat. A comparison results showed that the reaction energy barrier (TS2) for the decomposition of NH_2NO was greater than that of any other elementary reaction process. Thus, it could be concluded that NH_2NO decomposition was the rate-determining step for the $\text{MnO}_2\text{-CuO-Nb}_2\text{O}_5/\text{BCN}$ catalyst, exerting a relatively significant influence on the NH_3 -SCR reaction—consistent with the findings in the literature^[43].

In summary, for the $\text{MnO}_2\text{-CuO-Nb}_2\text{O}_5/\text{BCN}$ configuration, the absolute values of the reaction heats for all elementary reactions were greater than their corresponding reaction energy barrier values throughout the entire reaction process. This implied that the heat released at each stage could better compensate the energy barrier that needed to be overcome during the reaction. This was also a crucial reason for the excellent denitration activity.

2.4.3.2 L-H reaction mechanism pathway

From *in situ* IR spectra, the L-H reaction mainly occurred between NO_2 or nitrate species and adsorbed NH_4^+ species. Among them, NO_2 and nitrate species formed through consecutive elementary reactions: $\text{NO}(\text{ad}) + \text{O}(\text{a}) \rightarrow \text{NO}_2 + \text{O}(\beta) \rightarrow \text{NO}_3^-$. Since oxidizing NO to NO_2 represented a

critical step for further conversion to nitrates, the $\text{NO} \rightarrow \text{NO}_2$ reaction mechanism was explored (Figure 14). During the formation of NO_2 , gaseous NO molecules interacted with the Mn-1 sites on the surface through their N atoms to form adsorbed NO molecules. Subsequently, the O atom in the NO molecule rapidly bonded with the active O atom adsorbed on the Cu site, forming NO_2 . This process had a calculated reaction energy barrier of 11.3 kJ/mol and reaction heat of -6.2 kJ/mol . The relatively low reaction energy barrier indicated that NO could more easily capture active O atoms to form NO_2 under aerobic conditions.

After the formation of NO_2 , a portion of them was used for the “Fast-SCR” reaction (Equation 17). While the remainder further formed nitrate species through interaction with corresponding atoms on the surface. In view of the fact that the *in situ* infrared characterization results showed the highest peak intensity for bridged nitrate species (at 1628 cm^{-1}), only bridged nitrates were selected as representative for computational analysis. The specific reaction pathway, as shown in Figure 14, was as follows: The N atom in NO_2 bonded with the active O atom connected to the Cu-1 site. Meanwhile, one O atom in NO_2 directly linked to the active Mn-1 site, ultimately generating the NO_3^- species required for subsequent reactions. The reaction heat for this process was -27.1 kJ/mol . The formed NO_3^- ions well conformed to the structure of bridged nitrates: one O atom in NO_3^- bonded to the N atom *via* $\text{N}=\text{O}$ bond, while the other two O atoms bonded to the Mn and Cu ions on the surface, respectively. Notably, no transition state was observed during this process, indicating that the reaction was a rapid process.

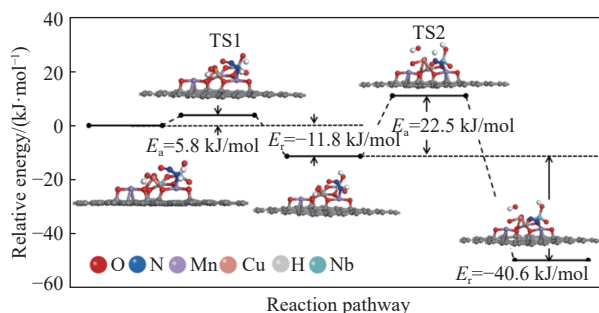


Fig. 13 Formation and decomposition processes of NH_2NO on the surface of the $\text{MnO}_2\text{-CuO-Nb}_2\text{O}_5/\text{BCN}$ configuration

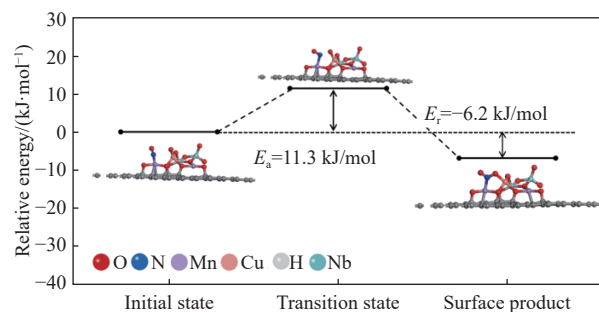


Fig. 14 The processes of NO_2 generation on the surface of the $\text{MnO}_2\text{-CuO-Nb}_2\text{O}_5/\text{BCN}$ configuration

Immediately after the formation of NO_3^- , it reacted with adsorbed NH_4^+ to generate NH_4NO_3 , with the specific process illustrated in Figure 15. When NH_4^+ approached NO_3^- , the bonds between NO_3^- and the active sites remained intact, retaining the Mn–O and Cu–O bond configurations. The bonding initiation between NH_4^+ and NO_3^- involved two pathways: (1) When NH_4^+ was close to NO_3^- , two O atoms in NO_3^- (the O atoms in N–O bonds) simultaneously bonded with the H atoms in NH_4^+ ; (2) The N atom in NO_3^- directly bonded with H atoms in NH_4^+ . The calculated heat released during the formation of NH_4NO_3 was 463.1 kJ/mol, significantly higher than that released during the NO_3^- formation. This revealed that NH_4NO_3 was more likely to form on the catalyst surface. Following the NO_3^- generation, it immediately reacted with adsorbed NH_4^+ to form NH_4NO_3 , which then underwent a continuous reaction of $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ and finally decomposed into non-toxic and harmless N_2 and H_2O . These reaction pathways effectively confirmed that the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst also operated *via* the L-H mechanism.

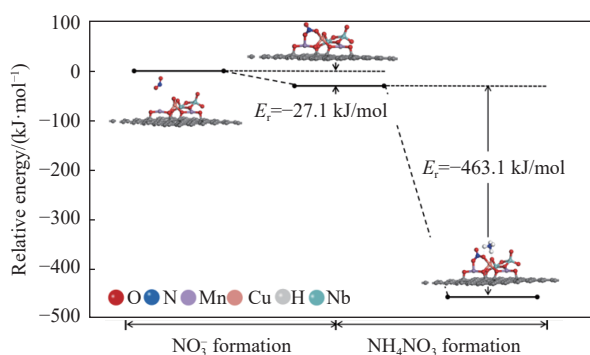


Fig. 15 The processes of NH_4NO_3 generation on the surface of $\text{MnO}_2\text{-CuO-Nb}_2\text{O}_5/\text{BCN}$ configuration

3 Conclusion

In this study, Nb was selected as a dopant to modify the $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ catalyst. The results showed that the $\text{Mn}_7\text{-Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst with Nb doping amount of 0.05% exhibited the best SCR denitration activity. *In situ* infrared spectroscopy and DFT molecular simulation calculations were further employed to systematically investigate the reaction mechanism. The main research conclusions were as follows:

(1) *In situ* spectra revealed that during the $\text{NO} + \text{O}_2 \rightarrow \text{NH}_3$ reaction, NH_3 existed as coordinated species with both Lewis and Brønsted acid sites. The $-\text{NH}_2$ intermediates promoted the NH_3 activation, which was consistent with the E-R mechanism. When NH_3 reacted with $\text{NO} + \text{O}_2$, NO was preferentially adsorbed to form nitrates with strong oxidizing properties, following the L-H mechanism. The catalyst exhibited both E-R and L-H dual pathways at low temperatures, achieving efficient conversion of NH_3 and NO through the synergistic effect of multi active sites.

(2) DFT calculations results demonstrated that the $\text{Mn}_7\text{-}$

$\text{Cu}_3\text{-Nb}_{0.05}/\text{BCN}$ catalyst followed the E-R mechanism, i.e. NH_3 was preferentially adsorbed on the Mn-2 site (adsorption energy: -299.1 kJ/mol) and underwent dehydrogenation with a low energy barrier (15.5 kJ/mol) to generate the key intermediate $-\text{NH}_2$. This intermediate reacted with NO to form NH_2NO . The decomposition of NH_2NO into N_2 and H_2O (energy barrier of 22.5 kJ/mol) was the rate-determining step of the reaction. Meanwhile, all elementary reactions in the E-R mechanism were exothermic and the heat released was higher than the corresponding energy barriers, ensuring the thermodynamic spontaneity and kinetic feasibility of the reaction. In the L-H mechanism, NO was preferentially adsorbed on the Mn-1 site, oxidized to NO_2 with a low energy barrier and rapidly converted into bridged nitrate NO_3^- . The NO_3^- species combined with NH_4^+ through dual pathways to efficiently form NH_4NO_3 , which ultimately decomposed into N_2 and H_2O . The entire reaction process exhibited significant exothermic characteristics. No transition state was observed in the key steps, confirming the high efficiency and rapid reaction characteristics of the L-H pathway.

Declaration of Competing Interest

The authors declare no conflict of interest.

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生物炭基 Mn-Cu-Nb 催化剂低温 NH_3 -SCR 脱硝机理研究

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摘 要: 在全球能源转型与碳中和背景下, 控制生物质燃烧产生的氮氧化物(NO_x)排放具有重要意义, 开发高效低温催化剂成为当前研究重点。本研究以 Nb 掺杂改性 $\text{Mn}_7\text{-Cu}_3/\text{BCN}$ 催化剂, 构建 $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$ 体系, 通过选择性催化还原 (SCR) 活性测试优选掺杂量, 并结合原位红外表征与密度泛函理论 (DFT) 模拟探究反应机理。结果表明, 0.05% Nb 掺杂的催化剂脱硝活性最佳, 150–275 $^{\circ}\text{C}$ 时 NO 转化率 $\geq 94\%$, 且抗碱金属 K 中毒性能提升。机理研究表明, 该催化剂在低温下同时存在 E-R 和 L-H 两种反应路径, 通过多活性位点协同作用促进 NH_3 与 NO 的高效转化。DFT 计算进一步证实, 两条路径均具有反应能垒低、放热显著的特征, 保障了低温反应的高活性与可行性。本研究为 Nb 改性 Mn-Cu 基负载型催化剂的设计与机理研究提供了理论支持。

关键词: 低温催化剂; 选择催化还原; $\text{Mn}_7\text{-Cu}_3\text{-Nb}_x/\text{BCN}$; DFT 计算; 反应机理

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