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Mechanism of O₂-promoted NO adsorption on activated carbon: An experimental and computational study



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ARTICLE INFO ABSTRACT Keywords: Activated carbon can be used to control NO_x emissions in low-temperature flue gas, while improving its per-NO formance is challenging. NO adsorption on activated carbon was found significantly promoted with the presence Activated carbon of O₂. Based on the analysis of NO adsorption characteristics under different atmospheres and corresponding Adsorption desorption characteristics, NO oxidation, NO2 migration and further conversion on activated carbon are pro-Oxidation posed to cause the significant increase in NO adsorption capacity. Quantum chemical calculations conducted on NO₂ the adsorption and reaction pathways of NO, O2, and NO2 on different carbonaceous models clarified that the Flue gas pathway of O2-promoted NO adsorption on activated carbon can be divided into two stages. In the first stage, O2 adsorbs on active carbon atoms near the hydroxyl functional group and undergoes an oxidation reaction with gaseous NO to generate NO₂. In the second stage, the desorbed NO_2 is re-absorbed on the saturated carbon atoms; the N-down adsorption configuration of NO_2 will not convert, while the O-down adsorption configuration of NO_2 will oxidize the active site to form C-O and release NO; the C-O further reacts with the gaseous NO₂ to form NO₂ which stably remains. There are two types of active sites involved in the pathway. The active carbon atoms near the hydroxyl functional groups mainly play a catalytic role in the oxidation of NO, while the saturated carbon atoms mainly store nitrogen-containing components. The results can help improve the performance of activated carbon in adsorbing NO in low-temperature flue gas.

1. Introduction

Nitrogen oxides (NO_x) are one of the main pollutants in the flue gas emitted from coal-fired power plants [1,2]. Current coal-fired power plants commonly use selective catalytic reduction (SCR) technology to control NO_x emissions [3]. However, when the technology is applied to flue gases from industrial boilers and kilns, it encounters a series of problems, such as a decrease in catalyst activity caused by low flue gas temperatures at the location where the SCR can be installed, catalyst poisoning caused by complex flue gas components, and high ammonia escape issues [4]. Therefore, more suitable technologies need to be developed for industrial flue gases with low temperatures and complex components.

Activated carbon (AC) is used to adsorb gaseous pollutants and is often used in industries such as metallurgy to control NO_x in flue gases [5]. In the metallurgical industry, the method achieves NO_x emissions below 100 mg·Nm⁻³. With increasing concern for air quality, emission limits for industrial flue gas pollutants are becoming more restrictive; for example, the ultralow emission standards promoted in China require

industrial flue gas NO_x emissions to be less than 50 mg·Nm⁻³ [6]. Therefore, the adsorption performance of AC needs to be further improved to achieve high efficiency and economy in NO_x emission control.

 NO_x in industrial flue gases is mainly in the form of NO. Experimental studies revealed that the adsorption of NO over AC at room temperature was weak (<0.01 mmol·g⁻¹ [7–9]). However, when NO coexisted with O₂, the adsorption of NO by AC was significantly enhanced, and the adsorption capacity reached 1.62 mmol·g⁻¹ [8]. This was 213 times larger than that of NO adsorption alone, and NO₂ appeared in the adsorbed gas products. The study of NO₂ adsorption over carbon black, wood-based activated carbon, and date pit charcoal at room temperature revealed that the adsorption capacity of NO₂ was large (0.31–6.15 mmol·g⁻¹ [10–12]) and comparable to the NO adsorption capacity over AC when coexisting with O₂. This suggests that the oxidation of NO is responsible for the significant enhancement of its adsorption.

When NO and O_2 coexist in the gas phase at room temperature and reach thermodynamic equilibrium, NO is fully oxidized to NO₂. However, in the flowing flue gas, due to the short residence time, the

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oxidation rate of NO in the gas phase was very low (only 1.6 % [13]). In the presence of O_2 , NO_2 was found in the product gas of NO adsorption over AC, indicating that the oxidation of NO occurred on the surface of AC [13,14]. NO oxidation experiments carried out at room temperature over polycrylonitrile-based activated carbon fibers, pitch-based activated carbon fibers, and coconut-based activated carbon revealed that the oxidation rate of NO reached 42.7 %, 86.5 %, and 80.7 %, respectively, when AC adsorption was saturated [15–17]. The oxidizing activity of NO varies significantly over different ACs.

The first step in the NO oxidation reaction is the adsorption of the reacting gas. Researchers [18–23] investigated the adsorption of NO and O₂ on carbonaceous models containing unsaturated carbon atoms, oxygen-containing functional groups, and nitrogen-containing functional groups as well as on pristine carbonaceous models and found that unsaturated carbon atoms and atoms with strong electron-donating ability could serve as active sites for the adsorption of NO or O₂. By transition state calculations, adsorbed NO was able to react with gaseous O₂, and adsorbed O₂ was able to react with gaseous NO, following the E-R mechanism [22–24]. In addition, adsorbed NO could also react with adsorbed O₂ or with adsorbed and dissociated O, following the L-H mechanism [24]. Both NO oxidation reaction mechanisms may occur over AC.

At the initial stage of NO adsorption over AC in an oxygen atmosphere, NO₂ did not appear in the product gas. This suggested that after the oxidation of NO occurred on the surface of the AC, the generated NO₂(ad) was not desorbed [25]. Desorption experiments on AC samples adsorbed for some time in a $NO + O_2$ atmosphere showed that the amounts of CO and CO₂ in the desorbed gases were significantly higher than those of AC samples left in air for the same time. This indicated that NO2 generated from NO oxidation on the surface of AC underwent subsequent transformations that promoted the formation of carbon--oxygen functional groups, which were desorbed as CO and CO2 in desorption experiments [25-27]. By analyzing the NO adsorption and oxidation reaction stages, Mochida [28] pointed out that NO₂(ad) generated from NO oxidation needed to undergo multiple conversion steps before it was released into the gas phase and speculated that NO2(ad) was converted to (NO-O-NO2)ad first, and then (NO-O-NO2)ad was converted to generate NO2(g). Based on Mochida's study, Adapa [29] proposed that NO₂(ad) was successively converted to NO₃(ad) and NO-NO₃(ad), and subsequently, NO-NO₃(ad) was converted to NO₂(g). The proposed NO₂(ad) conversion pathway has also been adopted by several researchers to understand the adsorption behavior of NO on sludge carbon and nitrogen-doped porous carbon [30,31]. However, in the in situ DRIFTS experiment [2,32], it was found that C-NO₂ and NO₃ functional groups appeared on the AC during the adsorption process, which means that the above speculation about the NO₂(ad) conversion pathway and intermediate products still needs further exploration.

The experiments of NO adsorption over AC find that the presence of O₂ can significantly promote the adsorption of NO. However, the current understanding of the mechanism of NO oxidation and NO2(ad) conversion cannot explain this phenomenon. Existing mechanistic research suggests that the active site where NO oxidation occurs can adsorb both NO and O₂, and the NO₂ generated after oxidation only undergoes subsequent conversion at this site, without involving other active sites that can adsorb NO_x. Therefore, it cannot explain why more NO is adsorbed in an atmosphere with oxygen. Exploring the promotion mechanism of O₂ on the adsorption of NO on AC is of great significance for regulating the structure of AC and developing high-performance adsorbents. Therefore, this article adopted an isothermal adsorption experimental system and a fixed-bed desorption experimental system to conduct NO adsorption and desorption experiments under different atmospheres and studied the influence of O2 on NO adsorption and desorption characteristics. Combining the in situ DRIFTS experiment of NO adsorption over AC, we explored the intermediate products and possible reaction pathways involved in the NO adsorption process on the surface of AC in the presence of O2. Using quantum chemical

calculations to investigate the adsorption of NO, O_2 , and NO₂ on AC, we further calculated the reaction pathways at each active site and ultimately revealed the promoting mechanism of O_2 on NO adsorption over AC.

2. Method

2.1. Experimental

2.1.1. Sample

The AC sample used in the experiment was produced by Shanghai Aladdin Biochemical Technology Co., Ltd. (CAS: 64365-11-3). Before the adsorption experiment, the AC was degassed at 200 °C for 2 h to remove water and volatile organic compounds adsorbed in the pores. The specific surface area, specific pore volume, and average pore diameter of the sample degassed are 1036.7 $\text{m}^2 \cdot \text{g}^{-1}$, 0.451 cm³·g⁻¹, and 2.005 nm, respectively.

2.1.2. Adsorption experiments

The isothermal adsorption experimental system is shown in Fig. 1. Ushaped tube made of quartz material (inner diameter φ 6 mm, length 250 mm) as the reactor. The U-shaped tube was placed in the isothermal water bath, and 0.04 g of AC sample was placed at the lowest end of the straight section of the U-shaped tube for the experiment. Both ends of the sample are filled with analytically pure quartz wool to ensure that the sample does not flow with the airflow. By measuring the temperature distribution inside the U-shaped tube under flowing conditions, the temperature distribution in the area where the sample is located is uniform and can be stable at 30 °C. The total flow rate of gas at the inlet of the reactor was 200 NmL·min⁻¹, consisting of three gases: NO, O2, and N2. The flow rate of each gas is accurately controlled by mass flow controllers. After the three gases are mixed, they first pass through a preheating section in a constant-temperature water bath to reach 30 °C before entering a U-shaped tube. The concentrations of NO and NO2 at the reactor outlet were analyzed using a Fourier transform infrared spectrometer (FTIR; Nicolet 6700, Thermo Fisher Scientific, USA), with a measurement error of < 3 %.

To study the effect of O_2 on the adsorption characteristics of NO, three experimental conditions are set up, namely, the introduction of 300 ppm NO, pre-adsorption of 5 % O_2 for 1 h, followed by the introduction of 300 ppm NO, and the introduction of 300 ppm NO and 5 % O_2 . The three experimental conditions are abbreviated as "NO", " O_2 -NO", and "NO + O_2 ". The adsorption under the above three conditions reached saturation after 3, 5, and 360 min, respectively. Once the adsorption reached saturation, the experiment would be ended.

After the adsorption experiment was completed, based on the concentration of NO and NO₂ at the outlet of the reactor measured by FTIR, the NO_x adsorption amount was calculated using Eq. (1).

$$N_{\text{NO}_{x,t}} = \int_0^t \left(\frac{(C_{\text{NO},\text{in}} - C_{\text{NO},\text{out}} - C_{\text{NO}_2,\text{out}}) \times 10^{-6} \times Q}{V_m \times m} \right) dt \tag{1}$$

where $N_{NO_x,t}$ represents the amount of NO_x adsorbed on AC at adsorption time *t* (mmol·g⁻¹), and $C_{NO,in}$, $C_{NO,out}$ and $C_{NO_2,out}$ represent the NO concentration at the reactor inlet, NO concentration and NO₂ concentration (ppm) at the reactor outlet, respectively. *Q* represents the gas flow rate (NmL·s⁻¹), V_m represents the molar volume at 0 °C (22.4 l·mol⁻¹), and *m* represents the weight of the loaded sample (g).

In situ DRIFTS experiments were conducted to observe the changes in functional groups on the surface of AC during the adsorption process. After mixing the AC sample powder with spectral pure KBr, it was placed in a PIKE DRIFT cell, and the spectrum was collected using an FTIR spectrophotometer to characterize the adsorption configuration on the surface of the AC during the adsorption process. Reaction conditions were set selectively: 300 ppm NO, 5 vol% O₂, N₂ balance with 200 NmL·min⁻¹. All spectra were recorded from 650 to 4000 cm⁻¹ by



Fig. 1. Schematic diagram of the isothermal adsorption experimental system.

accumulating 32 scans with a resolution of 4 cm^{-1} .

An X-ray photoelectron spectrometer (XPS; ESCALAB 250Xi, ThermoFisher, U.K.) apparatus with an Al K α anode was used to analyze the binding energy of O1s of AC. The XPS profile was calibrated using the C1s (284.8 eV) profile.

2.1.3. Desorption experiments

The fixed-bed experimental system used in the desorption experiment is shown in Fig. 2. The reactor consists of an outer quartz tube and an inner quartz tube, which are sealed with rubber plugs. A movable quartz tray is placed at the top of the inner quartz tube and sealed with frosting. The inner diameter of the outer quartz tube is 45 mm, and the inner diameter of the quartz tray is 35 mm. The quartz tray is located in the isothermal zone of the furnace body. The bottom of the quartz tray was equipped with a quartz sieve plate and a high-purity quartz filter membrane (MK360, Munktell, Sweden), which was used to stack the experimental samples. The heating program of the electric furnace was set to raise the experimental sample from room temperature to 500 °C at a heating rate of 2 $^{\circ}$ C·min⁻¹. Purge with N₂ at a flow rate of 200 NmL·min⁻¹. An FTIR spectrometer was used to detect the concentrations of NO and NO₂ at the experimental outlet.

The sample used in the desorption experiment was the AC sample after the adsorption experiment was completed. The adsorption experiment found that under two operating conditions: the introduction of 300 ppm NO and the pre-adsorption of 5 % O₂ for 1 h, followed by the introduction of 300 ppm NO, AC adsorption reached saturation within 5 min. However, with the introduction of 300 ppm NO + 5 % O₂, it took approximately 360 min to reach adsorption saturation. Therefore, seven types of samples were prepared for the desorption experiment, namely, AC samples that reached adsorption saturation under the above three adsorption conditions and AC samples that adsorbed for 5, 20, 70 and 110 min under 300 ppm NO + 5 % O₂ atmosphere, abbreviated as AC_{NO}, AC_{O2-NO}, AC_{NO+O2}, AC_{NO+O2-5} min, AC_{NO+O2-20} min, AC_{NO+O2-70} min and AC_{NO+O2-110} min, respectively.



Fig. 2. Schematic diagram of the fixed-bed experimental system.

2.2. Calculation details

2.2.1. Structural models

The original AC sample was analyzed by XPS and the O1s spectra are shown in Fig. 3. The spectra can be resolved in three peaks centered at 531.3–531.3 eV, 532.1–532.3 eV, and 532.2–532.8 eV, corresponding to C = O of carbonyl, C = O of lactone, and C-O of phenolic hydroxyl/ether [23,33], respectively. This indicated the presence of oxygen-containing functional groups such as carbonyl, lactone, phenolic hydroxyl, or ether groups on the surface of AC.

Considering the amorphous properties of AC, a typical structural unit of an amorphous carbon-based cluster model is constructed. According to references [18,34,35], a carbonaceous structure model containing seven aromatic rings is sufficient to ignore the impact of edge effects on computational accuracy. Considering both computational accuracy and efficiency, a pristine carbonaceous model containing seven aromatic rings was constructed to study the promotion mechanism of O2 on NO adsorption, as shown in Fig. 4a. Unsaturated carbon atoms are intrinsic defect sites generated under external forces or during the preparation of carbon materials (such as ball milling). Therefore, based on the pristine carbonaceous model, a carbonaceous model containing unsaturated carbon atoms is constructed, as shown in Fig. 4b. In addition to unsaturated carbon atoms, raw materials, posttreatment processes, and oxidation atmospheres may introduce oxygen-containing functional groups on AC, which can have an impact on NO oxidation on AC. Therefore, combined with the results of XPS characterization, carbonaceous models containing carbonyl, hydroxyl, lactone, and ether groups are constructed based on the pristine carbonaceous model, as shown in Fig. 4c-f [22-24,34-36]. These carbonaceous models are used to study the adsorption and conversion processes of NO, O_2 , and NO_2 on AC.

Before conducting adsorption calculations, it is necessary to first determine the active sites on these carbonaceous models. On the carbonaceous model containing unsaturated carbon atoms, the unsaturated carbon atoms (carbon atoms in the red circle) are the active sites of the model (Fig. 4b). For other carbonaceous models, the electron-donating ability of carbon surface atoms can be analyzed by calculating the electrophilic Fukui function, and atoms with strong electron-donating ability can be used as active sites for adsorption calculations [37,38]. Electrophilic Fukui functions of carbonaceous models are calculated using Multiwfn 3.7 [39]. After analysis, the Fukui function value of the carbon atom (carbon atom at the red circle) located at the



Fig. 3. High-resolution O1 s spectra of AC.

edge of the pristine carbonaceous model (Fig. 4a) is higher, while the oxygen atom of the carbonyl group (oxygen atoms at the red circle) has a higher Fukui function value on the carbonaceous model containing the carbonyl group (Fig. 4c). The carbonaceous model containing a hydroxyl group (Fig. 4d) has a higher Fukui function value for the edge carbon atom (carbon atom at the red circle) that is farther away from the hydroxyl group, while the carbonaceous model containing a lactone group (Fig. 4e) has a higher Fukui function value for the double bond oxygen atom (oxygen atom at the red circle) in the lactone group. The carbonaceous model containing an ether group (Fig. 4f) has a higher Fukui function value for the circle) adjacent to oxygen atom. Therefore, in the following calculations, the atoms at the red circle will be used as the active sites of the carbonaceous models for the adsorption calculation of NO, O₂, and NO₂.

2.2.2. Computational methods

Gaussian 09 was employed to complete all calculations in this study [40]. The B3LYP method is combined with the 6-31G (d) basis set to perform geometric optimization and frequency calculation, ensuring that the optimized structures are energy-minimum structures without any imaginary frequency. Calculate the transition state of the reaction path using the quadratic synchronous transit (QST) method. Frequency analysis is used to ensure that there is only one imaginary frequency in the transition state structure. Perform intrinsic reaction coordinate (IRC) calculations on the calculated transition states to ensure that each transition state corresponds to adjacent minimum energy structures. The single-point energies are obtained at the B3LYP/6-311G(d,p) level for adsorption energy calculation.

The adsorption energy of the adsorption process is calculated using Eq. (2):

$$E_{\rm ad} = E_{\rm complex} - E_{\rm gas} - E_{\rm model} \tag{2}$$

where E_{ad} represents the adsorption energy (kJ·mol⁻¹). $E_{complex}$, E_{gas} , and E_{model} represent the single point energies (kJ·mol⁻¹) of the adsorption configuration formed after gas molecule adsorption, the gas molecule, and the carbonaceous model, respectively.

3. Results and discussion

3.1. Effect of O₂ on NO adsorption and desorption characteristics

The dynamic adsorption characteristic curves obtained by conducting AC adsorption experiments under NO and NO + O₂ atmospheres and pre-adsorption of O2 followed by NO atmosphere are shown in Fig. 5. When 300 ppm NO was introduced into the reactor inlet, only NO was detected in the gas at the reactor outlet, and the NO concentration rapidly increased from 184 ppm at the beginning of the reaction to 300 ppm at the inlet after 3 min. At this time, the adsorption of NO on AC reached saturation, with an adsorption capacity of only 0.016 mmol g^{-1} indicating that the number of active sites directly adsorbing NO on AC was small. When 300 ppm NO + 5 % O₂ was introduced into the reactor inlet, NO and NO₂ were detected in the gas at the reactor outlet. The NO concentration rapidly increased from 248 ppm at the beginning of the reaction to approximately 271 ppm at 25 min, followed by a slow increase, reaching a maximum of 279 ppm at 108 min. Then, it slowly decreased and gradually flattened out, stabilizing at 265 ppm after 360 min. At the initial stage of adsorption, the NO₂ concentration in the outlet gas was 0. After 10 min of adsorption, the NO₂ concentration began to rise and gradually stabilized. At 360 min, the NO₂ concentration stabilized at 31 ppm. At this point, the sum of NO and NO₂ concentrations in the outlet gas of the reactor was 296 ppm, which was equivalent to the inlet NO concentration. This indicated that the adsorption of AC reached saturation under an atmosphere of 300 ppm NO + 5 % O₂ in the inlet gas, with an adsorption capacity of 1.55 mmol·g⁻¹. At this time, the oxidation rate of NO was 11.66 %.



Fig. 4. (a) pristine carbonaceous model, (b) carbonaceous models containing unsaturated carbon atoms, (c) carbonyl functional group, (d) hydroxyl functional group, (e) lactone functional group, and (f) ether functional group.



Fig. 5. NO and NO₂ concentrations in the outlet gas versus time during AC adsorption process. (NO: adsorption under 300 ppm NO, O₂-NO: adsorption under 300 ppm NO after 1 h of pre-adsorption under 5 % O₂, NO + O₂: adsorption under 300 ppm NO + 5 % O₂).

In the presence of oxygen, the surface of AC underwent significant NO oxidation, thereby significantly increasing the adsorption capacity of NO_x. The phenomenon observed in the experiment where the outlet NO concentration first increased and then decreased may be due to the reaction of NO₂ generated by NO oxidation with other reducing active sites on the surface of AC. This reaction not only generated oxygen-containing functional groups on the surface of AC but also released NO into the gas phase. As the reducing active sites were consumed, the NO released by the NO₂ reduction reaction would also decrease, leading to a trend of first increasing and then decreasing NO concentration at the outlet. At the initial stage of adsorption, NO₂ was not detected in the outlet gas, and later, the concentration of NO₂ gradually increased to a stable level, which may also be due to the occurrence of this reaction.

From the adsorption capacity of AC under 300 ppm NO atmosphere, it can be seen that the number of active sites for NO adsorption on AC is small, and there was a phenomenon of a large amount of NO adsorption occurring under a NO + O₂ atmosphere. This may be due to the transfer of NO₂ generated after NO adsorption and oxidation to other active sites for adsorption. It may also be because the AC had a large number of active sites for O₂ adsorption, and after adsorbing O₂ on the active site, it underwent a reaction with NO, generating NO₂ and adsorbing at the active site. Therefore, experiments were conducted to pre-adsorb O₂ for 1 h and then adsorb NO to verify whether the active sites for O₂ adsorption can adsorb a large amount of NO_x.

From Fig. 5, the dynamic adsorption characteristic curve obtained by pre-adsorbing O2 and then adsorbing NO is similar to that obtained by only adsorbing NO. The NO concentration at the outlet of the reactor increased to the inlet concentration within 5 min, and no NO2 was detected. At this time, the NO_x adsorption capacity on AC was 0.026 mmol g^{-1} . The NO_x adsorption capacity of pre-adsorbed O₂ and then adsorbed NO was slightly greater than that of only adsorbed NO, indicating the existence of active sites for O₂ adsorption that can adsorb O₂ and further adsorb NO for the oxidation reaction. However, the NO_x adsorption capacity of pre-adsorbed O2 and re-adsorbed NO is much smaller than that of simultaneous adsorption of NO and O₂, indicating that the number of active sites for O2 adsorption that can react with NO is limited, which cannot cause a large amount of NO_x adsorption. This means that the oxidation of NO occurs at the active sites of limited NO and O₂ adsorption, and the generated NO₂ must undergo subsequent conversion and migration to other active sites, resulting in a significant increase in NO_x adsorption when O₂ coexists.

Temperature-programmed desorption experiments were conducted on AC samples that reached saturation adsorption under NO and NO + O₂ atmospheres and pre-adsorbed O₂ before reaching saturation adsorption under a NO atmosphere. Considering the different adsorption conversion processes that may occur in the early and later stages of adsorption under a NO + O₂ atmosphere, temperature-programmed desorption experiments were also conducted on an AC sample that was adsorbed under a NO + O₂ atmosphere for 5, 20, 70 and 110 min. The nitrogen-containing components in the desorption gas product were NO and NO₂. The NO and NO₂ desorption curves are shown in Fig. 6a and b respectively.

Only NO was observed in the product gas of AC_{NO} and AC_{O2-NO} desorption, and no NO₂ was detected. There were two desorption peaks for NO, located near 100 and 175 °C, with peak heights of 1–2 ppm. The desorption curves of the two types of AC samples almost overlap, indicating that the NO_x adsorption configurations over AC were consistent. There should be adsorbed NO and its oxidation products on AC saturated with pre-adsorbed O₂ and then adsorbed under a NO atmosphere, while only adsorbed NO should exist on the AC sample saturated with adsorption under a NO atmosphere. However, the similarity of the desorption curves between the two AC samples indicated that the



Fig. 6. (a) NO and (b) NO₂ evolution curves during temperature-programmed desorption processes of AC_{NO} , AC_{O_2-NO} , $AC_{NO+O_2-5 \text{ min}}$, $AC_{NO+O_2-20 \text{ min}}$, $AC_{NO+O_2-70 \text{ min}}$, $AC_{NO+O_2-70 \text{ min}}$, $AC_{NO+O_2-10 \text{ min}}$ and AC_{NO+O_2}

adsorption configurations of the two types of AC samples were consistent, and NO oxidation products also appeared on the surface of the AC sample saturated with adsorption under a NO atmosphere. This may be due to the oxidation of the NO adsorbed state occurring when the saturated adsorbed sample came into contact with air during transfer to the desorption reactor, which also indicated that the NO adsorbed state on the surface of AC was easily oxidized.

The desorption of AC_{NO+O2-5 min} also just release NO; NO desorption peaks appeared at 100 and 175 °C, with peak heights of 2–3 ppm. The position of the NO desorption peak of AC_{NO+O2-5 min} was consistent with that of AC_{NO} and AC_{O_2-NO} , indicating that when NO and O_2 were adsorbed simultaneously, no new NO_x adsorption configuration appeared on the AC during the initial adsorption stage. Due to the higher NO desorption peak on AC $_{\rm NO+O_2-5\ min}$ compared to AC $_{\rm NO}$ and AC $_{\rm O_2-NO},$ it represented more adsorption configurations on AC_{NO+O2}-5 min. However, due to the saturation of the active sites adsorbed by NO and O2 during the preparation of AC_{O_2-NO} , this meant that when NO and O_2 were adsorbed for 5 min in an atmosphere, in addition to the saturation of the active sites adsorbed by NO and O2, there were also other active sites to adsorb the oxidation products of NO. Because the simultaneous adsorption of NO and O₂ only involves the three gases NO, O₂, and NO₂, it was speculated that these active sites were the active sites for NO₂ adsorption. From the position of the NO desorption peak, it can be seen that AC_{O2-NO}, AC_{NO}, and AC_{NO+O2-5 min} had the same adsorption configuration. These meant that during the preparation process of AC_{O2-NO}, AC_{NO}, and AC_{NO+O2-5 min}, NO₂(ad) was easily transferred after oxidation on the active site for NO or O2 adsorption and ultimately adsorbed on the active site for NO2 adsorption.

As for $AC_{NO+O_2-20 \text{ min}}$, although the desorbed gas only contained NO, a new NO desorption peak appeared at 200–500 °C, besides those at 100 and 175 °C. As the adsorption time further increased, NO₂ appeared in the desorption product gases of $AC_{NO+O_2-70 \text{ min}}$, $AC_{NO+O_2-110 \text{ min}}$ and AC_{NO+O_2} , with a desorption peak at 100 °C. The newly generated desorption peaks during the adsorption process indicated the formation of the new NO_x adsorption configurations. This also meant that after NO was oxidized to NO₂(ad), it would not only transfer to the active site for NO₂ adsorption but also undergo further conversion reactions. To further investigate the evolution of adsorption configurations on AC during this process, an in situ DRIFTS experiment was conducted on AC in a NO + O₂ atmosphere.

The in situ DRIFTS experiment on AC under 300 ppm NO + 5 % O₂ atmosphere was conducted at 30 °C, and the observed spectra at different adsorption times are shown in Fig. 7. During the first 20 min of adsorption, the spectrum remained unchanged within the range of 2000–650 cm⁻¹, with only slight fluctuations in intensity. At 40 min, a peak appeared in the spectrum at 1360 cm⁻¹, which is the vibration



Fig. 7. In situ DRIFTS spectra of AC under 300 ppm NO + 5 % O_2 atmosphere at 30 °C.

 v_{as} (C-NO₂) of NO₂ adsorbed [23,32]. The adsorbed NO₂ should be the product of NO oxidation. At 80 min, the peak at 1360 cm⁻¹ continued to increase, and multiple small peaks appeared in the range of 1480–1415 cm⁻¹, representing the vibration of linear and monodentate nitrite [41]. This indicated that the amount of adsorbed NO₂ gradually increased during the adsorption process and there existed different adsorption forms of NO₂. A small peak also appeared at 833 cm⁻¹, representing the vibration of v_2 (NO₃) [32]. The appearance of NO₃ indicated a further conversion of adsorbed NO₂. At 120 min, the peak at 1360 cm⁻¹ increased significantly. In addition, a v_3 (NO₃) vibration peak of NO₃ appeared at 1384 cm⁻¹, and a vibration peak of (NO)₂ appeared at 1767 cm⁻¹. The appearance of (NO)₂ may be related to the accumulation and dimerization of NO filled in micropores [32]. (NO)₂ only appears in small amounts in the later stage of adsorption, indicating that its contribution to NO adsorption conversion is insignificant.

The gas–solid contact condition in the in situ DRIFTS experiment was different from the adsorption experiments conducted at a fixed-bed reactor, so the adsorption time in the in situ DRIFTS experiment cannot fully correspond to the adsorption time in the fixed-bed experiment. However, the adsorption process that occurred in the two experiments was consistent. The in situ DRIFTS experiment indicates that C-NO₂ will first appear on AC during the adsorption process, and the generated C-NO₂ can be transformed into NO₃.

Comparing the adsorption curves of AC under different adsorption conditions, it was found that only when O_2 and NO were adsorbed

simultaneously would the NO_x adsorption capacity on the AC significantly increase. According to the literature [22-24,34-36], NO and O₂ can adsorb on unsaturated carbon atoms and atoms with strong electron donating ability and then undergo a NO oxidation reaction to generate NO₂(ad). Based on the analysis of the desorption experimental results, the generated NO₂(ad) is easily transferred to the active sites of NO₂ for adsorption. Combining the results of desorption experiments with in situ DRIFTS experiments, it was found that as adsorption progresses, the adsorbed NO2 will undergo further conversion reactions to generate NO₃. Due to the oxidation of NO and the migration and transformation of NO₂ generated on the surface of AC under the action of oxygen, the adsorption of NO on AC is significantly promoted. However, further research is needed on the specific active sites and pathways involved in NO oxidation and migration transformation. Therefore, in Sections 3.2 and 3.3 of this article, quantum chemical calculations are used to study the various adsorption configurations and reaction pathways on the surface of AC, respectively.

3.2. Adsorption of NO, O2 and NO2 over activated carbon

This section considers the adsorption of NO, O₂, and NO₂ on the pristine carbonaceous model, the carbonaceous model containing unsaturated carbon atoms, and the carbonaceous models containing oxygen-containing functional groups.

Ouantum chemical calculations of NO adsorption on AC have found that NO cannot be chemically adsorbed on the active sites of the pristine carbonaceous model. On the carbonaceous model containing unsaturated carbon atoms, three adsorption configurations are formed by the interaction between N or O atoms in NO and unsaturated carbon atoms (N-down adsorption configuration of NO, O-down adsorption configuration of NO, and parallel adsorption configuration of NO), as shown in Fig. 8a-c. The adsorption energies corresponding to the three adsorption configurations are -339.8, -203.1, and -547.1 kJ·mol⁻¹. On the carbonaceous models containing oxygen-containing functional groups, calculations have shown that NO can only be chemically adsorbed on the carbonaceous models containing carbonyl or ether groups, as shown in Fig. 8d and f. On the carbonaceous model containing carbonyl group, the adsorption configuration of NO is formed by the interaction between the N atom in NO and the O atom in carbonyl group, with an adsorption energy of $-55.4 \text{ kJ} \cdot \text{mol}^{-1}$. On the carbonaceous model containing ether group, the adsorption configuration of NO is formed by the interaction between the N atom in NO and the saturated carbon atom, with an adsorption energy of -91.8 kJ·mol⁻¹.

Quantum chemical calculations of O_2 adsorption on AC have found that O_2 cannot be chemically adsorbed on the pristine carbonaceous model. On the carbonaceous model containing unsaturated carbon atoms, two adsorption configurations (single atom downward adsorption configuration of O_2 and parallel adsorption configuration of O_2) are formed by the interaction between O atoms in O_2 and unsaturated carbon atoms, as shown in Fig. 9a and b. The adsorption energies corresponding to the two adsorption configurations are -336.4 and -742.7 kJ·mol⁻¹, respectively. On the carbonaceous models containing oxygen-containing functional groups, O₂ can only be chemically adsorbed on the carbonaceous models containing hydroxyl or ether groups, as shown in Fig. 9c and d. Through the interaction between the O atom in O₂ and the saturated carbon atom near the hydroxyl functional group, a single-atom downward adsorption configuration of O₂ is formed on the carbonaceous model containing hydroxyl group, with an adsorption energy of + 69.1 kJ·mol⁻¹. On the carbonaceous model containing ether group, a single-atom downward adsorption configuration of O₂ is formed by the interaction between the O atom in O₂ and the saturated carbon atom, with an adsorption energy of -251.2 kJ·mol⁻¹.

Quantum chemical calculations of NO2 adsorption on AC have found that on the pristine carbonaceous model, two adsorption configurations (N-down adsorption configuration of NO2 and O-down adsorption configuration of NO₂) are formed by the interaction between N or O atoms in NO2 molecules and saturated carbon atoms, as shown in Fig. 10a and b. The adsorption energies corresponding to the two adsorption configurations are + 60.4 and + 68.9 kJ·mol⁻¹. The adsorption configurations formed by NO2 adsorption on the carbonaceous model containing unsaturated carbon atoms are shown in Fig. 10c–f. Four adsorption configurations are formed by the interaction between N or O atoms in NO2 molecules and unsaturated carbon atoms (N-down adsorption configuration of NO2, O-down adsorption configuration of NO2, N and O atoms downward adsorption configuration of NO₂, and two O atoms downward adsorption configuration of NO₂). The adsorption energy distribution of these NO2 adsorption configurations ranges from -516.42 - -384.17 kJ·mol⁻¹. On the carbonaceous models containing oxygen-containing functional groups, NO2 can adsorb on carbonaceous models containing carbonyl, hydroxyl, or ether groups, as shown in Fig. 10g-l. On the carbonaceous model containing carbonyl groups, two adsorption configurations (N-down adsorption configuration of NO₂ and O-down adsorption configuration of NO₂) are formed by the interaction between N or O atoms in NO2 and O atoms in carbonyl groups, as shown in Fig. 10g and h. The adsorption energies of these two adsorption configurations are -32.53 and + 99.66 kJ·mol⁻¹, respectively. On the carbonaceous model containing hydroxyl groups, two adsorption configurations (N-down adsorption configuration of NO2 and O-down adsorption configuration of NO₂) are formed by the interaction between N or O atoms in NO2 and saturated carbon atoms near the hydroxyl group, as shown in Fig. 10i and j. The adsorption energies of these two adsorption configurations are + 61.65 and + 70.89 kJ·mol⁻¹, respectively. On the carbonaceous model containing ether groups, two adsorption configurations (N-down adsorption configuration of NO2 and O-down adsorption configuration of NO₂) are formed by the interaction between N or O atoms in NO2 and saturated carbon atoms, as shown in Fig. 10k and l. The adsorption energies of these two adsorption configurations are -173.9 and -182.8 kJ·mol⁻¹, respectively.

From the above adsorption calculations of NO, O2, and NO2 on AC,



Fig. 8. The adsorption configurations of NO on AC. (a) N-down adsorption configuration and (b) O-down adsorption configuration on the carbonaceous model containing unsaturated carbon atoms. (c) parallel adsorption configuration on the carbonaceous model containing unsaturated carbon atoms. (d) adsorption configuration on the carbonaceous model containing ether group.



Fig. 9. The adsorption configuration of O_2 on AC. (a) single atom downward adsorption configuration and (b) parallel adsorption configuration on the carbonaceous model containing unsaturated carbon atoms. (c) adsorption configuration on the carbonaceous model containing hydroxyl group. (d) adsorption configuration on the carbonaceous model containing ether group.



Fig. 10. The adsorption configurations of NO_2 on AC. (a) N-down adsorption configuration and (b) O-down adsorption configuration on the pristine carbonaceous model. (c) N-down adsorption configuration. (d) O-down adsorption configuration, (e) N and O atoms downward adsorption configuration and (f) two O atoms downward adsorption configuration on the carbonaceous model containing unsaturated carbon atoms. (g) N-down adsorption configuration and (h) O-down adsorption configuration on the carbonaceous model containing carbonyl group. (i) N-down adsorption configuration and (j) O-down adsorption configuration on the carbonaceous model containing carbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) O-down adsorption configuration on the carbonaceous model containing earbonyl group. (i) N-down adsorption configuration on the carbonaceous model containing earbonyl group.

the pristine carbonaceous model cannot chemically adsorb NO and O_2 and has no contribution to NO oxidation. NO and O_2 can be chemically adsorbed on unsaturated carbon atoms, and according to published literature [23,24], the oxidation reaction of NO can occur at this site.

However, the adsorption energies of the generated NO₂ on unsaturated carbon atoms are less than $-105 \text{ kJ} \cdot \text{mol}^{-1}$, which is very stable. The adsorption energy is negative and the value is large, making it difficult to complete the NO₂ desorption reaction due to the long time required

[42]. This means that although unsaturated carbon atoms can catalyze the oxidation of NO, the generated NO₂ cannot undergo subsequent migration and transformation. Therefore, unsaturated carbon atoms do not contribute to the significant increase in NO adsorption capacity in the presence of an O₂ atmosphere. The carbonaceous model containing carbonyl or ether groups can chemically adsorb NO, while the carbonaceous model containing hydroxyl or ether groups can chemically adsorb O2. If NO oxidation reactions occur on the carbonaceous model containing ether group, the adsorption energies of generated NO₂ are less than -173.5 kJ·mol⁻¹. The generated NO₂ is also difficult to desorb, which means that the active sites on the carbonaceous model containing ether group also do not contribute to the significant increase in NO adsorption capacity in an O2 atmosphere. However, if NO oxidation reactions occur at active sites on carbonaceous models containing carbonyl or hydroxyl groups, the adsorption energies of generated NO₂ are greater than -32.53 kJ·mol⁻¹, making it easy to desorb. Desorbed NO2 can be adsorbed on saturated carbon atoms, unsaturated carbon atoms, and saturated carbon atoms near ether group, which can increase the adsorption capacity of NO_x on AC. Therefore, in Section 3.3, the NO oxidation reaction on carbonaceous models containing carbonyl or hydroxyl groups and the subsequent NO₂ conversion reaction are studied through quantum chemical calculations.

3.3. Pathways of NO oxidation and NO₂ conversion

According to the adsorption calculations of NO and O_2 in Section 3.2, only NO can be chemically adsorbed on the carbonaceous model containing carbonyl groups, and only O₂ can be chemically adsorbed on the carbonaceous model containing hydroxyl groups. Taking these two adsorption configurations as the initial adsorption configurations for the NO oxidation reaction, the calculated oxidation reaction pathways are shown in Fig. 11. Fig. 11a shows the oxidation pathway on the carbonaceous model containing carbonyl groups. After NO is adsorbed on the O atom of the carbonyl group, it is activated. After breaking through the energy barrier of 185.6 kJ·mol⁻¹ the adsorbed NO can remove one O atom of a gaseous O2, and the other O atom of the gaseous O2 will combine with a gaseous NO. The oxidation process will generate one Ndown adsorption configuration of NO2 and one O-down adsorption configuration of NO₂. The energy barrier of this oxidation pathway is high, making it difficult to spontaneously occur at room temperature. Fig. 11b shows the oxidation pathway on the carbonaceous model containing hydroxyl groups. After O2 is adsorbed and activated on the saturated carbon atom adjacent to the hydroxyl functional group, the C-O-O formed can provide an O atom to a gaseous NO, generating a C-O and an O-down adsorption configuration of NO₂. The energy barrier for this oxidation process is only 40.6 kJ·mol⁻¹, and the energy barrier for NO₂ desorption is 87.1 kJ·mol⁻¹. The oxidation reaction between the C-O-O and NO and the desorption of NO₂ can occur at room temperature. Subsequently, the generated C-O can react with gaseous NO after breaking through the energy barrier of 96.9 kJ·mol⁻¹, generating an O-

down adsorption configuration of NO₂, and the energy barrier for NO₂ desorption is only $5.5 \text{ kJ} \cdot \text{mol}^{-1}$. The oxidation reaction between the C-O and NO, as well as the desorption of generated NO₂, can also occur at room temperature. Therefore, it can be determined that the oxidation of NO and the desorption of NO₂ can occur continuously on the carbonaceous model containing hydroxyl groups.

After the NO₂ generated by NO oxidation on the carbonaceous model containing hydroxyl groups is desorbed to the gas phase, according to the calculation of the NO₂ adsorption configuration in Section 3.2, it can be chemically adsorbed on the saturated, unsaturated carbon atoms on the surface of AC. Considering that unsaturated carbon atoms and saturated carbon atoms near ether group can adsorb NO, it can be concluded that the adsorption of gaseous NO₂ on saturated carbon atoms is the main pathway for a significant increase in NO adsorption under a NO + O₂ atmosphere. Therefore, taking the pristine carbonaceous model as an example, we investigate the subsequent conversion of NO₂ adsorbed on the saturated carbon atom of this model. In the pristine carbonaceous model, there are two types of NO₂ adsorption configurations, namely, the N-down adsorption configuration of NO₂.

According to the calculation of adsorption energy for the two adsorption configurations in Section 3.2, the heat absorbed during the formation of the N-down adsorption configuration of NO₂ is less than that of the O-down adsorption configuration of NO₂, indicating that the N-down adsorption configuration of NO₂ is more stable. Through calculations, it is found that the more stable N-down adsorption configuration of NO₂ can undergo conversion. The reaction pathway is shown in Fig. 12. From Fig. 12, after the O-down adsorption configuration of NO₂ breaks through the energy barrier of $81.3 \text{ kJ} \cdot \text{mol}^{-1}$, the N-O bond of NO₂ close to the carbon atom breaks, forming a C-O and NO molecule. The generated NO molecule is released



Fig. 12. NO2 conversion pathway on the pristine carbonaceous model.



Fig. 11. NO oxidation pathways on the carbonaceous models containing (a) carbonyl or (b) hydroxyl groups.

into the gas phase after breaking through the energy barrier of 9.8 kJ·mol⁻¹, while the C-O can combine with another gaseous NO₂ molecule to form NO₃⁻ after breaking through the energy barrier of 100.4 kJ·mol⁻¹, and the generated NO₃⁻ can be chemically adsorbed on the pristine carbonaceous model.

Based on the analysis of the adsorption configurations and reaction pathways of NO, O₂, and NO₂ on different carbonaceous models, the main pathway through which O₂ promotes NO adsorption on AC can be proposed. First, O₂ adsorbs on active carbon atoms near the hydroxyl functional groups on the surface of AC and then reacts with gaseous NO molecules to generate NO₂, which is desorbed and released into the gas phase. NO₂ in the gas phase can be adsorbed on saturated carbon atoms, forming a N-down adsorption configuration of NO₂ and an O-down adsorption configuration of NO₂. The N-down adsorption configuration of NO₂ can exist stably at this site and no longer react. The O-down adsorption configuration of NO₂ will oxidize the active site to form a C-O and release NO into the gas phase. The C-O will further react with the gaseous NO₂ to form NO₃ and remain stable.

The proposed path can effectively explain the experimental phenomenon of O₂ promoting NO adsorption on AC. On the active carbon atoms near the hydroxyl functional groups on the surface of AC, continuous adsorption of O2, oxidation reaction with gaseous NO, and desorption of generated NO2 occur. During the initial stage of the adsorption experiment, all the desorbed NO2 will be adsorbed by saturated carbon atoms, causing an increase in the NO adsorption amount, but NO2 cannot be observed in the outlet gas of the reactor. A portion of NO2 adsorbed by saturated carbon atoms is stably adsorbed in the Ndown adsorption configuration, which explains the C-NO₂ observed in the in situ DRIFTS experiment. The other portion is adsorbed in the Odown adsorption configuration and gradually oxidizes the active sites to form a C-O, releasing NO into the gas phase. Therefore, in the middle stage of the adsorption experiment, a slight increase in the concentration of NO at the reactor outlet can be observed. The generated C-O further reacts with gaseous NO₂ to generate NO₃; thus, the in situ DRIFTS experiment shows the appearance of NO₃ on the surface of the AC during the later stage of the adsorption experiment. As an increasing number of saturated carbon atoms are occupied by the N-down adsorption configuration of NO₂ and NO₃, the number of active sites available for adsorption of NO₂ decreases, while the O-down adsorption configuration of NO2 and NO generated through oxidation of active sites decreases. Therefore, as the adsorption reaction progresses, a gradual increase in NO2 concentration and a phenomenon of NO concentration first increasing and then decreasing until stable will be observed at the reactor outlet.

The desorption characteristics can also be well explained by the proposed path. The nitrogen-containing components present on the AC samples at the initial stage of adsorption in the $NO + O_2$ atmosphere are mainly the N-down adsorption configuration of NO2 and the O-down adsorption configuration of NO2. Therefore, NO desorption peaks at 100 and 175 °C appear in the desorption experiment of $AC_{NO+O_2-5 min}$. As the adsorption proceeds, the O-down adsorption configuration of NO2 will oxidize the active site to form C-O, and C-O will further react with gasphase NO₂ to form NO₃. The generated NO₃ corresponds to the NO₂ desorption peak at 100 °C newly observed in the desorption experiment of $AC_{NO+O_2\mbox{-}70\mbox{ min}}.$ As the adsorption further continues, the N-down adsorption configuration of NO_2 and NO_3^- will accumulate on the surface of the activated carbon, corresponding to the significant rise in the NO and NO2 desorption peaks at 100 °C observed in the desorption experiments of AC_{NO+O2}-110 min and AC_{NO+O2}. The nitrogen-containing components present in the saturated AC samples adsorbed in the NO + O₂ atmosphere are mainly N-down adsorption configurations of NO2 and NO₃, which correspond to the observed NO and NO₂ desorption peaks at 100 °C in the corresponding sample desorption experiments.

From the main pathway through which O₂ promotes NO adsorption on AC, there are two types of active sites involved in this process, namely, active carbon atoms near the hydroxyl functional groups and saturated carbon atoms. The active carbon atoms near the hydroxyl functional group mainly play a catalytic role in the oxidation of NO, while the saturated carbon atoms mainly store nitrogen-containing components. Therefore, increasing the number of hydroxyl functional groups on AC and improving the adsorption activity of saturated carbon atoms through surface modification can help improve the adsorption rate and capacity of NO on AC under an oxygen atmosphere.

4. Conclusion

This study proposes the main pathway through which O₂ promotes NO adsorption on activated carbon. The adsorption experiments show that O₂ can significantly promote the adsorption of NO on activated carbon. However, compared to untreated activated carbon, the activated carbon treated with preabsorbed O₂ has a slightly stronger ability to adsorb NO. This indicates that the active sites of O₂ adsorption have a limited contribution to the adsorption of NO, and NO oxidation occurs on a limited number of active sites of NO or O₂ adsorption. New NO and NO₂ desorption peaks appear in the temperature-programmed desorption of samples adsorbed under a $NO + O_2$ atmosphere. This indicates that after NO oxidation occurs on the surface of activated carbon to form NO₂, NO₂ not only migrates to active sites for NO₂ adsorption but also undergoes further conversion reactions. The in situ DRIFTS experiment on the adsorption process of activated carbon under a $NO + O_2$ atmosphere indicates that C-NO2 appears first on the surface of the activated carbon, and the generated C-NO2 is then transformed into NO3. Through calculation and analysis of the adsorption sites and configurations of NO, O₂, and NO₂ on activated carbon, although saturated carbon atoms near ether groups and unsaturated carbon atoms can adsorb NO or O₂, the NO₂ generated by oxidation reaction is difficult to desorb. Therefore, the contribution of these two active sites to the significant increase in NO adsorption capacity under an O2 atmosphere is very small. However, after adsorbing NO on the active site near the carbonyl group or O₂ on the active site near the hydroxyl group, the NO₂ generated by the oxidation reaction can be desorbed and further adsorbed on the saturated carbon atom. This may be the main pathway for O₂ to promote the adsorption of NO on activated carbon. By calculating the reaction pathway on activated carbon, the NO oxidation reaction on the carbonaceous model containing carbonyl groups has a high energy barrier and is difficult to occur. The O2 adsorbed on the carbonaceous model containing hydroxyl groups can undergo an oxidation reaction with gasphase NO molecules, and the generated NO₂ has a low energy barrier for desorption and can be desorbed. There are two adsorption configurations for NO2 adsorbed on the pristine carbonaceous model. The Ndown adsorption configuration of NO₂ is stable and no longer converts, while the O-down adsorption configuration of NO₂ oxidizes the active site to form C-O and releases NO into the gas phase. The C-O structure generated on the active site further reacts with the gas phase NO₂ to form NO_3^- and remains stable. There are two types of active sites involved in the main pathway through which O₂ promotes NO adsorption on AC, namely, active carbon atoms near hydroxyl functional groups and saturated carbon atoms. The active carbon atoms near the hydroxyl functional groups mainly play a catalytic role in the oxidation of NO, while the saturated carbon atoms mainly store nitrogencontaining components. The results can help improve the performance of activated carbon in adsorbing NO in low-temperature flue gas.

CRediT authorship contribution statement

Zhongwei Li: Conceptualization, Data curation, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Guochang Song:** Data curation, Methodology, Software, Validation. **Xingyu Yang:** Investigation, Visualization, Writing – review & editing. **Qiang Song:** Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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References

- Z. Zeng, P. Lu, C. Li, L. Mai, Z. Li, Y. Zhang, Removal of NO by carbonaceous materials at room temperature: A review, Catal, Sci. Technol. 2 (2012) 2188–2199, https://doi.org/10.1039/C2CY20183F.
- [2] R. Zhang, F. Gao, X. Tang, H. Yi, Y. Zhou, Temperature responses of two synergistic pathways for low-temperature catalytic oxidation of high-concentration NO over ACFs: Nano-confinement and nitrogen-containing groups, Fuel 325 (2022), 124878, https://doi.org/10.1016/j.fuel.2022.124878.
- [3] D. Damma, P.R. Ettireddy, B.M. Reddy, P.G. Smirniotis, A Review of Low Temperature NH₃-SCR for Removal of NO_x, Catalysts 9 (2019) 349, https://doi. org/10.3390/catal9040349.
- [4] Y. Peng, J. Li, L. Chen, J. Chen, J. Han, H. Zhang, W. Han, Alkali metal poisoning of a CeO₂–WO₃ catalyst used in the selective catalytic reduction of NO_x with NH₃: an experimental and theoretical study, Environ. Sci. Technol. 46 (2012) 2864–2869, https://doi.org/10.1021/es203619w.
- [5] M. Jeguirim, M. Belhachemi, L. Limousy, S. Bennici, Adsorption/reduction of nitrogen dioxide on activated carbons: textural properties versus surface chemistry – a review, Chem. Eng. J. 347 (2018) 493–504, https://doi.org/10.1016/j. cei.2018.04.063.
- [6] Z. Wang, L. Pan, Implementation results of emission standards of air pollutants for thermal power plants: a numerical simulation, Huan Jing Ke Xue 35 (2014) 853–863, https://doi.org/10.13227/j.hjkx.2014.03.007.
- [7] A. Claudino, J.L. Soares, R. Moreira, H.J. Jose, Adsorption equilibrium and breakthrough analysis for NO adsorption on activated carbons at low temperatures, Carbon 42 (2004) 1483–1490, https://doi.org/10.1016/j.carbon.2004.01.048.
- [8] B. Li, L. Zhang, Z. Wang, C. Ma, NO adsorption over powder activated carbon in a fluidized bed, Asia-Pacific Power and Energy Engineering Conference 2011 (2011) 1–4.
- [9] S. Wang, S. Xu, S. Gao, P. Xiao, M. Jiang, H. Zhao, B. Huang, L. Liu, H. Niu, J. Wang, D. Guo, Simultaneous removal of SO₂ and NO_x from flue gas by lowtemperature adsorption over activated carbon, Sci. Rep. 11 (2021) 11003, https:// doi.org/10.1038/s41598-021-90532-9.
- [10] M. Jeguirim, V. Tschamber, J.F. Brilhac, P. Ehrburger, Interaction mechanism of NO₂ with carbon black: effect of surface oxygen complexes, J. Anal. Appl. Pyrolysis 72 (2004) 171–181, https://doi.org/10.1016/j.jaap.2004.03.008.
- [11] K. Kante, E. Deliyanni, T.J. Bandosz, Interactions of NO₂ with activated carbons modified with cerium, lanthanum and sodium chlorides, J. Hazard. Mater. 165 (2009) 704–713, https://doi.org/10.1016/j.jhazmat.2008.10.092.
- [12] M. Belhachemi, M. Jeguirim, L. Limousy, F. Addoun, Comparison of NO₂ removal using date pits activated carbon and modified commercialized activated carbon via different preparation methods: effect of porosity and surface chemistry, Chem. Eng. J. 253 (2014) 121–129, https://doi.org/10.1016/j.cej.2014.05.004.
- [13] Z. Zhang, J.D. Atkinson, B. Jiang, M.J. Rood, Z. Yan, Nitric oxide oxidation catalyzed by microporous activated carbon fiber cloth: An updated reaction mechanism, Appl. Catal. B Environ. 148–149 (2014) 573–581, https://doi.org/ 10.1016/j.apcatb.2013.10.050.
- [14] S.A. Dastgheib, H. Salih, T. Ilangovan, J. Mock, NO Oxidation by activated carbon catalysts: impact of carbon characteristics, pressure, and the presence of water, Acs Omega 5 (2020) 21172–21180, https://doi.org/10.1021/acsomega.0c02891.
- [15] I. Mochida, S. Kisamori, M. Hironaka, S. Kawano, Y. Matsumura, M. Yoshikawa, Oxidation of NO into NO₂ over active carbon fibers, Energy Fuels 8 (1994) 1341–1344, https://doi.org/10.1021/ef00048a024.
- [16] I. Mochida, Y. Kawabuchi, S. Kawano, Y. Matsumura, M. Yoshikawa, High catalytic activity of pitch-based activated carbon fibres of moderate surface area for oxidation of NO to NO₂ at room temperature, Fuel 76 (1997) 543–548, https://doi. org/10.1016/S0016-2361(96)00223-2.
- [17] Z. Guo, Y. Xie, I. Hong, J. Kim, Catalytic oxidation of NO to NO₂ on activated carbon, Energy Convers. Manage. 42 (2001) 2005–2018, https://doi.org/10.1016/ S0196-8904(01)00058-9.

- [18] J. Wang, M. Yang, D. Deng, S. Qiu, The adsorption of NO, NH₃, N₂ on carbon surface: a density functional theory study, J. Mol. Model. 23 (2017) 262, https:// doi.org/10.1007/s00894-017-3429-2.
- [19] H. Zhang, J. Liu, X. Wang, L. Luo, X. Jiang, DFT study on the C(N)-NO reaction with isolated and contiguous active sites, Fuel 203 (2017) 715–724, https://doi. org/10.1016/j.fuel.2017.05.023.
- [20] J. Yang, S. Yuan, S. Wang, M. Yang, B. Shen, Q. Zhang, Z. Zhang, F. Wang, L. Xu, Z. Wang, Density functional theory study on the effect of sodium on the adsorption of NO on a char surface, Energy Fuels 34 (2020) 8726–8731, https://doi.org/ 10.1021/acs.energyfuels.0c00987.
- [21] L. Chen, J. Yang, M. Zhang, M. Gao, J. Su, Y. Huang, Z. Zhang, Z. Wang, L. Xu, B. Shen, Theoretical study of NO adsorption by hydroxyl-containing char with the participation of Na/K, Langmuir 38 (2022) 9940–9954, https://doi.org/10.1021/ acs.langmuir.2c01244.
- [22] Z. Qu, F. Sun, X. Pi, X. Li, D. Wu, J. Gao, G. Zhao, One-step synergistic optimization of hierarchical pore topology and nitrogen dopants in activated coke for efficient catalytic oxidation of nitric oxide, J. Clean. Prod. 335 (2022), 130360, https://doi. org/10.1016/j.jclepro.2022.130360.
- [23] X. Zhu, L. Zhang, T. Wang, J. Li, X. Zhou, C. Ma, Y. Dong, An updated study on NO catalytic oxidation over activated carbon: The effect of pore structure and a dualsite mechanism, Fuel 311 (2022), 122627, https://doi.org/10.1016/j. fuel.2021.122627.
- [24] Z. Li, W. Zhang, Z. Chen, Q. Zhang, X. Yang, S. Mao, W. Jian, Reaction mechanism for NO oxidation on the soot surface using a quantum chemistry, Fuel 313 (2022), 123032, https://doi.org/10.1016/j.fuel.2021.123032.
- [25] W.J. Zhang, S. Rabiei, A. Bagreev, M.S. Zhuang, E. Rasouli, Study of NO adsorption on activated carbons, Appl. Catal. B Environ. 83 (2008) 63–71, https://doi.org/ 10.1016/j.apcatb.2008.02.003.
- [26] W.-J. Zhang, A. Bagreev, F. Rasouli, Reaction of NO₂ with activated carbon at ambient temperature, Ind. Eng. Chem. Res. 47 (2008) 4358–4362, https://doi.org/ 10.1021/ie800249s.
- [27] J.D. Atkinson, Z. Zhang, Z. Yan, M.J. Rood, Evolution and impact of acidic oxygen functional groups on activated carbon fiber cloth during NO oxidation, Carbon 54 (2013) 444–453, https://doi.org/10.1016/j.carbon.2012.11.060.
- [28] I. Mochida, N. Shirahama, S. Kawano, Y. Korai, A. Yasutake, M. Tanoura, S. Fujii, M. Yoshikawa, NO oxidation over activated carbon fiber (ACF). Part 1. extended kinetics over a pitch based ACF of very large surface area, Fuel 79 (2000) 1713–1723, https://doi.org/10.1016/S0016-2361(00)00034-X.
- [29] S. Adapa, V. Gaur, N. Verma, Catalytic oxidation of NO by activated carbon fiber (ACF), Chem. Eng. J. 116 (2006) 25–37, https://doi.org/10.1016/j. cei.2005.10.007.
- [30] W. Deng, C. Tao, K. Cobb, H. Zhou, Y. Su, R. Ruan, Catalytic oxidation of NO at ambient temperature over the chars from pyrolysis of sewage sludge, Chemosphere 251 (2020), 126429, https://doi.org/10.1016/j.chemosphere.2020.126429.
- [31] X. Zou, S. Lou, C. Yang, N. Liu, X. Wang, L. Shi, X. Meng, Catalytic oxidation of NO on N-doped carbon materials at low temperature, Catal. Lett. 151 (2021) 487–496, https://doi.org/10.1007/s10562-020-03297-7.
- [32] F. You, G. Yu, Z. Xing, J. Li, S. Xie, C. Li, G. Wang, H. Ren, Y. Wang, Enhancement of NO catalytic oxidation on activated carbon at room temperature by nitric acid hydrothermal treatment, Appl. Surf. Sci. 471 (2019) 633–644, https://doi.org/ 10.1016/j.apsusc.2018.12.066.
- [33] A.P. Terzyk, The influence of activated carbon surface chemical composition on the adsorption of acetaminophen (paracetamol) in vitro: Part II. TG, FTIR, and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the neutral pH, Colloids Surf. A Physicochem. Eng. Asp. 177 (2001) 23–45, https://doi. org/10.1016/S0927-7757(00)00594-X.
- [34] X. Pi, F. Sun, J. Gao, Z. Qu, A. Wang, Z. Qie, L. Wang, H. Liu, A new insight into the SO₂ adsorption behavior of oxidized carbon materials using model adsorbents and DFT calculations, Phys. Chem. Chem. Phys. 21 (2019) 9181–9188, https://doi.org/ 10.1039/C8CP07782G.
- [35] X. Zhu, L. Zhang, M. Zhang, C. Ma, Effect of N-doping on NO₂ adsorption and reduction over activated carbon: An experimental and computational study, Fuel 258 (2019), 116109, https://doi.org/10.1016/j.fuel.2019.116109.
- [36] Z. Qu, F. Sun, J. Gao, X. Pi, Z. Qie, G. Zhao, A new insight into SO₂ lowtemperature catalytic oxidation in porous carbon materials: non-dissociated O₂ molecule as oxidant, Catal, Sci. Technol. 9 (2019) 4327–4338, https://doi.org/ 10.1039/C9CY00960D.
- [37] P. Bultinck, S. Fias, C. Van Alsenoy, P.W. Ayers, R. Carbó-Dorca, Critical thoughts on computing atom condensed Fukui functions, J. Chem. Phys. 127 (2007), https://doi.org/10.1063/1.2749518.
- [38] S. Liu, Conceptual density functional theory and some recent developments, Acta Phys.-Chim. Sin. 25 (2009) 590–600, https://doi.org/10.3866/PKU. WHXB20090332.
- [39] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580–592, https://doi.org/10.1002/jcc.22885.
- [40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W.

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Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 09, ReVision C.01, Gaussian, Inc., Wallingford, CT, 2009.

- [41] H. Liang, K. Gui, X. Zha, DRJFTS study of γFe₂O₃ nano-catalyst for low-temperature selective catalytic reduction of NO_x with NH₃, Can. J. Chem. Eng. 94 (2016) 1668–1675, https://doi.org/10.1002/cjce.22546.
- [42] P.H. Scudder, Electron Flow in Organic Chemistry: A Decision-Based Guide to Organic Mechanisms, third ed., John Wiley & Sons, New Jersey, 2023.