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journal homepage: www.elsevier.com/locate/pnsmiPerformance and mechanism of nitrogen-doped carbon-based catalysts in NH₃-SCR reactionYuejin Li^{a,b}, Xu Liu^a, Anshe Zhang^{c,***}, Weimin Zhao^{b,**}, Fangjun Shao^a, Shijie Zhang^a, Zihao Yao^{a,*}^a State Key Laboratory of Green Chemical Synthesis and Conversion, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310032, People's Republic of China^b College of Chemical Engineering and Materials, Shandong University of Aeronautics, Binzhou, 256603, People's Republic of China^c Binzhou Science and Technology Innovation Development Research Institutes, Binzhou 256600, People's Republic of China

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ABSTRACT

The present study investigates the performance and mechanism of nitrogen-doped carbon-based catalysts in selective catalytic reduction (SCR) reactions for removing nitrogen oxides (NO_x) through a combination of experiments and density functional theory (DFT) calculations. A series of catalysts with a gradient distribution of nitrogen content were prepared, and the types, contents, and structural characteristics of their nitrogen-containing functional groups were characterised. The experimental findings demonstrated that with an increase in nitrogen content, there was an initial rise and subsequent decrease in NO conversion among the catalysts. The AC-N-3 catalyst exhibited the highest NO conversion, with an observed value of 83.0 %. DFT calculations revealed that nitrogen doping enhanced the adsorption capacity of the catalysts for NO and O₂ through the introduction of functional groups. The active centre is located at the nitrogen functional group and its adjacent carbon atom. The centre of the molecule is responsible for driving the charge migration process, which in turn causes a stretching of the bond length of the reactants. This effect leads to the efficient pre-activation of the reactants, thereby significantly enhancing their catalytic activity. Through the analysis of the NH₃-SCR reaction pathway, the fundamental steps of the reaction were presented in a comprehensible manner.

1. Introduction

The treatment of nitrogen oxides has emerged as a prominent area of interest among both the public and researchers. Among the various treatment methods, selective catalytic reduction (SCR) using NH₃ represents the prevailing technology for NO_x removal, particularly in the context of industrial flue gas denitrification [1]. The choice of catalyst is of paramount importance in this technology, influencing both the efficiency of denitrification and the overall cost of operation [2]. Vanadium-based catalysts are typically used in the conventional SCR process. However, they are prone to poisoning due to contamination by sulphur and fly ash [3,4]. Consequently, there is an urgent need to develop new and efficient denitrification catalysts.

Carbon-based materials, characterized by high reserves, substantial specific surface area, well-developed microporous structure, exceptional

adsorption properties, and high strength, have been observed to exhibit catalytic activity for denitrification at low temperatures [5,6]. Further research into using carbon-based materials as denitrification catalysts or catalyst supports represents a promising avenue [7,8]. However, the primary disadvantage lies in their low SCR reactivity, necessitating modifications to enhance catalytic activity [9,10]. The structural nature and surface chemical properties of carbon-based materials significantly influence SCR performance [11,12]. Specifically, the surface chemical properties determine adsorption, catalytic, acid-base, and redox properties, as well as hydrophilicity and hydrophobicity [13–15]. The functional groups on their surfaces are closely related to these properties [16,17], and heteroatom doping is a common strategy to introduce such groups [18,19]. Heteroatom doping, particularly with O, N, B, and S, can significantly alter the electronic structure and create new defects, thereby enhancing catalytic activity [20–22]. Li [23] established that

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the incorporation of sulphur groups into carbon materials is the primary factor contributing to the enhanced activity of SCR catalysts. This is due to the promotion of NH_3 adsorption on the catalyst by the presence of sulphur groups. Li and He found that doping with oxygen functional groups is related to the oxidation degree and denitrification activity of the catalysts [24–26]. In recent years, there has been a marked increase in the level of interest surrounding nitrogen-doped carbon materials [27, 28]. Nitrogen doping, in particular, has garnered significant interest due to its similarity in atomic radius but difference in electronic configuration and electronegativity compared to carbon [29]. The principal types of N doping include pyridine-type, pyrrole-type, graphite-type, and pyridine oxide-type [30]. The research of Li and Zhang indicates that pyrrole-like or pyridine-like structures facilitate NO adsorption and the formation of intermediary products [31,32]. Verma demonstrated that nitrogen doping of activated carbon is more effective at room temperature than at high temperatures [33]. Huang has identified the pyridine nitrogen (N-6) surface group as the primary factor contributing to the enhanced activity of SCR at low temperatures. The introduction of N-6 results in the generation of numerous oxygen vacancies and promotes the formation of reactive oxygen species, thereby facilitating the oxidation of NO to NO_2 and the adsorption of NO_x [34]. A synthesis of previous research underscores the advantages of nitrogen doping for the denitrification reaction. Nevertheless, the mechanisms through which nitrogen doping in carbon materials impacts the denitrification performance of SCR remain largely unelucidated. Consequently, further research is warranted to comprehensively understand the effects of diverse nitrogen types and concentrations on the catalytic performance of the SCR reaction.

In this study, a range of carbon material catalysts exhibiting varying levels of nitrogen content were successfully synthesized through the incorporation of nitrogen-containing groups into the carbon matrix via dicyandiamide treatment. A comprehensive analysis of the structural characteristics and compositional alterations of these catalysts was conducted using a range of analytical techniques. Subsequently, the catalytic performance of the catalysts was rigorously evaluated in the NH_3 -SCR process. In order to gain insights into the adsorption behaviour, the adsorption of NO, NH_3 , and O_2 by the different carbon material catalysts was simulated using DFT. This methodological approach facilitated the analysis of the underlying reasons for the enhanced adsorption promoted by nitrogen doping in carbon materials. Through the integration of experimental findings with DFT calculations, the underlying causes and mechanisms by which nitrogen in carbon materials influences denitrification performance in SCR were elucidated. This finding provides a novel perspective for investigating the mechanistic underpinnings of NH_3 -SCR catalysis in nitrogen-doped carbon materials, with potential implications for developing more efficient and cost-effective SCR catalysts.

2. Methods

2.1. Catalysts preparation

Green Source Co., Ltd. provided the raw carbon materials used in this study. The initial stage of material preparation involved preparing nitrogen-containing solutions of varying concentrations by adding different masses of dicyandiamide (DCD) to deionized water. The synthesis of the catalysts proceeded in three distinct steps: (1) 400 g of columnar activated carbon was soaked separately in each nitrogen-containing solution at 80 °C for 12 h; (2) the impregnated activated carbon was subsequently filtered, washed with deionized water, and dried at 110 °C for 10 h; (3) the dried samples were then calcined under nitrogen protection at 300 °C for 2 h. The resulting catalysts were designated AC-N-0 (no nitrogen added), AC-N-1, AC-N-2, AC-N-3, AC-N-4, AC-N-5, and AC-N-6, based on the concentration of the nitrogen-containing solutions used during synthesis. The original, untreated AC and the AC-Ns samples were collectively referred to as ACs for simplicity.

2.2. Characterization

X-ray Photoelectron Spectroscopy (XPS) is a versatile technique utilized for a broad spectrum of analytical applications, encompassing both qualitative and quantitative elemental analysis, surface characterization of solids, and structural elucidation of compounds. The fundamental mechanism of XPS can be elucidated as follows: upon irradiation of a photon onto the surface of the specimen under investigation, electrons residing in the atomic orbitals of a specific element within the sample absorb the photon energy. This absorption leads to the emission of electrons from within the atom, transforming them into free photoelectrons. The energy of these photoelectrons enables the acquisition of valence state information about the corresponding element.

The X-ray photoelectron spectrometer utilized in this study was a ThermoFisher Scientific ESCALAB 250Xi, manufactured in the United States. The vacuum level in the analysis chamber was maintained at 8×10^{-10} Pa, and the excitation source was Al-K α rays ($h\nu = 1486.6$ eV). The C1s binding energy of 284.80 eV was adopted as the reference for charge compensation.

The Brunauer-Emmett-Teller (BET) method is a widely used technique for determining the physical properties, such as the specific surface area and pore size distribution, of porous materials. The BET model employed in this thesis is the ASAP2460 manufactured by Micromeritics Instrument Corporation. Before testing, the sample was degassed under ultra-high vacuum conditions at 250 °C for 10 h. The actual mass of the sample after degassing was recorded. Subsequently, the entire sample tube was inserted into the instrument and cooled with liquid nitrogen, thereby initiating the test and enabling the acquisition of nitrogen adsorption and desorption isotherms. The specific surface area and pore size distribution of the catalyst sample were obtained through the analysis method provided by the BET software.

The Element Analyzer (EA) is capable of quantitatively determining the elemental composition of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) in organic substances. It is a widely used instrument in the fields of chemistry, pharmacology, and environmental monitoring. The EA employs a high-temperature combustion method to ascertain the concentrations of these organic elements within the sample. The sample is decomposed through catalytic oxidative combustion in an environment that is both high in temperature and oxygen-rich, resulting in the formation of stable products, namely CO_2 , H_2O , N_2 , and SO_2 . The specific model of the instrument utilized in this thesis is the Elementar Vario EL Cube.

Fourier transform infrared spectroscopy (FTIR) is a spectral analysis technique that determines infrared spectra by measuring an interferogram and subsequently performing a Fourier transform on it. This technique can be utilized as an optical analytical method for detecting the type and content of functional groups present on the surface of a sample. Additionally, it is capable of acquiring infrared absorption and emission spectra of solids, liquids, and gases.

The test is conducted by combining a minute quantity of the sample with pure potassium bromide to form a tablet, which is then introduced into the optical path of the instrument for analysis. This process generates an infrared spectrogram, displaying distinctive absorption peaks corresponding to various chemical bonds or groups across a specific wavelength range. By analyzing the spectral pattern, the specific chemical bonds or groups present in the substance can be identified. The instrument employed in this thesis is the Thermo Scientific Nicolet iS 50.

In this study, the fixed-bed evaluation device for desulfurization and denitrification comprises a gas distribution system, a reaction system, a detection system, and a control system. The latter is configured with multiple inlets to simulate the composition of flue gas, as illustrated in Fig. S1.

The length of the reaction tube was 1100 mm, with an outer diameter of 60 mm and an inner diameter of 50 mm. The catalyst loading in the reactor amounted to 350 g, and the reaction was conducted at a temperature of 140 °C for 420 min. N_2 served as the equilibrium gas. The

rate of gas flow was 4418 cm³/min in total, with a specific NO: NH₃ ratio of 8.6:20 cm³/min. Upon completion of the conversion experiments, a flue gas analyser was used to measure the outlet NO_x gas concentration. (Afriso-M60, Afriso Euro Index GmbH). Samples were collected at 15-min intervals to determine the concentration of the exit NO_x gas. In cases where specific circumstances warranted, the sampling frequency was increased as necessary.

The equation for calculating the NO conversion rate is presented in Equation (1):

$$NO_{Conversion} = \left(NO_{in} - \frac{NO_{in}}{NO_{out}} \right) \times 100\% \quad (1)$$

In this context, "NO_{in}" and "NO_{out}" represent the concentrations of NO (in parts per million) present in the inlet and outlet gases, respectively.

2.3. Computational modeling

In this study, all simulations are based on DFT and calculated using the Vienna Ab initio Simulation Package (VASP). The projected augmented wave (PAW) method is employed for the interaction between electrons and nuclei, while a combination of the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) functional is used for the energy interaction between electrons [35,36]. Notably, in our preceding studies, the impact of van der Waals interactions proved pivotal in terms of the simulations [37,38]. Therefore, all calculations were conducted using DFT-D3, which incorporates van der Waals corrections [39].

The simulations of the carbon material prototype utilized a 5 × 4 × 1 sawtooth and armchair type supercell structure with a single-cycle orientation. The k-points were determined using a 2 × 2 × 1 Monkhorst-Pack k-point mesh, and the projected density of states (PDOS) was calculated on a 10 × 10 × 1 mesh. The total energy convergence criterion was set to 10⁻⁵ eV, and the force convergence criterion was set to 0.01 eV/Å. The truncated kinetic energy of the plane-wave basis set was set to 450.0 eV. To prevent interaction between neighboring graphene layers and their periodic images, a vacuum region of 15 Å was established in the z-direction.

The following equation provides a definition of the adsorption energies (*E_{ads}* or *E_a*) of NO, NH₃, or O₂ on ACs:

$$E_{ads} = E_{total} - (E_c + E_g) \quad (2)$$

E_{total} represents the total energy of the adsorption system. *E_c* denotes the energy of the stabilized configuration of the ACs catalysts (e.g., AC and AC-Ns), whereas *E_g* represents the energy of the NO, O₂, or NH₃ gas molecules. A decrease in the value of *E_{ads}* or *E_a* signifies an increase in the adsorption capacity, indicating a stronger interaction between the gas molecules and the catalyst surface.

3. Results and discussion

3.1. Physical properties of carbon materials

The physical properties of the catalysts, including specific surface area and pore size, significantly influence their performance. Consequently, the ACs catalysts employed in all experiments were analyzed using an accelerated surface area and porosimetry system (BET). The results of this analysis are summarized in Table 1 and Fig. 1.

Treating carbon materials with nitrogen-containing solutions of varying concentrations, prepared using dicyandiamide, can lead to alterations in their properties, particularly in their specific surface area. As shown in Table 1, this hypothesis is confirmed. The specific surface area of the catalysts used in the denitrification experiments ranged from 143.82 to 170.95 m²/g, exhibiting a notable variation. Notably, the specific surface area of both AC-N-5 and AC-N-6 declined by approximately 16 % relative to a baseline. Fig. 1a illustrates the pore size

Table 1

Surface area and pore volume of catalysts.

Sample	S _{BET} (m ² /g)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)
AC-N-0	195.33	137.74	57.58	0.13
AC-N-1	187.97	133.29	54.68	0.13
AC-N-2	173.12	119.65	53.47	0.12
AC-N-3	167.80	114.15	53.65	0.12
AC-N-4	144.85	98.37	46.48	0.10
AC-N-5	143.82	101.58	42.24	0.10
AC-N-6	130.86	87.19	43.67	0.10

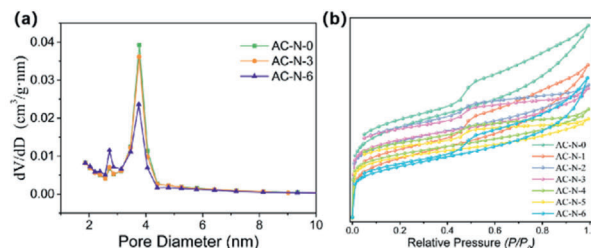


Fig. 1. (a) BJH pore diameter and (b) N₂ adsorption-desorption isotherms.

distribution for three representative catalysts, designated AC-N-0, AC-N-3, and AC-N-6. As observed, the pore size peaks of the three catalysts are approximately 3.8 nm, while the average pore sizes of all catalysts fall within the range of 3.66–4.31 nm. Notably, the peaks of AC-N-6 display a value of approximately 2.7 nm, which is markedly larger than those observed in other catalyst types. The catalysts exhibit predominantly mesoporous characteristics, accompanied by the presence of micropores. The total pore volume ranged from 0.10 to 0.12 cm³/g. As the dicyandiamide concentration increased, the specific surface area of the nitrogen-doped carbon materials gradually decreased, accompanied by varying degrees of reduction in pore size and total pore volume.

Fig. 1b provides a visual representation of the adsorption-desorption isotherms of the AC samples. All ACs samples displayed type IV adsorption isotherms, indicative of a mesoporous structure and confirming the coexistence of mesopores and micropores within the ACs. The larger BET-specific surface area and pore volume of these materials facilitated the exposure of a greater number of active sites, thereby enhancing the catalytic reaction, as reported in previous studies [40]. Overall, the modification of carbon materials with dicyandiamide was found to influence the structural properties of the catalysts, and this impact had a negative defect.

3.2. EA and XPS analysis

The results of the elemental analysis of the nitrogen-doped ACs are summarized in Table 2. The primary constituents of the ACs are carbon (exceeding 85 %) and nitrogen (ranging from 1 % to 10 %), with a negligible amount of hydrogen (less than 2 %). Notably, an increase in the concentration of dicyandiamide during synthesis is accompanied by a corresponding decrease in carbon content. These observations lend

Table 2

Chemical composition (wt%) of catalysts by EA and XPS.

Sample	EA (wt%)				XPS (wt%)	
	C	N	H	Others	C	N
AC-N-0	93.14	1.57	0.85	4.43	96.00	4.00
AC-N-1	92.34	2.03	0.87	4.77	95.40	4.60
AC-N-2	90.59	2.19	0.85	6.38	94.00	6.00
AC-N-3	90.08	3.01	1.05	5.86	92.30	7.70
AC-N-4	88.83	5.44	1.09	4.64	91.90	8.10
AC-N-5	86.75	7.91	0.94	4.40	91.70	8.30
AC-N-6	85.25	9.30	0.92	4.53	91.00	9.00

support to the hypothesis that nitrogen can be effectively doped into catalysts through the utilization of dicyandiamide-treated carbon materials. Additionally, trace amounts of nitrogen were detected in the unmodified carbon material, as exemplified by the AC-N-0 sample, which exhibited a carbon content of 93.14 % and a nitrogen content of 1.57 %. The nitrogen doping of AC-N-6 resulted in a significant increase in nitrogen content, from 1.57 % to 9.30 %, while the carbon content decreased correspondingly, from 93.14 % to 85.25 %. It is noteworthy that the hydrogen content remained relatively constant across the samples, despite the increasing concentration of dicyandiamide, suggesting minimal direct contribution of hydrogen from the precursor.

The carbon and nitrogen contents exhibit a similar trend to their respective elemental analysis results. The original AC had a carbon content of approximately 96.00 %, whereas AC-N-6 showed a decrease of 91.00 %. The discrepancy between the EA and XPS results stems from the fact that XPS, as a surface analysis technique, is primarily utilized to investigate the elemental composition and chemical state of a material's outermost layers. In contrast to the notable alteration in nitrogen content, the concentrations of other elements remained relatively stable throughout the treatment of the carbon materials with dicyandiamide. Given these findings, future investigations into alterations in denitrification performance from a catalyst composition perspective should prioritize analyzing the impact of nitrogen and nitrogen-bearing groups on catalytic activity.

Fig. 2a illustrates four potential structural configurations of nitrogen-containing functional groups in ACs. To gain further insight into the variations in nitrogen-containing group content across all ACs, we conducted a detailed analysis of the XPS test results. The fitted results for C1s and N1s are presented in Fig. 2b–c and Fig. S2. Typical XPS peaks for N1s can be decomposed into four components: a C=N peak of 398.5 eV (pyridine nitrogen, N-6), a C-N peak of 401.1 eV (pyrroloid nitrogen, N-5), and a N-H peak of 401.1 eV. The typical XPS peaks for C1s can be decomposed into three: 284.8 eV (C=C), 286.8 eV (C-O/C=N), and 288.5 eV (C=O/C-N) [41]. Additionally, the following peaks have been identified: 401.1 eV (graphitized nitrogen, N-Q), and an N-O peak of 403.8 eV (nitrogen oxide, N-X) [42,43]. All ACs catalysts with C1s and N1s exhibit these structures, with the sole distinction being the size of their respective peak areas, which suggests that nitrogen is incorporated into the carbon material.

Table 3 summarizes the nitrogen functional groups present in the ACs as determined by XPS analysis, with their compositions calculated from the peak areas. The data reveal a positive correlation between the concentration of dicyandiamide and the increase in the N-6 peak, suggesting that the introduction of dicyandiamide enhances the nitrogen-containing functional groups on the AC surface. The N-5 peak exhibits a trend of initial decline followed by an increase, with the AC-N-6 sample displaying the highest N-5 content. Notably, the AC-N-6 sample has markedly lower N-Q and N-X peak contents compared to the AC-N-0 sample. In conclusion, the treatment with dicyandiamide results in the substitution of oxygen functional groups (N-X) on the AC surface, favoring the formation of the N-6 structure. Concurrently, the creation of numerous surface defects contributes to an increase in the N-5 content. The N-6 and N-5 structures constituted the majority of the four structures, ranging from approximately 60 % to nearly 90 %.

Table 3

Concentration of nitrogen-containing groups in N1s spectra.

Sample	N-6		N-5		N-Q		N-X	
	N _I ^a	N _I ^b	N _{II} ^a	N _{II} ^b	N _{III} ^a	N _{III} ^b	N _{IV} ^a	N _{IV} ^b
AC-N-0	28.1	1.1	37.6	1.5	19.9	0.8	14.3	0.6
AC-N-1	36.3	1.7	24.2	1.1	29.3	1.3	10.1	0.5
AC-N-2	31.3	1.9	32.4	2.0	19.2	1.2	17.1	1.0
AC-N-3	30.4	2.3	32.9	2.5	12.9	1.0	23.8	1.8
AC-N-4	45.0	3.7	24.1	2.0	16.8	1.4	14.1	1.1
AC-N-5	48.3	4.0	38.4	3.2	11.1	0.9	2.1	0.2
AC-N-6	43.8	3.9	45.5	4.1	5.3	0.5	5.4	0.5

^a Percentage of each deconvoluted peak in relation to N1s total area (%).

^b N concentration (wt.%). The N concentration is calculated by multiplying the percentage of deconvoluted peak by O or C concentration shown in XPS results.

3.3. FTIR

The introduction of doped nitrogen allows for the formation of a multitude of potential bonding configurations. The possible configurations include -CN, -NO, -NH_x, and -OOH. Nitrogen can substitute for a C atom in the graphite lattice, forming mainly pyridine or pyrrole configurations [44]. To further illustrate the formation of new functional groups in the ACs catalysts due to nitrogen doping, Fourier infrared spectroscopy (FTIR) was employed for analysis, and the results are presented in Fig. 3. The absorption peaks at 3520 cm⁻¹ and 3410 cm⁻¹ are indicative of the O-H versus N-H stretching vibrations [45], respectively, which suggest that some nitrogen atoms have undergone hydrogenation. Furthermore, the peaks of AC-N-0 are observed to be weak or absent at these two locations, which is more indicative of the addition of nitrogen to form new nitrogen groups. Additionally, the peak

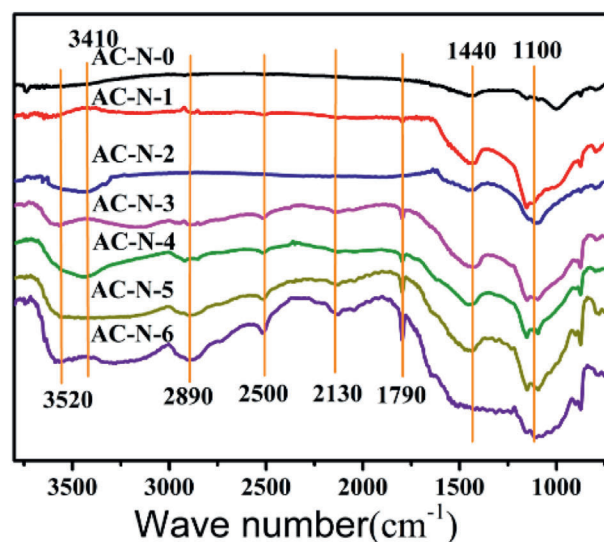


Fig. 3. FTIR spectra of nitrogen-containing ACs.

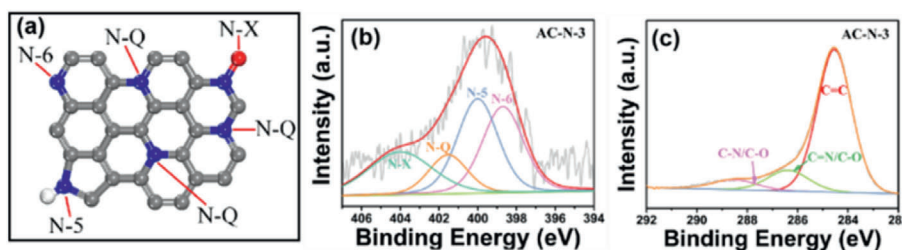


Fig. 2. (a) Structures corresponding to nitrogen functional groups; (b) Deconvolution of N1s(AC-N-3); (c) Deconvolution of C1s (AC-N-3).

intensities appear to increase as the nitrogen content increases. The bond at 2890 cm^{-1} is indicative of the stretching vibration of the C-H group. The bands at 2500 cm^{-1} and 2130 cm^{-1} are attributed to the stretching vibrational modes of the cyano terminus of $\text{C}\equiv\text{N}$. The peaks at 1790 cm^{-1} between the spectral peaks are indicative of the presence of $\text{C}=\text{O}$, which suggests the existence of carboxyl, ester, or ketone groups in the modified carbon material. In the case of AC-N-0, no such peak is observed. However, bands at 1440 and 1100 cm^{-1} are attributed to C-N [46]. Fig. 3 illustrates that the AC-N-0 peaks are weak at all positions where nitrogen-containing groups are evident. This suggests that new carbon functional groups have been introduced into the modified carbon material. As the DCD concentration increases, the peak intensity also rises, indicating an increase in its content. This is consistent with the XPS results.

In conclusion, the successful doping of nitrogen onto the carbon material catalysts was confirmed through a series of analytical techniques, including elemental analysis, XPS, and FTIR forming nitrogen-containing functional groups primarily consisting of pyridine nitrogen (N-6) and pyrrole nitrogen (N-5), thereby demonstrating the reliability of the material preparation process.

3.4. Reduction of NO with NH_3

To investigate the impact of nitrogen content and functional groups in carbon-based catalysts on denitrification reactions, a series of catalysts with varying nitrogen contents were prepared, and their denitrification performance was compared. Fig. 4 illustrates the NO conversion of various ACs catalysts.

The AC-N-0 catalyst exhibited a denitrification efficiency ranging from 64.0% to 67.0% , positioning it in the middle of the performance spectrum among all catalysts tested. Notably, the AC-N-3 catalyst demonstrated the highest denitrification efficiency, reaching 83.0% , significantly outperforming the other catalysts in the series and exhibiting enhanced stability. The AC-N-2 catalyst also showed high efficacy, with its denitrification efficiency ranging from 77.0% to 81.5% . In contrast, the AC-N-1 catalyst displayed considerable variability in its efficiency, initially achieving 81.0% but later decreased to 72.6% . The AC-N-1, AC-N-2 and AC-N-3 catalysts outperformed the unmodified carbon material catalysts.

As illustrated in Fig. 4, the denitrification performance of the AC-N-4, AC-N-5, and AC-N-6 catalysts displayed a modest decrease compared to the unmodified AC-N-0 catalyst. Specifically, the AC-N-6 catalyst exhibited a lower denitrification efficiency, ranging from 58.6% to 63.5% . Meanwhile, the denitrification efficiencies of the AC-N-4 and

AC-N-5 catalysts were nearly equivalent, ranging from 61.9% to 64.5% . Notably, as the nitrogen content in the catalysts increased sequentially from AC-N-0 to AC-N-6, the NO conversion rate initially increased, before subsequently declining. This trend underscores the importance of optimizing nitrogen content to achieve optimal denitrification performance.

A comprehensive analysis of denitrification experiments shows that the addition of nitrogen can initially enhance the denitrification performance of ACs catalysts. However, excessive nitrogen content diminishes their SCR activity, highlighting the need for careful optimization. Zhang et al. have demonstrated that the conversion rate of NO is closely correlated with the structural properties of activated carbon catalysts [47]. As shown in Table 1, the incorporation of nitrogen affects the physical structural properties of modified carbon catalysts, with the extent of this effect varying with nitrogen content. Initially, the increase in nitrogen content appears to enhance the denitrification performance. However, excessive nitrogen content impairs the physical structural properties of the catalysts, which in turn results in a decline in denitrification performance. This observation underscores the importance of balancing nitrogen content to achieve optimal denitrification performance.

The experimental analysis conducted indicates that the incorporation of nitrogen into carbon materials has the potential to significantly enhance their NH_3 -SCR activity. However, the specific mechanism through which this enhancement in performance occurs remains to be elucidated. The present study employs density functional theory calculations to systematically investigate the mechanism of nitrogen-doped carbon materials catalytic performance from a theoretical perspective, with a view to revealing the fundamental principle behind nitrogen doping and enhancing denitrification activity.

3.5. Reactants adsorption

In catalytic reactions, the adsorption of reactants onto the catalyst surface is crucial. In order to conduct a more in-depth examination of the impact of nitrogen-doped carbon catalysts on the denitrification reaction, a comparative analysis of the adsorption behaviour of NO, NH_3 and O_2 on unmodified carbon materials (AC) was conducted in our previous research. [48]. The results showed that the reactants mainly exist in a physical adsorption state on the surface of unmodified carbon materials. However, this physical adsorption is detrimental to the catalytic reaction because the weak adsorption force fails to provide sufficient activation energy, making it difficult to promote effective intermolecular interactions and transformations between reactants. This represents a significant drawback for catalytic reactions. Therefore, it is particularly necessary to modify carbon materials to enhance their adsorption capacity and thereby improve catalytic reaction activity.

It has been demonstrated that heteroatom doping in carbon materials leads to charge redistribution, with edge atoms exhibiting a higher electron transfer rate than basal atoms [49–51]. Consequently, the higher charge density at edge atoms provides a greater number of active sites than basal atoms, making catalytic reactions in carbon materials more likely to occur at the edges. Strelko et al. have shown that incorporating nitrogen atoms into the graphite lattice reduces the energy gap and enhances electron mobility compared to pure carbon, thereby reducing the electron work function at the carbon/gas interface and enhancing catalytic performance. Both the carbon atom clusters and the clusters containing pyridine nitrogen atoms exhibit high energy gap values (4.88 eV and 4.91 eV , respectively). However, when the carbon atom clusters incorporate pyrrole nitrogen atoms, the energy gap value decreases to 2.98 eV . Furthermore, when the carbon atom clusters contain both pyrrole and pyridine nitrogen atoms, the energy gap value decreases to 2.88 eV . This observation suggests that the presence of both nitrogen-containing groups at graphene edges leads to the lowest energy gap and potentially the highest catalytic activity [52]. Based on the aforementioned literature and XPS/FTIR characterization findings.

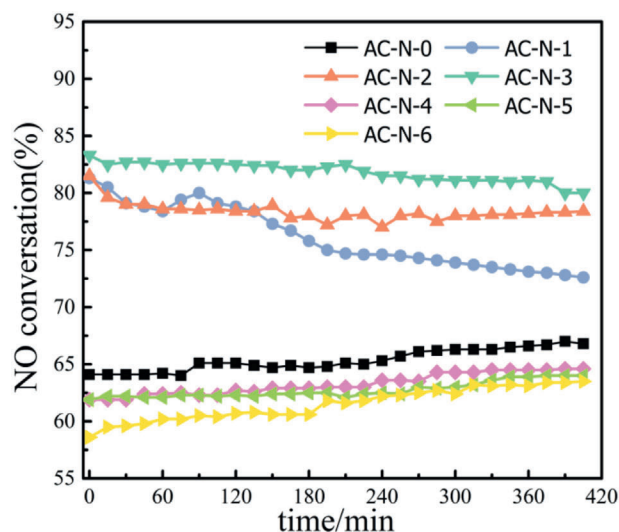


Fig. 4. NO conversion rate.

Catalyst models are classified into two typical categories based on their edge configurations: the zigzag type (Fig. S3a), and the armchair type (Fig. S3b). 0.12 models were devised and designated as follows:

Zigzag-AC (Z), Zigzag-AC-N-5 (Z-5), Zigzag-AC-N-6 (Z-6), Zigzag-AC-N-Q (Z-Q), Zigzag-AC-N-G (Z-G), Zigzag-AC-N-O (Z-O); collectively designated as Z-AC-Ns. Armchair-AC (A), Armchair-AC-N-5 (A-5), Armchair-AC-N-6 (A-6), Armchair-AC-N-Q (A-Q), Armchair-AC-N-G (A-G), Armchair-AC-N-O (A-O); collectively designated as A-AC-Ns. Both the Z-AC-Ns and the A-AC-Ns are, in fact, ACs.

As demonstrated in Fig. 5. There are two primary instances of adsorption on AC models. One such example is when the adsorbate and catalyst model are on the same plane, as is the case with Z-5 and Z-6. The second scenario is characterised by the presence of the adsorbate and the catalyst in a parallel state. The adsorption energy of NO at the edge of the Z model is -0.89 eV than that in the base plane of the untreated Z model. The adsorption energies for Z-5, Z-6, and Z-O are -3.64 eV, -1.27 eV, and -1.04 eV, respectively. The adsorption effects of all three substances are superior to those of the Z model and are attributable to chemical adsorption. In the Z-5 model, NO molecules selectively adsorb onto carbon sites adjacent to nitrogen functional groups; the Z-6 model exhibits a configuration that is entirely different, with NO directly anchored on the nitrogen functional group; in the Z-O system, NO forms a bond between the N atom and the surface oxygen atom, while its O atom cooperates with the adjacent nitrogen atom to construct a two-site adsorption, forming a stable adsorption configuration. The adsorption energy of -0.81 eV for Z-Q is comparable to that of the untreated Zigzag-AC model. Furthermore, the adsorption energy of -0.33 eV for Z-G is also more favorable than that within the untreated Z substrate, and the active sites are nitrogen atoms adjacent to carbon atoms. Therefore, Zigzag-type catalysts containing nitrogen functional groups can significantly enhance the adsorption of the reactant NO.

For the A-AC-Ns model, it is notable that the overall adsorption energy is relatively high, the adsorption is relatively weak, and it is of a physical adsorption. The adsorption energy of NO at the edge of the Armchair-AC model is -0.12 eV, which is similar to the adsorption energy observed for the untreated Armchair-AC substrate. The adsorption energies of A-Q, A-G, and A-O are -0.36 eV, -0.47 eV, and -0.31 eV, respectively. The adsorption effect of A-Q, A-G, and A-O is slightly more favorable than that of the untreated Armchair-AC model.

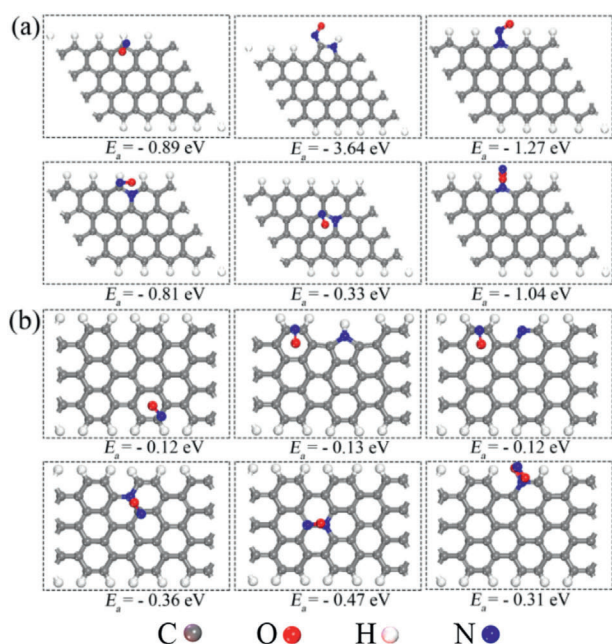


Fig. 5. Optimized structures and adsorption energies of NO on the ACs: (a) Zigzag, (b) Armchair.

NO molecules have been observed to adsorb onto the carbon atom adjacent to the nitrogen functional group, or onto the nitrogen functional group itself. The adsorption energies of A-5 and A-6 are -0.13 eV and -0.12 eV, respectively, which are comparable to those of the untreated A model. Armchair-type catalysts, comprising nitrogen functional groups, have been shown to possess the capacity to enhance the adsorption of the reactant NO to a certain extent.

By analyzing the NO adsorption sites on the ACs catalysts, it can be seen that there are two main distributions of active sites. One of these distributions is on nitrogen-containing functional groups, such as in Z-5, and the other is on adjacent positions to nitrogen functional groups. This is because the incorporation of nitrogen changes the properties of the neighboring carbon atoms [53].

The preceding analysis demonstrates that, in combination with N doping, the adsorption performance of NO on AC-Ns was superior to that of unmodified AC. Consequently, nitrogen doping enhanced the catalyst's adsorption capacity for NO, thereby facilitating the denitrification catalytic reaction.

Fig. 6 shows the adsorption results of O_2 on the ACs model. In the calculation process, the main adsorption positions considered are the nitrogen functional groups themselves and their adjacent sites. The molecular configuration is characterised by two distinct situations: the O_2 molecule is oriented horizontally or vertically relative to the catalyst model.

The adsorption energy of O_2 at the edge of the Zigzag-AC model is -0.37 eV, which indicates stronger adsorption compared to within the untreated Zigzag-AC substrate. Z-5 and Z-Q exhibit adsorption energies of -2.65 eV and -1.11 eV, respectively, both superior to the Zigzag-AC model, indicating chemisorption. In the Z-5 model, O_2 molecules have been observed to preferentially anchor to the carbon atom adjacent to the nitrogen functional group and coplanar with the substrate; In the Z-Q model, O_2 spans the carbon sites on both sides of the nitrogen functional group and is stably adsorbed in a parallel configuration. Z-6, Z-G, and Z-O have adsorption energies of -0.28 eV, -0.28 eV, and -0.27 eV, respectively; these models also demonstrate superior adsorption capacities compared to the undoped Z model. It shows that introducing nitrogen significantly improves the catalyst's O_2 adsorption performance. The active centre is located at the nitrogen functional group or a neighboring carbon atom.

The A-AC-Ns models all show weak adsorption of O_2 , which is usually unfavorable for catalytic reactions. The adsorption energy at the edge of the A model is -0.10 eV, indicating weak adsorption. It is further observed that the adsorption energies at the A-5, A-6, and A-O models are -0.11 eV, -0.11 eV, and -0.12 eV, respectively, and these values indicate that the adsorption of O_2 is likewise weak in all three models. Notably, the adsorption energies of O_2 were elevated to -0.28 eV and -0.30 eV for the A-Q and A-G models, indicating a slight enhancement in adsorption capacity at these models compared to the undoped Armchair-AC model. Its adsorption structure and configuration resemble those of NO.

The preceding analysis demonstrates that upon N doping, the adsorption of O_2 on AC-Ns exhibited superior performance compared to unmodified AC. While the adsorption of O_2 on the modified carbon material catalyst did not reach the same level of effectiveness achieved by NO, the introduction of nitrogen still enhanced the catalytic activity for denitrification of the catalyst.

The results of the NH_3 adsorption configuration on the AC models are presented in Fig. 7. During the calculation process, various adsorption positions and geometrical configurations were considered, ultimately yielding stable adsorption structures.

The adsorption energy of NH_3 at the edge of the Zigzag-AC model was found to be -0.14 eV, which was comparable to the adsorption energy within the basal plane of the undoped Z model. The adsorption energies of Z-5 and Z-6 were -0.37 eV and -0.23 eV, respectively, exhibiting slight enhancements over the Zigzag-AC model. The adsorption energies of Z-Q, Z-G, and Z-O are all -0.14 eV, which is comparable

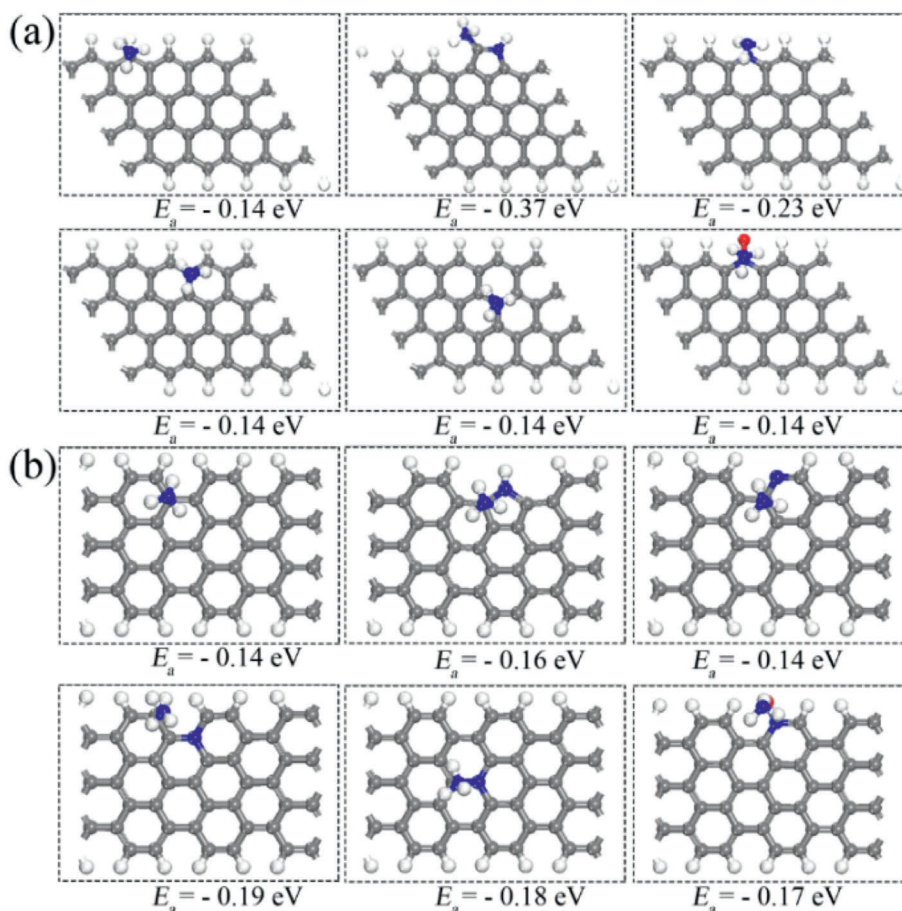


Fig. 6. Optimized structures and adsorption energies of O_2 on the ACs: (a) Zigzag, (b) Armchair.

to that of the untreated Z model.

In the case of the A model, the adsorption of NH_3 is observed to be generally weak, with a range of -0.14 eV to -0.19 eV. This is physically adsorbed, and the observed energy is similar to that of the adsorption within the undoped Z substrate.

The aforementioned analysis indicates that, in conjunction with nitrogen doping, the adsorption of NH_3 on AC-Ns is nearly equivalent to that of undoped AC, exhibiting minimal variation. This suggests that nitrogen doping does not significantly enhance the adsorption capacity of the catalyst for NH_3 .

Thorough analysis of the adsorption energy and configuration of the reactants, NO , NH_3 , and O_2 on ACs reveals that the nitrogen-doped model exhibits a higher propensity for the adsorption of NO and O_2 . The findings of this study indicate the presence of strong interactions that are predominantly governed by chemical adsorption. It has weak adsorption of NH_3 and exhibits weak van der Waals coupling. Further analysis of the adsorption site indicates that the active center is confined to the nitrogen functional group and its neighboring carbon atoms. Due to the introduction of nitrogen, this region undergoes local charge rearrangement, providing effective adsorption sites for NO and O_2 , but lacking effective coupling sites for NH_3 . According to the results of the adsorption energy calculation, nitrogen-doped carbon materials demonstrate significantly stronger adsorption of reactants. This thermodynamically favors the activation of reactants on the catalyst surface and facilitates the efficient progression of the denitrification reaction.

The strength of the catalyst adsorption of reactants can be quantified by the distance between the catalyst surface and the reactant molecules (adsorption distance) and the electron gain/loss between the catalyst and the reactants (charge transfer), in addition to the conventional comparison of adsorption energy [54]. Consequently, the adsorption

capacity of the catalyst can be further confirmed by analyzing the adsorption distance and charge transfer.

As illustrated in Fig. 8 a and Table S1, the adsorption distance between the reactant NO and the catalyst increases concurrently with a reduction in adsorption energy. The charge transfer varies, which is attributed to the different adsorption positions of NO on the Z-O catalyst model. While the adsorption position of NO on the other catalysts is either N or C, it is exclusively O on Z-O. The electronegativities of oxygen, nitrogen, and carbon are in the order of 2.55, 3.04, and 3.44, respectively. Electronegativity varies greatly in its ability to gain or lose electrons [55]. This is as evidenced by Table S1, which shows that NO is an electron-losing species (-0.11 |e|) only on the Z-O catalyst model. The adsorption distance between the reactant O_2 and the catalyst in Fig. 8 (b) is largely consistent with the variation pattern of adsorption energy, yet the pattern of charge transfer is not consistent (Table S2). A similar, but more pronounced, difference in charge transfer is also observed for the Z-O catalyst model.

The Z-5 type catalyst has been demonstrated to exhibit the most effective adsorption effect on NO , characterised by an N–C distance of 1.37 Å, an N–O bond length that extends from 1.17 Å to 1.27 Å, and a charge transfer of 0.74 |e|. It has been demonstrated that the greater the degree of stretching applied to a bond, the more fully activated it is, and the easier it is to break and rearrange. The Z-6 model catalyst also stretched the NO bond length from 1.17 Å to 1.22 Å, but the charge transfer amount decreased to 0.15 |e|, and the activation depth decreased slightly. Catalysts with high adsorption energy, such as A-6, have a distance of 2.90 Å between NO and their active sites, and the NO bond length remains at 1.17 , with no charge transfer, thus failing to play an effective activating role. A comparison of the calculation results of the Z and Z-Q models reveals that both models exhibit a high degree of

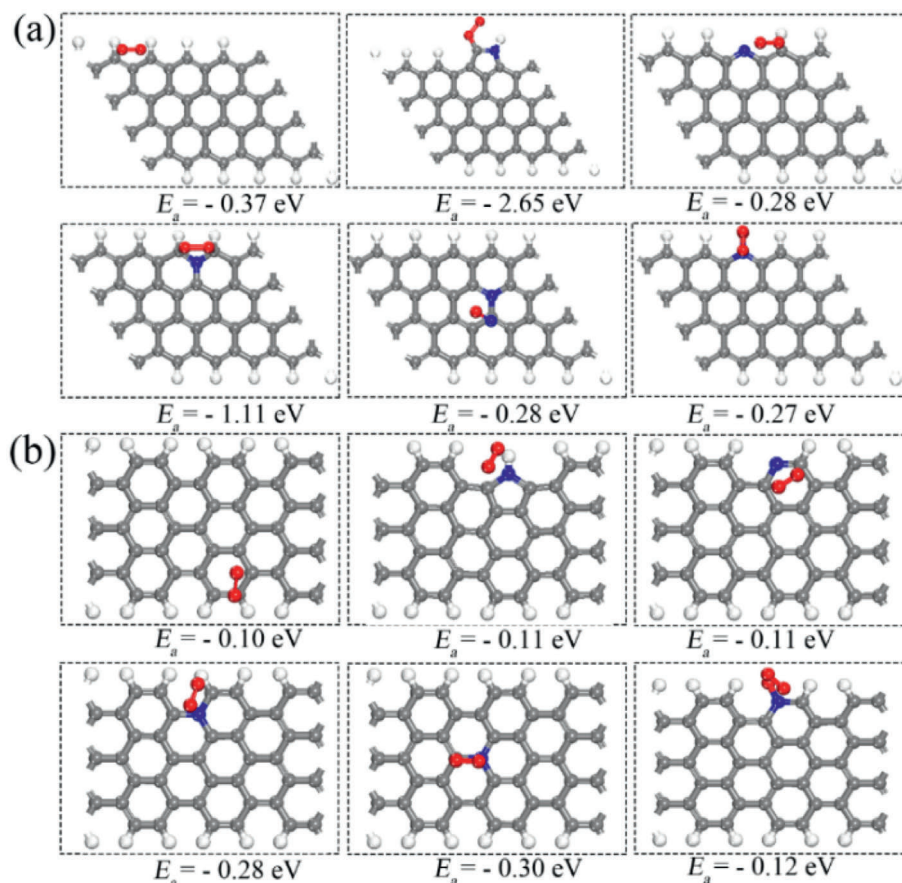


Fig. 7. Optimized structures and adsorption energies of NH_3 on the ACs: (a) Zigzag, (b) Armchair.

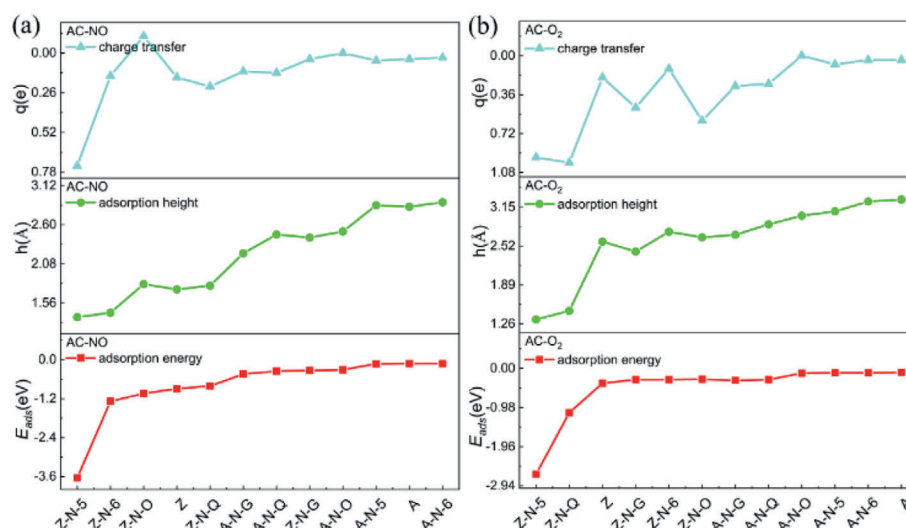


Fig. 8. Adsorption energies, adsorption distance, and charge transfer of NO and O_2 with ACs: (a) NO and (b) O_2 .

consistency with regard to adsorption energy and adsorption distance. However, the Z-Q system undergoes a more significant charge transfer, thereby exerting a stronger activating effect on NO. This is evidenced by a stretching of the N-O bond length from 1.17 Å to 1.21 Å, which provides a more favorable geometric structure for subsequent bond breaking and reactions. It can thus be concluded that the introduction of nitrogen does not merely enhance the adsorption of reactants by the catalyst; rather, it achieves deep activation of the reactants through

efficient charge transfer and bond length regulation. This, in turn, provides the foundation for subsequent reactions.

The results for O_2 are presented in Fig. 8 b and Table S2, illustrating that O_2 exhibits the highest degree of adsorption on the Z-5 model catalyst. The adsorption distance between O_2 and the active site is 1.33 Å, with the bond length of O_2 elongated from 1.21 Å to 1.40 Å. Notably, the Z-Q model, resulting from nitrogen doping, alters the properties of the neighboring carbon atoms [56]. O_2 is horizontally

adsorbed on the two carbon atoms adjacent to the doped nitrogen. In this case, the adsorption distance is 1.47 Å, accompanied by the highest charge transfer of 0.99 |e|, the O-O bond length was stretched to 1.51 Å. The results related to ammonia adsorption are not included in this analysis due to inadequate adsorption by the catalyst and their limited relevance to the primary discussion.

Further confirmation of the importance of nitrogen doping is provided by the analysis of the adsorption energy, adsorption distance, and charge transfer of NO and O₂ on the catalyst. Specifically, it enhances the adsorption capacity of the catalyst towards the reactants and further elongates the bond lengths of the adsorbed reactants through charge transfer between the reactants and the catalysts. This process favorably prepares the reactants for subsequent bonding reactions, thereby optimizing their reactivity.

To further elucidate the reasons for the bonding between reactants and the catalyst, taking NO as an illustrative example, the PDOS of the catalyst with NO was calculated. The results are depicted in Fig. 9.

The incorporation of heteroatomic nitrogen triggered a redistribution of electronic charge within the catalyst. Therefore, the PDOS relationship between the active center C (or N, O) and NO was analyzed. Frontier molecular orbital theory emphasizes that the vicinity of the Fermi energy level plays a pivotal role in bond formation [57,58]. As evident in Fig. 9, a hybridization occurs between portions of the catalyst and adsorbed NO in proximity to the Fermi energy level.

In the Z model, the presence of three matching peaks at -0.88, -1.99, and -2.31 eV below the Fermi energy level for both NO and C (or N, O) signifies a strong bonding interaction between the p-bands of NO and Z. This observation underscores a substantial covalent interaction between NO and the active sites (C, N, or O) of Z.

In contrast, the PDOS analysis of the Armchair-AC model reveals no matching peaks between NO and C (or N, O), indicating that the p-bands of NO and C (or N, O) do not contribute significantly to bond formation. Similarly, A-5 and A-6 exhibit comparable results to Armchair-AC, with weak interactions between the p-bands of NO and C (or N, O) during bond formation. This finding aligns well with the adsorption energy profiles presented in Fig. 6. On the other hand, A-Q, A-G, and A-O catalysts demonstrate slightly improved adsorption compared to the A model, reflected in the emergence of weaker matching peaks in their

PDOS profiles between NO and C (or N, O).

The Z-5 structure, with peaks approximately at 0.39, -0.35, and -1.32 eV, the Z-6 structure, exhibiting peaks at 0.97, -0.81, -1.21, and -1.85 eV, the Z-Q structure, featuring peaks around -1.44, -1.82, and -2.60 eV, and the Z-O structure, displaying a peak at approximately -1.94 eV, all demonstrate similar outcomes to Z, suggesting a strong interaction between the NO p-band and these catalysts. While the Z-G structure, with peaks around 0.91 and -2.58 eV, also exhibits matching peaks, its adsorption efficacy is superior when compared to the undoped substrate due to its status as a basal plane atom, less efficient than edge atoms in terms of electron transfer rates, as evidenced by previous studies [59–61] (Fig. 4). However, it lags behind other Zigzag-type structures in this regard (Fig. 5).

Nitrogen doping significantly enhances the hybridization between the reactant NO and the active sites of the catalyst, constituting the primary reason for the improved adsorption capabilities of the modified catalyst towards reactants.

In summary, a rigorous analysis, grounded in adsorption energy calculations, underscores that nitrogen doping in catalysis triggers charge redistribution [62], which in turn fosters the adsorption of NO onto the catalyst surface. The facilitation of adsorption can be attributed to the favorable hybridization bonding between the two entities, as corroborated by the PDOS analysis. Additionally, the ensuing charge transfer and the elongation of the reactant bond length create conducive environments for subsequent reactions, thereby ensuring their seamless progression.

3.6. NH₃-SCR reaction pathway

Previous studies have emphasized the pivotal role of NO and NH₃ adsorption on catalysts in the SCR reaction [63,64]. Currently, two widely accepted mechanisms for catalytic reactions are the Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms, both of which have been applied to denitrification reactions. In the literature on denitrification reactions, the E-R mechanism suggests that NH₃ initially adsorbs onto the active sites of the catalyst, followed by its reaction with NO in the gas phase. In this study, we conducted a comprehensive analysis of the adsorption energies of NO, O₂, and NH₃ on a range of

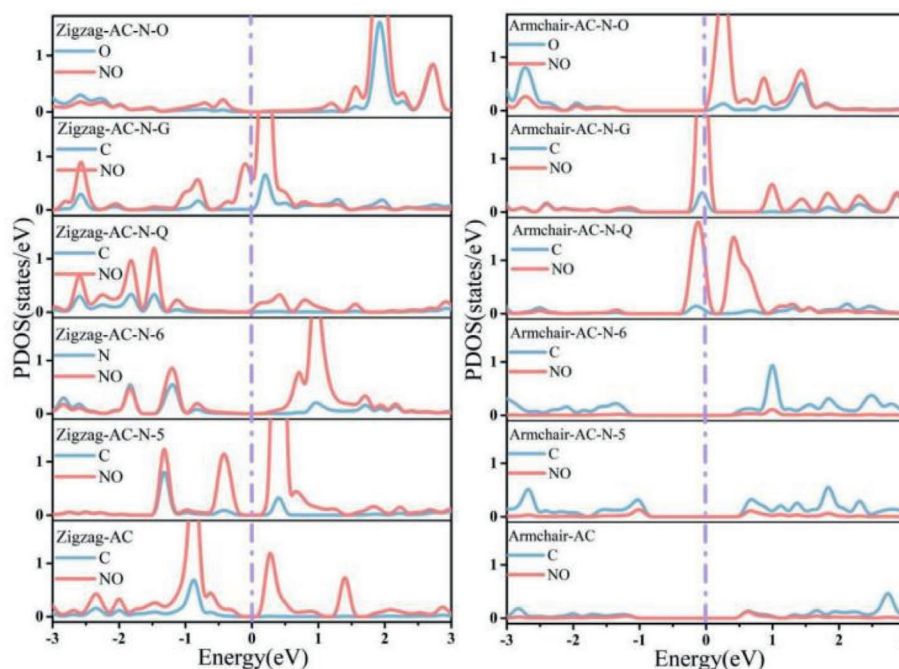


Fig. 9. Partial density of states of (PDOS) of NO adsorbed on Acs.

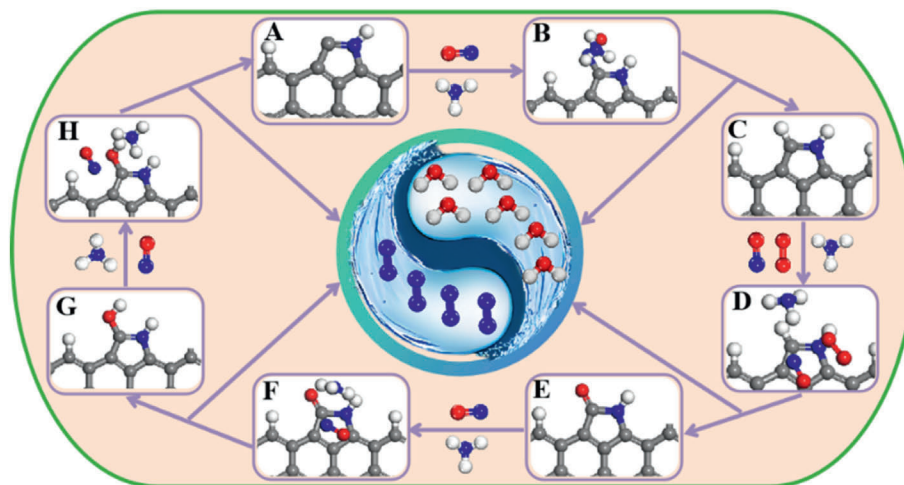


Fig. 10. Pathway of the NH_3 -SCR reaction on catalysts.

catalysts. Notably, NH_3 adsorption on our catalysts was suboptimal, in contrast to previous reports, underscoring the novelty of our integrated theoretical and experimental methodology.

The L-H mechanism can be conceptually described as the adsorption of reactants A and B onto adjacent active sites on the catalyst surface. Based on our preceding analysis, NO exhibits favorable adsorption on Z-5 (−3.64 eV), Z-6 (−1.27 eV), and Z-O (−1.04 eV) catalysts. Similarly, O_2 achieves chemical adsorption on Z-5 (−2.65 eV) and Z-Q (−1.11 eV) catalysts. Experimental analyses utilizing EA, XPS, and FTIR spectroscopy verified the existence of these structures within the catalysts. Hence, a comprehensive assessment of adsorption energies and catalyst functionalities indicates a stronger alignment with the E-R mechanism for the catalytic reaction process. In the system under scrutiny in this study, density functional theory (DFT) calculations suggest that NO demonstrates robust chemical adsorption on the catalyst, while the adsorption of NH_3 is comparatively feeble. Consequently, the reaction is more consistent with an E-R mechanism pathway where NO serves as the adsorbate species: the NO molecule first adsorbs onto the catalyst active site, followed by reaction with NH_3 molecules in the gas phase.

Reaction pathway analysis offers a visual insight into the fundamental steps underpinning the catalytic process. Taking the Z-5 model as an illustrative example, the specific pathway is outlined in Fig. 10. In the initial A-B phase, NO adsorbs onto the unsaturated carbon site of the pyrrolic nitrogen (N-5), while NH_3 approaches NO, leading to the formation of the intermediate product C-NO/N- NH_3 depicted in B. Subsequently, this intermediate undergoes decomposition, yielding N_2 and H_2O , with hydrogen saturating the carbon attached to the pyrrolic nitrogen, resulting in the structure shown in C. This structure exhibits weak adsorption capabilities towards NO, O_2 , and NH_3 , fostering intense competitive adsorption dynamics. This step represents a pivotal juncture in the overall reaction sequence.

During the C-D transition, a C-NO/N- O_2 /H- NH_3 configuration emerges, which, upon decomposition, results in the substitution of hydrogen for oxygen. Progressing to the E-F stage, a C-NO-C/C- NH_3 -N structure is formed. Following its decomposition, a hydroxyl group occupies the vacant carbon site previously associated with the pyrrolic nitrogen. This intermediate, featuring both Z-OH and Z-5 configurations, presents an intriguing scenario where the close properties of oxygen and nitrogen might induce antagonistic effects, detracting from the adsorption efficiency of reactants. Consequently, in the G-H step, the adsorption behavior of NO and NH_3 differs significantly from that observed in structures with a single functional group, yielding an OH-NO/H- NH_3 intermediate. This intermediate subsequently dissociates into N_2 and H_2O , ultimately restoring the initial A structure, thus completing the catalytic cycle.

4. Conclusion

The present study focuses on the performance of catalysts prepared using dicyandiamide. DFT calculations are employed to elucidate the mechanisms behind the enhanced activity of nitrogen-doped SCR catalysts, as well as their reaction pathways.

AC-Ns were synthesized successfully through a straightforward method. Comprehensive characterization of the prepared materials confirmed the successful incorporation of nitrogen into the catalysts, forming various nitrogen functionalities. During this process, the introduction of other heteroatoms was minimized, and the nitrogen doping had a certain impact on the physical structure of the carbon material. The denitrification experiments revealed a correlation between the denitrification efficiency and nitrogen content. Specifically, the untreated AC-N-0, without DCD treatment, exhibited a moderate denitrification efficiency of approximately 67 %. Catalysts with lower nitrogen content, namely AC-N-1, AC-N-2, and AC-N-3, exhibited superior performance in comparison to the unmodified carbon material. It is noteworthy that AC-N-3 attained the maximum denitrification efficiency of 83.0 %. However, for AC-N-4, AC-N-5, and AC-N-6, which contained higher nitrogen levels, their denitrification efficiencies were slightly lower than that of AC-N-0. This phenomenon is attributed to alterations in the physical properties such as specific surface area and pore volume during the modification process, which may hinder the exposure of active sites and thus inhibit catalytic reactions. However, the incorporation of nitrogen has been demonstrated to exert a favorable influence on the reaction. Consequently, the judicious control of nitrogen incorporation is imperative for the optimization of denitrification performance of the catalysts. Theoretical calculations corroborated that the presence of nitrogen facilitates the adsorption of reactants onto the catalyst, particularly when catalysts contain pyridinic nitrogen (N-6), pyrrolic nitrogen (Z-5), graphitized nitrogen (N-Q) and nitrogen oxide (N-X). The observations of charge transfer, adsorption distance, and bond length changes indicate that nitrogen doping not only improves the catalyst's adsorption of reactants but also produces efficient interfacial charge transfer and significantly stretches the bond length of reactants. A comprehensive investigation into the PDOS reveals that nitrogen doping significantly enhances orbital hybridisation between reactant and active sites, thereby promoting the formation of reactant-catalyst bonds. Furthermore, by analysing the denitrification reaction pathways, a more profound comprehension of the fundamental steps involved in the reaction process was obtained.

In summary, this work provides valuable insights into the design of efficient nitrogen-containing carbon-based SCR catalysts for low-temperature applications and sheds light on their activity origins.

Moreover, it establishes a theoretical framework for investigating the impact of physical structure and chemical properties on catalyst performance during modification processes.

CRedit authorship contribution statement

Yuejin Li: Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Xu Liu:** Software, Methodology, Investigation. **Anshe Zhang:** Data curation, Resources, Supervision. **Weimin Zhao:** Methodology, Conceptualization. **Fangjun Shao:** Writing – original draft, Investigation. **Shijie Zhang:** Resources, Formal analysis. **Zihao Yao:** Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.pnsc.2025.12.003>.

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