



Density functional theory on the mechanism of NO reduction by hydroxyl groups during oxy-fuel combustion

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ABSTRACT

To further clarify the influence mechanism of the hydroxyl group on NO heterogeneous reduction over char, this study demonstrates that the hydroxyl group affects the NO reduction over char through two different pathways based on density functional theory (DFT). For the first pathway, termed “Adsorption-only”, the hydroxyl group merely adsorbs onto the char surface as a surface functional group. Conversely, for the second pathway, termed “Modification”, the hydroxyl group engages in reactions with the char, inducing a redistribution of active sites on the char surface. Kinetics calculations reveal that the “Adsorption-only” pathway inhibits NO heterogeneous reduction over char, while the “Modification” pathway substantially enhances the reduction process. From the standpoint of the reaction pathway, the “Modification” mechanism shortens the reduction reaction pathway. Additionally, wave function analysis shows that this mechanism involves Coulomb attraction during bond formation and Coulomb repulsion during bond breaking, potentially lowering the energy barrier.

1. Introduction

Oxy-fuel combustion has been extensively studied as a highly promising means to reduce CO₂ emissions. In oxy-fuel combustion, the fuel is burned in a mixture of O₂ and recycled flue gas (mainly composed of H₂O and CO₂). The significant changes in the atmospheric conditions of oxy-fuel combustion, characterized by higher levels of H₂O and CO₂ compared to conventional air combustion, call for a reevaluation of the various chemical reactions during the combustion process (Yadav and Mondal, 2022; Deng et al., 2022; Ling et al., 2023; Liu et al., 2019; Toftagaard et al., 2010; Liu et al., 2019). NO is one of the major pollutants from fossil fuel combustion, and controlling NO emissions is key to achieving clean and efficient combustion of fossil energy. During combustion, the NO heterogeneous reduction by char accounts for a significant portion of total NO reduction (Shu et al., 2015; Xu et al., 2023). Biomass is receiving increasing attention as a readily available renewable carbon-based energy source. It has been found that certain biomass chars contain a large number of oxygen-containing functional groups on their surfaces. These functional groups play a crucial role in regulating acidic pollutants like nitrogen oxides (Chen et al., 2017; Wang et al., 2020; Li et al., 2022). Some researchers used alkaline solutions to modify char, and the experimental results showed that the concentration of hydroxyl groups and other oxygen-containing

functional groups on the surface of the modified char was significantly increased, and the adsorption capacity of nitrogen oxides was also significantly enhanced by a factor of 3.3–3.5 (Anthonysamy et al., 2022). Gong et al. (Gong et al., 2021) conducted the experimental study employing three distinct biomass chars for NO reduction, observing that the biomass char with the highest concentration of oxygen-containing functional groups demonstrated the most substantial reduction rate of NO.

Quantum chemical method has been more and more widely applied to the field of combustion as computer technology has advanced (Zhao et al., 2020; Gao et al., 2017; Chen et al., 2023; Zhang et al., 2020). Quantum chemical methods can predict chemical reaction pathways, quantitatively calculate chemical reaction rates, and better understand chemical reaction mechanisms, thus greatly compensating for the inadequacy of experimental studies in describing chemical reaction mechanisms. Zhang et al. (Zhang et al., 2014) calculated the effect of the presence of hydroxyl groups in the environment on the NO heterogeneous reduction on char using density functional theory and traditional transition state theory and found that hydroxyl groups help release active sites on the surface of char, increasing the surface reactivity of char. In addition, Chen et al. (Chen et al., 2021) calculated the pathway of the NO heterogeneous reduction on nitrogen-containing char with and without hydroxyl groups and found that hydroxyl groups changed

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the pathway of generation of the reduction product N_2 and increased the rate of N_2 desorption on the surface of char.

The influence of the reaction atmosphere on the concentration of oxygen-containing functional groups on the carbon surface cannot be neglected during oxy-fuel combustion (Luo et al., 2023; Qing et al., 2019). Previous research has demonstrated that oxygen in the reaction atmosphere can promote the production of oxygen-containing functional groups on the surface of the char, such as hydroxyl, carbonyl, quinone, and carboxyl groups, increasing the reactivity of char (Zhang et al., 2014; Ibarra and Miranda, 1996; Suzuki et al., 1994). Besides, water molecules can decompose into hydrogen atoms and hydroxyl radicals at high temperatures, and the resulting free hydroxyls adsorb onto the char surface to form oxygen-containing functional groups (Wang et al., 2019). Yue et al. (Yue et al., 2022; Yue et al., 2022) further demonstrated by Fourier transform infrared spectroscopy (FTIR) that the concentration of hydroxyl groups on the pyrolyzed char surface increased significantly in the presence of H_2O in the atmosphere. In their kinetic simulation calculations, Hong et al. (Hong et al., 2020) revealed that the presence of both H_2O and O_2 in the atmosphere promotes reaction (1), resulting in a drastic increase in the concentration of hydroxyl radicals in the atmosphere.



According to existing studies, hydroxyl groups on the char surface can significantly influence the heterogeneous reduction of NO. However, before the gas-solid reaction can occur, hydroxyl groups in the reaction atmosphere must first be adsorbed onto the char surface. A critical aspect of understanding how hydroxyl groups affect the NO heterogeneous reduction on char is clarifying the adsorption process of these groups and their subsequent behavior on the char surface. Unfortunately, existing research has not focused specifically on this subject. Therefore, this paper initially investigates the hydroxyl group adsorption process on char using quantum chemical calculations, identifies two distinct mechanisms through which the hydroxyl group influences the heterogeneous reaction between char and NO, and finally elucidates the reasons behind the differing effects of these mechanisms on the chemical reaction through kinetic analysis and wave function analysis.

2. Computation and methods

To ensure the accuracy of the results derived from quantum chemical calculations, selecting an appropriate computational model is vital. Existing studies have shown that during the pyrolysis of coal or biomass, aliphatic hydrocarbons in the molecular structure of char are destroyed and small aromatic rings are continuously polymerized to form large-sized aromatic systems (Xu et al., 2016; Li et al., 2006). Additionally, solid-state Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR) investigations have shown that the molecular structure of char is mainly composed of interconnected aromatic structures. The percentage of aromatic carbon in the total carbon content further increases with the rise in pyrolysis temperature and duration, reaching up to 97 % (Munira et al., 2021; Mafu et al., 2017). The study by Plencia et al. (Plencia et al., 2023) demonstrated that biochar derived from biomass pyrolysis contains a significant amount of graphite structures, and these graphite structures increase with the rise in pyrolysis temperature. Similarly, Liu et al. (Liu et al., 2015) conducted XRD, Raman, and FTIR characterizations on coal pyrolysis char and found that as the carbon conversion efficiency exceeded 0.9, the majority of amorphous carbon had been consumed, leaving graphite carbon as the only predominant carbon type in the char residues. Furthermore, the studies by Yin et al. (Yin et al., 2022) and Zhang et al. (Zhang et al., 2024) investigated the structural evolution of coal during the pyrolysis process. They found that with the increase in pyrolysis temperature, the amorphous carbon in coal char gradually transforms into graphite-like structures, leading to a significant rise in the degree of graphitization of the char. Additionally, as the

temperature increases, heteroatoms (O) are further eliminated, primarily reflected in the decreasing relative content of $C=O$ and $-COOH$ groups.

Therefore, a graphite structure containing 6–7 benzene rings (Fig. 1) was selected as the computational model. Additionally, studies by Chen et al. (Chen and Yang, 1998) and Yang et al. (Yang and Yang, 2002) showed that when using this model, the computational data closely matched the experimental data. The unsaturated carbon atoms at the top of this computational model are used to simulate the active sites present on the char surface.

In density functional theory methods, the choice of basis set and functional significantly impacts computational precision and cost. In the selection of functional, the B3LYP functional offers advantages such as low spin contamination, robustness, and broad applicability, effectively balancing accuracy and computational expense in calculations (Stephens et al., 1994). However, B3LYP has limitations in accurately computing weak interactions, and the dispersion correction term of DFT-D3 is introduced to address this shortcoming (Grimme et al., 2010; Goerigk et al., 2017). For the selection of the basis sets, the 6-31G(d) basis set is employed for geometry optimization and vibrational analysis due to its efficiency in these aspects. On the other hand, the def2-TZVP basis set is selected for single-point energy calculations, as these calculations are more sensitive to the choice of basis set. Employing this combination enables significant cost reductions while maintaining a high level of computational accuracy.

During quantum chemical calculations, each transition state structure in the chemical reaction pathway was verified to have one and only one imaginary frequency and the intrinsic reaction coordinates (IRC) were calculated to ensure that each transition state structure connected to the correct reactants and products. The thermodynamic parameters of each structure at different temperatures were calculated using the Shermo program (Lu and Chen, 2021). The thermodynamic parameters of each structure were corrected with zero point energy correction (frequency scaling factor of 0.981) to eliminate systematical errors introduced by the harmonic approximation and the calculation level itself. Since this study does not involve vibrational spectra, the fundamental frequency correction was not considered.

The transition state theory (TST) was used in the reaction kinetics analysis, with the formula for calculating the reaction rate constant of elementary reactions as (Gao et al., 2017):

$$k(T) = \lambda \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

Eq. (2) can be rewritten in an equivalent thermodynamic form:

$$k(T) = \sigma \frac{k_B T}{h} \left(\frac{RT}{P_0}\right)^{\Delta n} \exp\left(-\frac{\Delta G^{0,\ddagger}}{k_B T}\right) \quad (3)$$

$$\Delta G^{0,\ddagger}(T) = \Delta G^{0,\ddagger}(T) - G_{Reactant}^0(T) \quad (4)$$

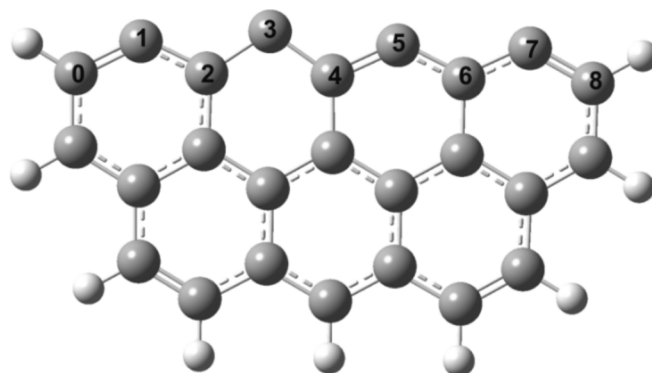


Fig. 1. The Char model.

In where, $\Delta G^{0\ddagger}(T)$ is standard-state activation free energy. k_B is the Boltzmann constant. h is the Planck constant. T is the thermodynamic temperature. $Q^\ddagger$ is the partition function of the transition state. Q_A and Q_B are the total partition functions of the reactants, which are the product of the translational partition function Q_t , rotational partition function Q_r , and vibrational partition function Q_v . E_a is the activation energy of the reaction. R is the universal gas constant. σ is the reaction pathway degeneracy, which is generally 1 for large molecular systems. Δn , a constant, is defined as the number of reacting molecules (n) minus 1.

3. Results and discussions

3.1. The NO heterogeneous reduction over char with hydroxyl groups

The hydroxyl radicals in the ambient atmosphere have been shown to affect the heterogeneous reduction of NO by char in previous studies (Zhang et al., 2014; Yue et al., 2022; Yue et al., 2022). This section discusses the adsorption of hydroxyl groups onto the char surface and their subsequent behavior.

First, there are multiple pathways for hydroxyl groups to adsorb onto the char surface. Fig. 2 illustrates four possible adsorption products of $\cdot\text{OH}$ on the char surface, naming them as Z1, Z2, Z3, and Z4, respectively. The energy of the adsorption process is represented by E_{ads} , with units of kJ/mol . A negative E_{ads} value indicates that heat is released during the adsorption process. The greater the magnitude of the negative heat of adsorption ($|E_{ads}|$), the more stable the adsorbed structure. Therefore, Z4 is selected as the adsorption product and labeled as IM1 for subsequent reaction pathway calculations.

In the above, the most likely adsorption products were determined based on the adsorption energy. However, theoretical calculations suggest that the hydroxyl group adsorbed on the char surface may behave differently, implying that the chemical reactions could proceed via different mechanisms once the hydroxyl group is adsorbed on the char surface. Fig. 3 illustrates two different reaction pathways after hydroxyl group adsorption on the char surface, denoted as pathway 1 and pathway 2, respectively. In this paper, the notation used to represent various species in the chemical reactions is as follows: “R” denotes the reactants, “P” represents the products, “IM” is used for intermediates, and “TS” indicates the transition states. This notation will be consistently employed throughout the document to maintain clarity and consistency in describing the chemical processes under discussion.

In pathway 1, the hydroxyl group is adsorbed on the char surface only as a surface oxygen-containing functional group and does not participate in the generation of products. After the reaction product N_2 is

desorbed from the char surface while the hydroxyl group remains intact, this mechanism is referred to as the “Adsorption-only” mechanism for ease of description in subsequent discussions.

In pathway 2, the hydroxyl group reacts with char following adsorption. This reaction destroys the surface structure of the char and alters the subsequent processes of adsorption and reduction of NO molecules. This mechanism, hereafter termed the “Modification” mechanism for simplicity, is discussed in more detail in the following sections.

Next, the influence of two different behaviors of hydroxyl groups on the char surface on the NO heterogeneous reduction reaction on char is explored.

3.1.1. Chemical reaction pathway of the “Adsorption-only” mechanism – Pathway 1

In this section, the reaction pathway of the “Adsorption-only” mechanism, denoted by pathway 1, is described. In this mechanism, the hydroxyl group adsorbs solely as a surface functional group on the char surface, not participating in the generation of product N_2 . Following the reaction, the hydroxyl group remains on the char surface.

Bond order analysis is a way to quantitatively represent the strength of chemical bonds. Laplacian bond order (LBO) has been widely used because of its remarkable advantage of being able to reflect the strength of chemical bonds well and its value is relatively close to the formal bond order (Lu and Chen, 2013). To better describe the chemical reaction process, Table 1 presents both the LBO and bond lengths of some key chemical bonds. The potential energy surface of pathway 1 is shown in Fig. 4, and the imaginary frequencies of relevant transition state structures in pathway 1 are provided in Table S1.

After the hydroxyl group adsorbs on the R surface to form IM1, there are continuous active sites C1, C3, and C5 on the surface of IM1. When there are continuous active sites on the surface of the char, NO molecules tend to adsorb on the surface of the char in a parallel manner (Oyarzún et al., 2015). Among the three continuous active sites on the surface of IM1, the energy released when NO adsorbs on the C3 and C5 active sites to form the I-IM2 structure is the largest, which is 384.23 kJ/mol . Then, the second NO molecule adsorbs on the C1 active site on the surface of I-IM2 to form the I-IM3 structure, releasing 70.00 kJ/mol of energy.

The following is the process of N11-O12 bond breaking and N11-N13 bond formation. I-IM3 forms I-IM4 structure via transition state structure I-TS1, during which N11 and O12 atoms gradually move apart, the LBO decreases from 0.139 to 0, the bond length increases from $1.46 \text{ \AA}$ to $2.92 \text{ \AA}$, while N11 atom and N13 atom gradually approach each other, the LBO increases from 0 to 0.909, and the bond length decreases from

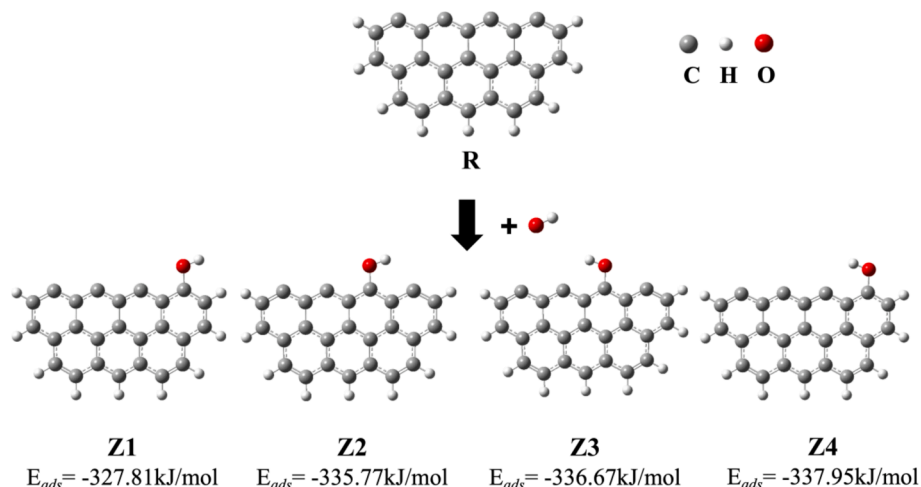


Fig. 2. Structures and energies of hydroxyl radical adsorption on char surface.

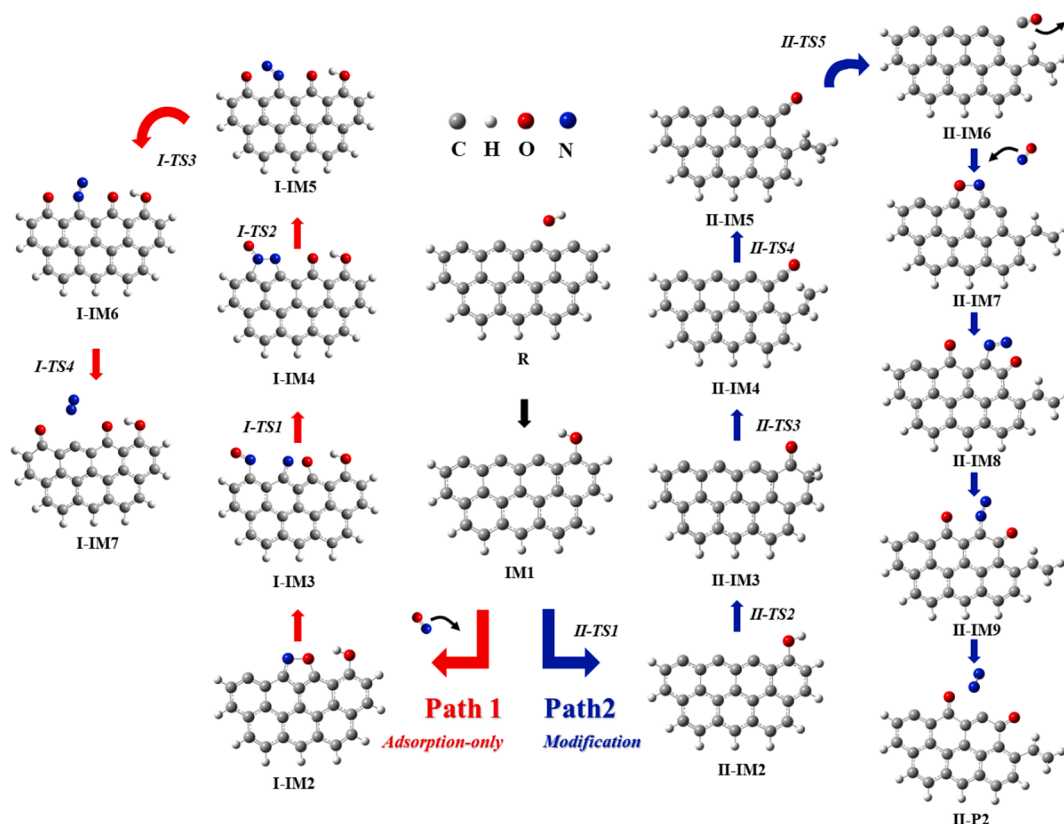


Fig. 3. Possible reaction pathways after IM1 structure.

Table 1

LBO and bond length variation in pathway 1.

Elementary reaction	Chemical bond	The LBO variation	Bond length variation (Å)
I-IM3 → I-TS1 → I-IM4	N11-O12	0.139 → 0.03 → 0	1.46 → 2.08 → 2.92
I-IM4 → I-TS2 → I-IM5	N11-N13	0 → 0 → 0.909	2.90 → 2.29 → 1.33
I-IM4 → I-TS2 → I-IM5	N11-N13	0.909 → 0.425 → 2.205	1.33 → 1.49 → 1.17

2.90 Å to 1.33 Å. This process requires overcoming an energy barrier of 56.00 kJ/mol while releasing 124.96 kJ/mol of energy. Subsequently, the O14 and C1, both on the char surface, bind via the transition state structure I-TS2 to form a quinone group. The LBO of N11-N13 increases from 0.909 to 2.205, the bond length decreases from 1.33 Å to 1.17 Å. This process requires overcoming an energy barrier of 330 kJ/mol while releasing 59.23 kJ/mol of energy. After this process, the O12 and O14 atoms in the two sequentially adsorbed NO molecules are adsorbed onto the char surface, forming two quinone groups, while N11 and N13 polymerize to form the N-N structures, which are essential precursors of

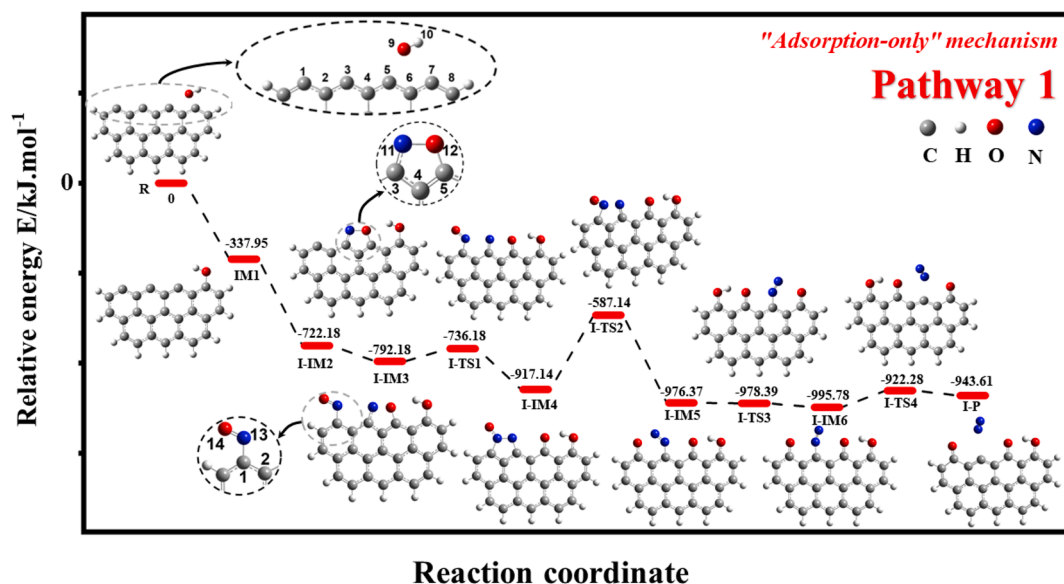


Fig. 4. The chemical reaction potential energy surface of pathway 1.

the reduction product N_2 . I-IM5 $\rightarrow$ I-TS3 $\rightarrow$ I-IM6 is the “twisting” process of the C3-N13 bond, which prepares the N-N structure to separate from the surface of IM5. It is worth noting that the energy of the transition state I-TS3 in this process is lower than the energy of I-IM5, which indicates that the occurrence of this process is barrierless. Finally, the N-N structure undergoes the I-IM6 $\rightarrow$ I-TS4 $\rightarrow$ I-P process, during which it overcomes an energy barrier of 33.50 kJ/mol and absorbs 52.17 kJ/mol of energy, leading to the formation of the reduction product N_2 that is desorbed from the char surface. After N_2 detaches from the char surface, the hydroxyl group is still retained on the I-P surface and does not participate in the generation of the gas product N_2 .

The chemical equation for the “Adsorption-only” mechanism is $R + 2NO + \cdot OH \rightarrow N_2 + I-P$. The rate-determining step of the total response is the elementary reaction I-IM4 $\rightarrow$ I-TS2 $\rightarrow$ I-IM5, corresponding to the process of formation of the N-N structure on the char surface. The energy barrier for this process is 330.00 kJ/mol.

3.1.2. Chemical reaction pathway of the “Modification” mechanism – pathway 2

In this section, the reaction pathway of the “Modification” mechanism, denoted as pathway 2, is described. In this mechanism, the hydroxyl group modifies the surface structure of the char, thereby altering the reaction pathway of NO heterogeneous reduction on the char. Table 2 shows the LBO and bond lengths of important chemical bonds during the pathway 2 process. Fig. 5 shows the chemical potential energy surface of pathway 2, and the corresponding imaginary frequencies are listed in Table S2.

Firstly, IM1 forms II-IM2 via the transition state II-TS1, during which the hydroxyl group on the surface of IM1 is rotated by 180° . Since this process does not involve the formation or breaking of chemical bonds, it only requires an energy barrier of 26.84 kJ/mol to be overcome, while releasing 10.13 kJ/mol of energy. Next, the migration of the H10 atom in the hydroxyl group occurs, where the H10 atom dissociates from the hydroxyl group, overcoming a large energy barrier of 274.61 kJ/mol, and combines with C8 to form the II-IM3 structure. During this process, the LBO of the O9-H10 bond decreases from 0.498 to 0, while the bond length is elongated from 0.97 Å to 2.65 Å. In addition, the process requires an energy absorption of 57.38 kJ/mol. The II-IM3 $\rightarrow$ II-TS3 $\rightarrow$ II-IM4 process is the ring-opening process of the char structure. The LBO of C7-C8 in the char structure decreases from 1.052 to 0, while the bond length gradually increases from 1.53 Å to 2.89 Å. The aromatic ring hosting the hydroxyl group breaks open, and a carbonyl group (C7 = O9) is formed on the char surface. This process requires overcoming an energy barrier of 158.83 kJ/mol while absorbing 121.53 kJ/mol of heat. Subsequently, the distance between C7 and C8 atoms further increases, and this process only requires overcoming an energy barrier of 9.96 kJ/mol while releasing 5.13 kJ/mol of energy. Finally, the chemical bond between C6 and C7 is broken, and CO desorbs from the surface of the char. This process requires overcoming an energy barrier of 129.56 kJ/mol and absorbing 115.82 kJ/mol of heat.

The above study has revealed the process of how the hydroxyl group

breaks the surface structure of the char. The following sections further investigate the process of the NO heterogeneous reduction on the broken char surface. It is evident that the distribution of II-P1 surface active sites, formed subsequent to the CO desorption from the II-IM6 surface, exhibits significant changes when compared to the original char structure R. These changes significantly alter the reaction process of the NO heterogeneous reduction on the char. First, NO adsorbs on the C3 and C5 active sites on the char surface to form II-IM7. This process releases 173.87 kJ/mol of energy. Then, the second NO adsorbs on the surface of II-IM7, leading to the formation of a five-element ring (C5-C6-N11-N13-O14) within the II-IM8 structure. It is important to note that, in contrast to the earlier mentioned simple adsorption process which occurs without transition states, this particular adsorption involves overcoming an energy barrier of 91.77 kJ/mol and necessitates passing through the transition state II-TS6 to yield the adsorption product II-IM8. During this process, the LBO between N11 and N13 increases from 0 to 1.719, and the bond length decreases from 3.03 Å to 1.23 Å. Concurrently, the formation of the N11-N13 structure on the surface of II-IM8 occurs, a step that is pivotal for the generation of the product N_2 . The subsequent process of II-IM8 $\rightarrow$ II-TS7 $\rightarrow$ II-IM9 is the ring-opening process of the five-element ring (C5-C6-N11-N13-O14), where the N13 and O14 atoms gradually separate. The LBO decreases from 0.077 to 0, and the bond length increases from 1.55 Å to 3.03 Å. Since the chemical bond between N13 and O14 in II-IM8 is fragile (LBO is only 0.077) and the bond-breaking process does not involve other complex chemical changes, the process only needs to overcome an energy barrier of 2.12 kJ/mol while releasing 59.81 kJ/mol of energy. Finally, C5 and N11 gradually move away from each other, and the bond order decreases from 0.989 to 0, while the bond length increases from 1.34 Å to 3.11 Å. The N11-N13 structure overcomes an energy barrier of 100.59 kJ/mol and desorbs from the char surface, forming N_2 molecules and absorbing 23.11 kJ/mol of energy.

The chemical equation for the “Modification” mechanism is $R + \cdot OH + 2NO \rightarrow CO + II-P2 + N_2$. The rate-determining step of the chemical reaction is II-IM9 $\rightarrow$ II-TS8 $\rightarrow$ II-P2, with the highest energy barrier of 100.59 kJ/mol, corresponding to the desorption of N_2 from the char surface. In addition, the energy barrier for the adsorption of the second NO molecule onto the char surface is 91.77 kJ/mol, which is close to the energy barrier of the rate-determining step. Therefore, this aspect is further analyzed in the subsequent kinetic analysis.

3.2. The NO heterogeneous reduction on char without hydroxyl groups

To facilitate a comparison with the process of NO heterogeneous reduction by the char in a hydroxyl group atmosphere, calculations were also performed for the NO reduction on char in an atmosphere without hydroxyl group, denoted as pathway 3. The chemical reaction pathway is shown in Fig. 6, and the LBO and bond lengths of important chemical bonds are presented in Table 3. The imaginary frequencies are provided in Table S3.

Firstly, due to the existence of continuous active sites on the R surface of the char, the first NO molecule adsorbs on the C3 and C5 sites of the char surface in a parallel manner, forming the III-IM1 structure and releasing 384.40 kJ/mol of energy (Oyarzún et al., 2015). Subsequently, the second NO molecule adsorbs on the C8 active site of the char surface by N-down absorption, forming the III-IM2 structure and releasing 46.10 kJ/mol of energy. After the adsorption of the two NO molecules, the N9 and O10 atoms gradually move away from each other during the III-IM2 $\rightarrow$ III-TS1 $\rightarrow$ III-IM3 process. In this process, the N9-O10 bond length increases from 1.44 Å to 2.91 Å, the LBO decreases from 0.171 to 0, and the covalent bond between N9 and O10 breaks. Meanwhile, the N9 and N11 atoms gradually approach each other, the N9-N11 bond length decreases from 2.92 Å to 1.43 Å, the LBO increases from 0 to 0.551, and the covalent bond between N9 and N11 is formed. This process requires overcoming a barrier of 93.87 kJ/mol and releases 47.47 kJ/mol of energy. The next stage corresponds to the formation of

Table 2
LBO and bond length variation in pathway 2.

Elementary reaction	Chemical bond	The LBO variation	Bond length variation (Å)
II-IM2 $\rightarrow$ II-TS2 $\rightarrow$ II-IM3	O9-H10	0.498 $\rightarrow$ 0.031 $\rightarrow$ 0	0.97 $\rightarrow$ 1.39 $\rightarrow$ 2.65
II-IM3 $\rightarrow$ II-TS3 $\rightarrow$ II-IM4	C7-C8	1.052 $\rightarrow$ 0.001 $\rightarrow$ 0	1.53 $\rightarrow$ 2.29 $\rightarrow$ 2.89
II-IM7 $\rightarrow$ II-TS6 $\rightarrow$ II-IM8	N11-N13	0 $\rightarrow$ 0.126 $\rightarrow$ 1.719	3.04 $\rightarrow$ 2.04 $\rightarrow$ 1.23
II-IM8 $\rightarrow$ II-TS7 $\rightarrow$ II-IM9	N13-O14	0.077 $\rightarrow$ 0.027 $\rightarrow$ 0	1.55 $\rightarrow$ 1.74 $\rightarrow$ 3.03
II-IM9 $\rightarrow$ II-TS8 $\rightarrow$ II-P2	C5-N11	0.989 $\rightarrow$ 0.035 $\rightarrow$ 0	1.34 $\rightarrow$ 1.86 $\rightarrow$ 3.11

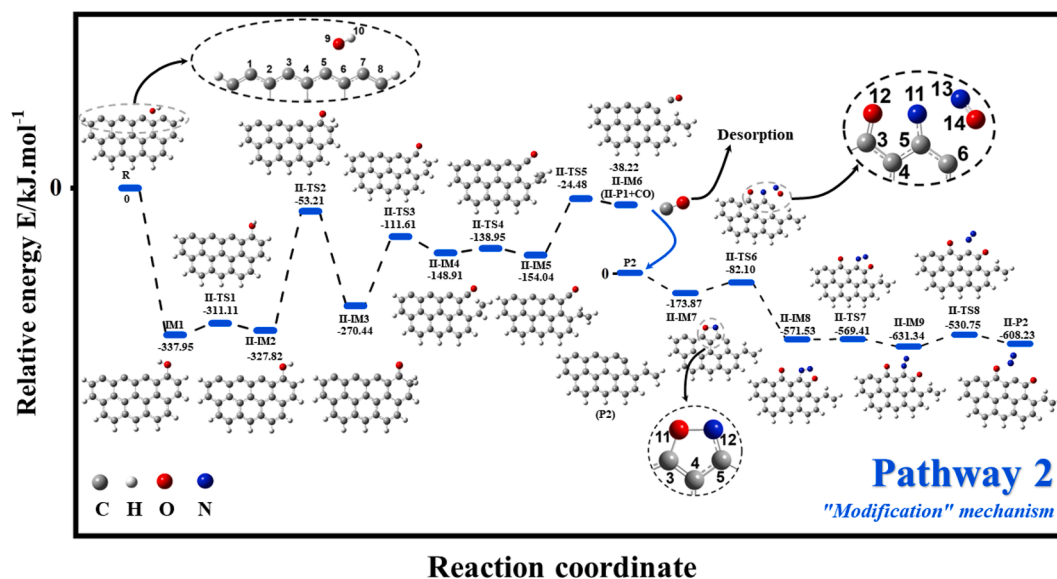


Fig. 5. The chemical reaction potential energy surface of pathway 2.

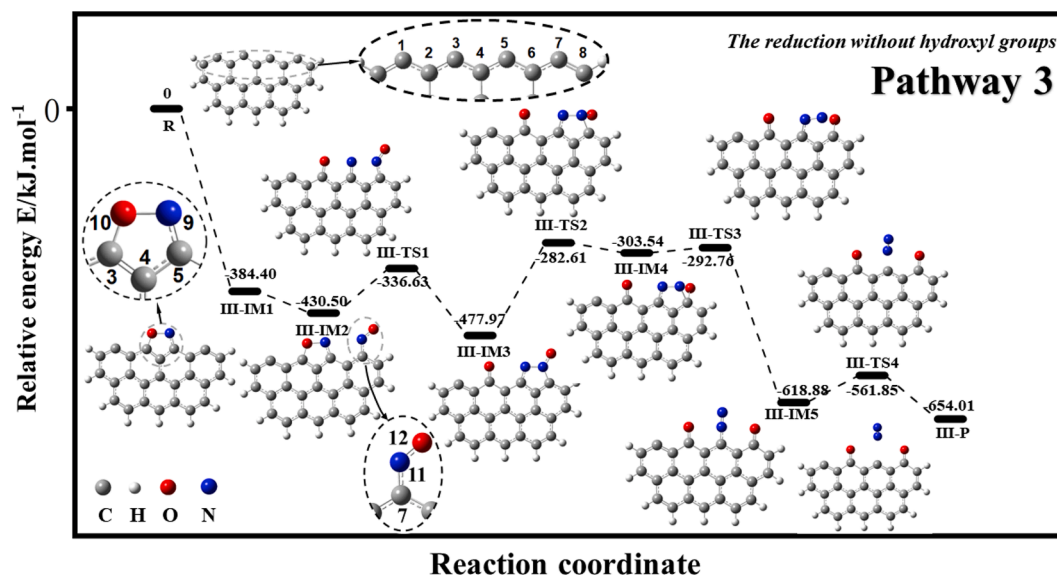


Fig. 6. The chemical reaction potential energy surface of pathway 3.

Table 3
LBO and bond length variation in pathway 3.

Elementary reaction	Chemical bond	The LBO variation	Bond length variation (Å)
III-IM2→III-TS1→III-IM3	N9-O10	0.171 → 0.001 → 0	1.44 → 2.20 → 2.91
	N9-N11	0 → 0.005 → 0.551	2.92 → 2.03 → 1.43
III-IM3→III-TS2→III-IM4	N11-O12	0.768 → 0.196 → 0.081	1.26 → 1.42 → 1.49
	C7-O12	0 → 0.013 → 0.207	2.38 → 1.72 → 1.44

the N-N structure. In this process, the O12 atom gradually approaches C7, the LBO of N11-O12 gradually decreases from 0.768 to 0.081, and the bond length increases from 1.26 Å to 1.49 Å. Meanwhile, the bond order of C7-O12 gradually increases from 0 to 0.207, and the bond length decreases from 2.38 Å to 1.44 Å. The gradual increase in the LBO

of C7-O12 during this process suggests a tendency for further bond formation between C7 and O12. This process requires overcoming an energy barrier of 195.36 kJ/mol and absorbing 174.43 kJ/mol of energy. Upon completion, the N9-N11 structure forms on the char surface, signaling the imminent formation of the product N₂. In the subsequent III-IM4 → III-TS3 → III-IM5 process, the N11 atom gradually moves away from the char surface, while the O12 atom further approaches it, leading to the formation of a quinone structure on the surface of III-IM5. Since this process does not involve complex chemical reactions, only requires overcoming an energy barrier of 10.78 kJ/mol while releasing 315.34 kJ/mol of energy. Finally, the C5 and N9 atoms gradually move away from each other, and N9-N11 desorbs on the char surface to form N₂, which requires overcoming an energy barrier of 57.03 kJ/mol and releases 35.13 kJ/mol of energy.

In an environment devoid of hydroxyl groups, the chemical equation representing the heterogeneous reduction of NO on the char surface can be expressed as $R + 2NO \rightarrow N_2 + III-P$. The rate-determining step of the total response is III-IM3 → III-TS2 → III-IM4, corresponding to the

formation process of N-N structure on the char surface, with an energy barrier of 195.36 kJ/mol.

3.3. Kinetic analysis for different reaction mechanisms

Reaction kinetics analysis, which quantitatively calculates rate constants indicative of the rates at which chemical reactions occur, is a crucial method in analyzing chemical reactions. In this section, the rate constants for several key elementary reactions and rate-determining steps in Pathways 1, 2, and 3 are calculated to elucidate the role of the hydroxyl group in the heterogeneous reduction of NO on the char surface. The formula for calculating the chemical reaction rate constants of elementary reactions is given in Eq. (2) in Section 2.

As outlined in Sections 3.1–3.2, the energy barriers for the rate-determining steps in the “Adsorption-only” mechanism, the “Modification” mechanism, and the absence of hydroxyl groups in the atmosphere are respectively identified as 330 kJ/mol, 100.59 kJ/mol, and 195.36 kJ/mol. From an energy barrier perspective, the presence of hydroxyl groups in the reaction atmosphere leads to divergent outcomes. Specifically, the “Adsorption-only” mechanism increases the reaction energy barrier, thereby inhibiting the reduction reaction, while the “Modification” mechanism reduces the energy barrier, thus promoting NO heterogeneous reduction on char.

To more clearly compare the effects of different mechanisms on chemical reaction rates, Fig. 7 illustrates the variation of the rate constants for the rate-determining steps of pathways 1, 2, and 3 with temperature in the range of 600–1800 K. As observed in Fig. 7, the rate constants k for all three chemical reactions increase with temperature, suggesting that higher temperatures enhance these reactions. Notably, at approximately 1200°C, the rate constant curves of two elementary reactions with higher energy barriers in the “Modification” mechanism intersect. This indicates a potential shift in the rate-determining step at this temperature. Below 1200°C, the reaction rate of the elementary reaction II-IM9 → II-TS8 → II-P2 is lower, making it the rate-determining step of the chemical reaction, which corresponds to the desorption of the product N₂ from the char surface. Above 1200°C, the elementary

reaction II-IM7 → II-TS6 → II-IM8 becomes slower, indicating that this process is now the rate-determining step, corresponding to the adsorption of the second NO molecule on the char surface.

Analysis of kinetic curves reveals that within the studied temperature range, the order of reaction rates for the three chemical pathways is as follows: “Modification” mechanism > chemical reactions in the absence of hydroxyl groups in the reaction atmosphere > “Adsorption-only” mechanism. This indicates that how hydroxyl groups in the reaction atmosphere affect the heterogeneous reduction of NO on the char surface is determined by their behavior on the char surface. The “Modification” mechanism enhances the reaction, while the “Adsorption-only” mechanism inhibits the chemical reaction.

3.4. Pathway and energy barrier analysis in the “Modification” mechanism

3.4.1. Shorter pathways in the “Modification” mechanism

Based on the kinetic analysis conclusions in Section 3.3, it is evident that the subsequent behavior of hydroxyl groups post-adsorption on the char surface exerts opposing effects on the reaction rate. Given that the N-N structure on the char surface serves as a precursor to the reduction product N₂, understanding its formation process is crucial to elucidating the reduction mechanism. This section analyzes the process from the adsorption of NO molecules to the formation of N-N structures in pathways 1, 2, and 3, to compare and elucidate why the “Modification” mechanism facilitates the chemical reactions.

As illustrated in Fig. 8, for the process transitioning from NO adsorption on the char surface to the formation of the N-N structure, both the “Adsorption-only” mechanism (pathway 1) and the reaction in the absence of hydroxyl groups (pathway 3) involve three similar elementary reactions. Specifically, pathway 1 proceeds through I-IM2 → I-IM3 → I-IM4 → I-IM5, while pathway 3 follows III-IM1 → III-IM2 → III-IM3 → III-IM4. Firstly, two NO molecules are adsorbed on the char surface in turn, then the N atoms of the two NO molecules approach each other to form covalent bonds, and finally, the N-O bond of the second NO molecule is broken and the N-N structure is formed on the char surface.

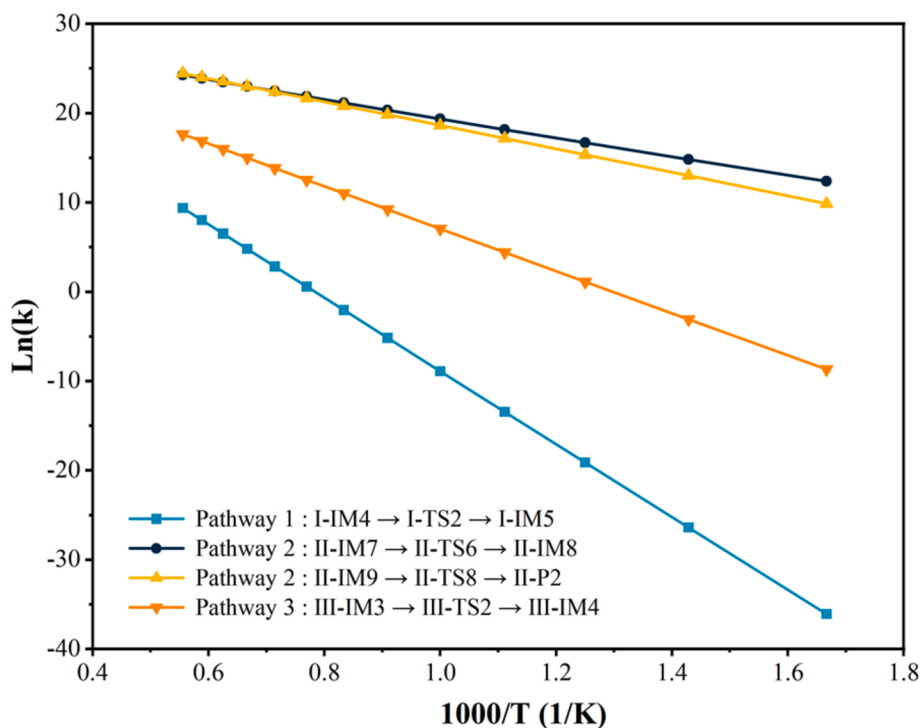


Fig. 7. Reaction rate constants for rate-determining steps (Pathway1: “Adsorption-only” mechanism Pathway2: “Modification” mechanism Pathway3: The reaction without hydroxyl groups).

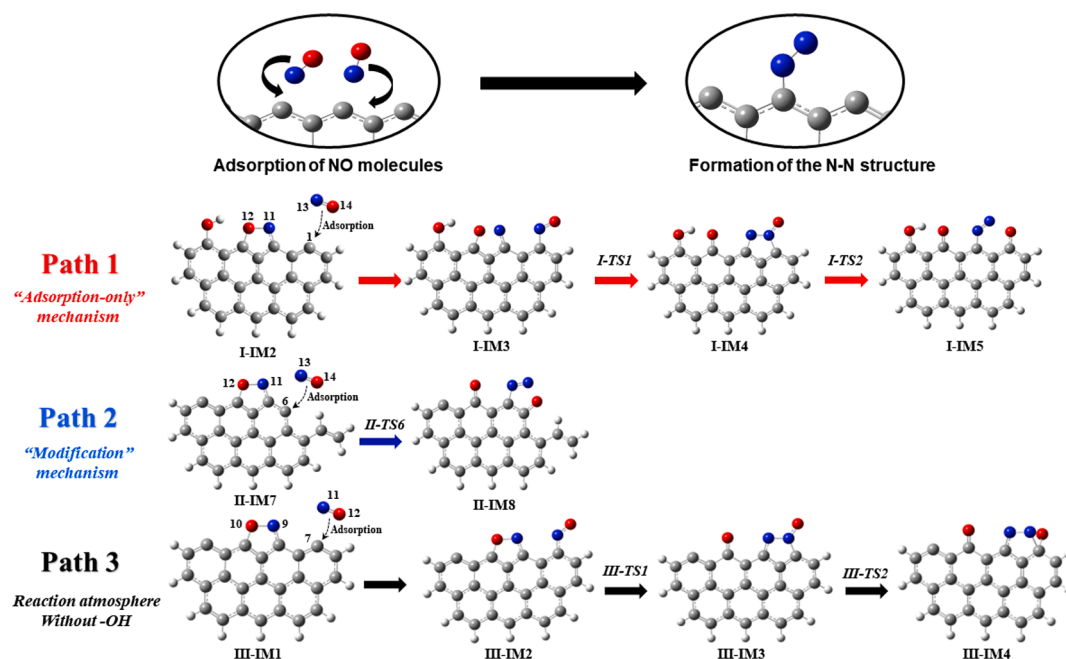


Fig. 8. The three reaction pathways from NO adsorption to N-O bond breakage.

However, in the "Modification" mechanism (pathway 2), the above three steps can be completed by only one elementary reaction (pathway 2: II-IM7 → II-TS6 → II-IM8). In terms of reaction pathways, the "turn three to one" phenomenon in the "Modification" mechanism greatly shortens the pathway of N_2 production.

To clarify the "Turn three to one" phenomenon in pathway 2, the spin densities of the transition state structure II-TS6 in the "Modification" mechanism were calculated, and contour maps with a contour value of 0.1 were drawn for it. Additionally, for comparison, contour

maps with the same contour value were also prepared for relevant structures in the other two mechanisms, all of which are presented in Fig. 9. The spin density is the difference between the densities of α and β electrons in the molecular system, which can reveal the distribution of unpaired electrons in the molecular system and help us better understand molecular properties. The green region in the figure represents a positive spin density, while the blue region represents a negative spin density. Analysis of Fig. 9(a) reveals the presence of unpaired β electrons in NO, distributed on p orbitals perpendicular to the molecular axis. On

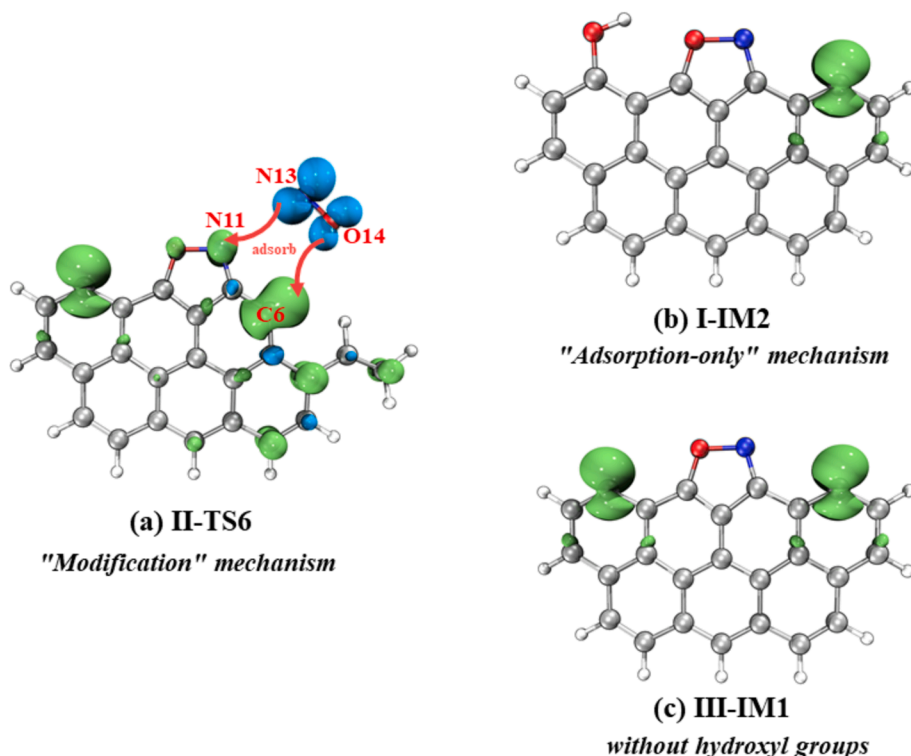


Fig. 9. Iso-surface maps of spin density for three structures.

the char surface, unpaired α electrons are present on the N11 and C6 atoms, which tend to pair with the unpaired β electrons of NO to form chemical bonds. Therefore, during the adsorption process, the N13 atom in NO can combine with the N11 atom on the char surface to form an N11-N13 covalent bond. In contrast, however, for I-IM2 (Fig. 9(b)) and III-IM1 (Fig. 9(c)), the absence of unpaired electrons in the N atoms on the char surface prevents the direct formation of N-N covalent bonds during adsorption, which need to be formed gradually in subsequent steps.

As is well known, the phenomenon of electron concentration in the bonding region is inevitably accompanied by the formation of covalent bonds, and the electron density difference map can describe this phenomenon well. In order to better explain the mechanism of bonding and bond breaking in the process of II-IM7 $\rightarrow$ II-TS6 $\rightarrow$ II-IM8, the electron density difference map of transition state II-TS6 during NO adsorption was plotted, as shown in Fig. 10. In Fig. 10, the green and blue regions correspond to the iso-surfaces of electron density difference of 0.003 a.u. and -0.003 a.u., respectively, indicating the main areas of electron density increase and decrease. Fig. 10 shows that as the NO molecule approaches the char surface, the electron density on the N13 and O14 atoms decreases, while it significantly increases in the regions between N11 and N13, and between C6 and O14. This indicates the direction of electron transfer during NO adsorption, namely from the NO molecule to the bonding region indicated by the red arrow in Fig. 10, where the significant increase in electron density often implies the formation of covalent bonds. Observation of the structure of II-IM8 reveals that N11-N13 and C6-O14 covalent bonds have been formed in the bonding region, confirming the above bonding mechanism.

3.4.2. Lower energy barriers in the “Modification” mechanism

The formation of N-N structures on the char surface is crucial for the NO heterogeneous reduction on char, and the previous subsection illustrated that the “Modification” mechanism can shorten the pathway of N-N structure formation. However, in addition to this, the energy barrier from the adsorption of NO to the formation of an N-N structure on the char surface is the lowest in the “Modification” mechanism. This implies a tendency for the reduction reaction to favor proceeding

through the “Modification” mechanism. Therefore, the atomic charges of the key intermediates in the formation of N-N structures on the char surface in the three mechanisms were calculated, aiming to discern the fundamental reason for the decrease of the energy barrier in the “Modification” mechanism, as illustrated in Fig. 11.

Atomic charges are point charges located at the center of an atom, which can intuitively describe the charge distribution in a chemical system and have significant implications for studying the properties of chemical systems. An atom with a more negative (positive) atomic charge is more likely to be the preferential site of an electrophilic (nucleophilic) reaction (Zhang et al., 2020). Atomic charges were calculated here with the ADCH (Atomic Dipole Moment Corrected Hirshfeld) method (Lu and Chen, 2012).

In the I-IM4 and III-IM3 structures, the formation of the N-N structure on the char surface requires the breaking of the N-O bond between the second NO molecule adsorbed on the char surface. Analyzing Fig. 11, in the “Adsorption-only” mechanism, the charge value of N13 atoms on the surface of I-IM4 is 0.315 and that of O14 atoms is -0.278 . There is a significant Coulombic attraction between N13 and O14 atoms due to carrying different kinds of charges. Similarly, in the reaction atmosphere without hydroxyl groups, the charge values of N11 and O12 atoms on the surface of III-IM3 are 0.256 and -0.221 , respectively, and there is also a significant coulombic attraction between the atoms. In the aforementioned two reaction mechanisms, breaking the covalent bond between N and O may require more energy due to the need to overcome the coulombic attraction between the atoms.

In the “Modification” mechanism, the formation of the N-N structure similarly requires the breaking of the N-O bond in the second NO molecule adsorbed on the char surface. Differently from the previous two reaction mechanisms, when the NO molecule approaches the surface of II-IM7, the N13 and O14 atoms carry the same type of charge, with values of 0.007 and 0.023, respectively. Therefore, the Coulombic repulsion between the N and O atoms in the NO molecule may be the main reason for the lowering of the chemical reaction energy barrier when the second NO molecule is adsorbed in the “Modification” mechanism.

To further clarify the charge changes in the “Modification”

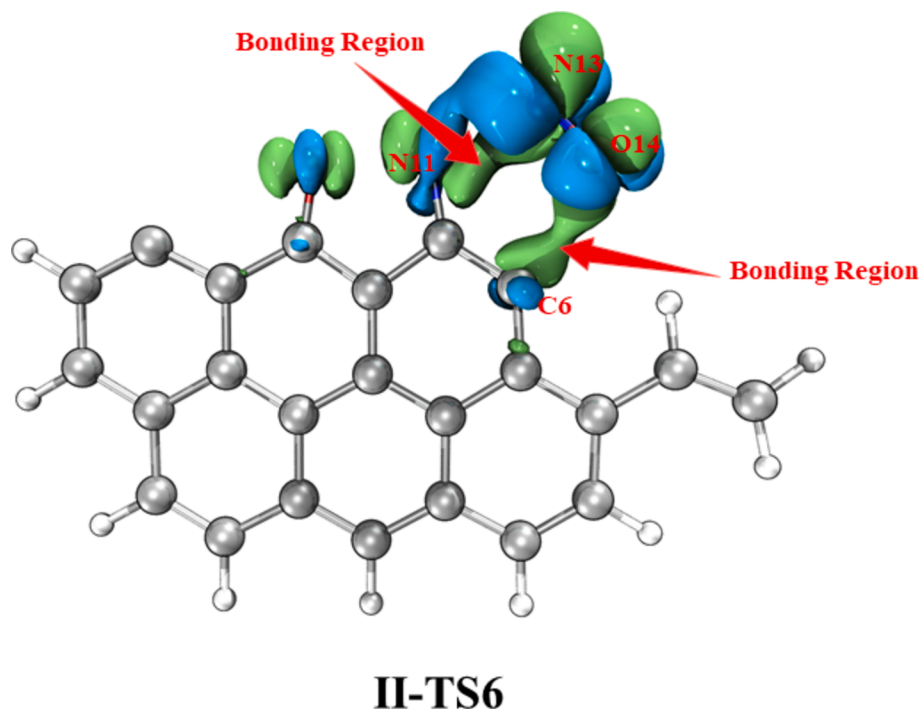


Fig. 10. The iso-surface maps of electron density difference of II-TS6.

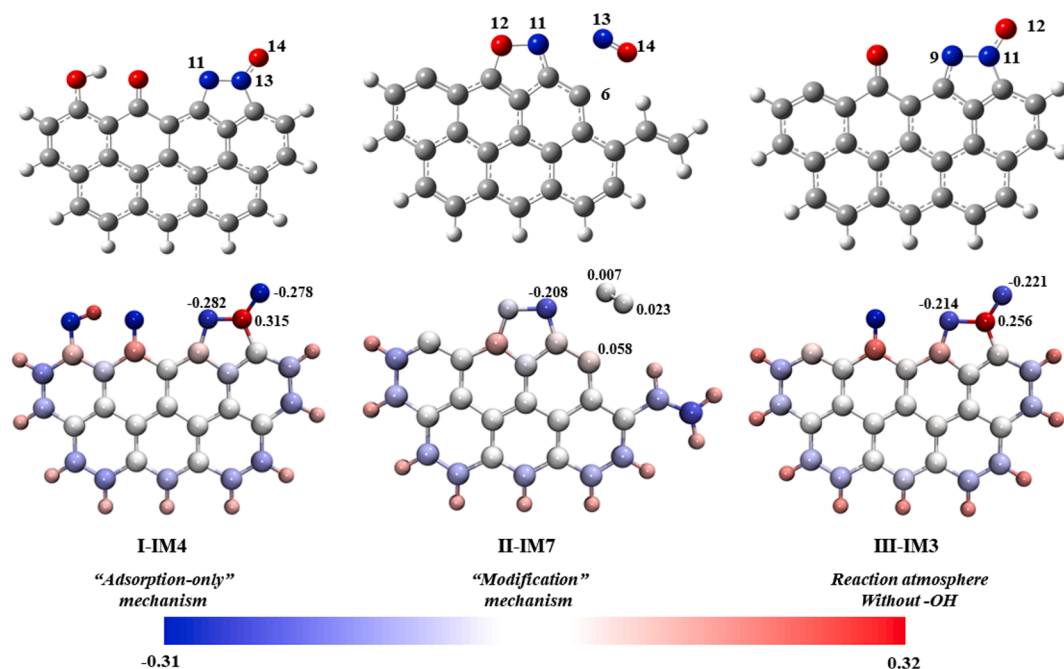


Fig. 11. ADCH atomic charge of I-IM4, II-IM7 and III-IM3.

mechanism, the ADCH charges of the II-IM7, II-TS6, and II-IM8 structures during the formation of N-N structures on the char surface were calculated, as illustrated in Fig. 12. From Fig. 12, it can be observed that as the NO molecule approaches the carbon surface, the electrons on the N13 atom undergo further transfer, resulting in a change in the charge value of the N13 atom from 0.007 to 0.097. Meanwhile, the C6 atom on the char surface gains electrons, causing its charge value to change from 0.058 to -0.092 . Surprisingly, it is found that the charges between the N11 and N13 atoms about to form a bond, as well as between the C6 and O14 atoms, have opposite values. This implies the presence of Coulombic attraction between the atoms, and the existence of Coulombic forces facilitates the formation of covalent bonds between N11-N13 and C6-O14. Therefore, in the "Modification" mechanism, when NO approaches the surface of II-IM7, electron transfer not only

contributes to original bond breaking but also assists in new bond formation. This point is one of the reasons why the energy barrier is lower in the "Modification" mechanism.

In summary, during the formation of the N-N structure in the "Modification" mechanism, the Coulombic attraction between bonding atoms and the Coulombic repulsion between bond-breaking atoms may be key factors contributing to its significantly lower energy barrier compared to other mechanisms.

4. Conclusions

In this study, DFT was employed to investigate how hydroxyl groups in the reaction atmosphere can influence the reduction reaction through various mechanisms. Notably, these mechanisms have been found to

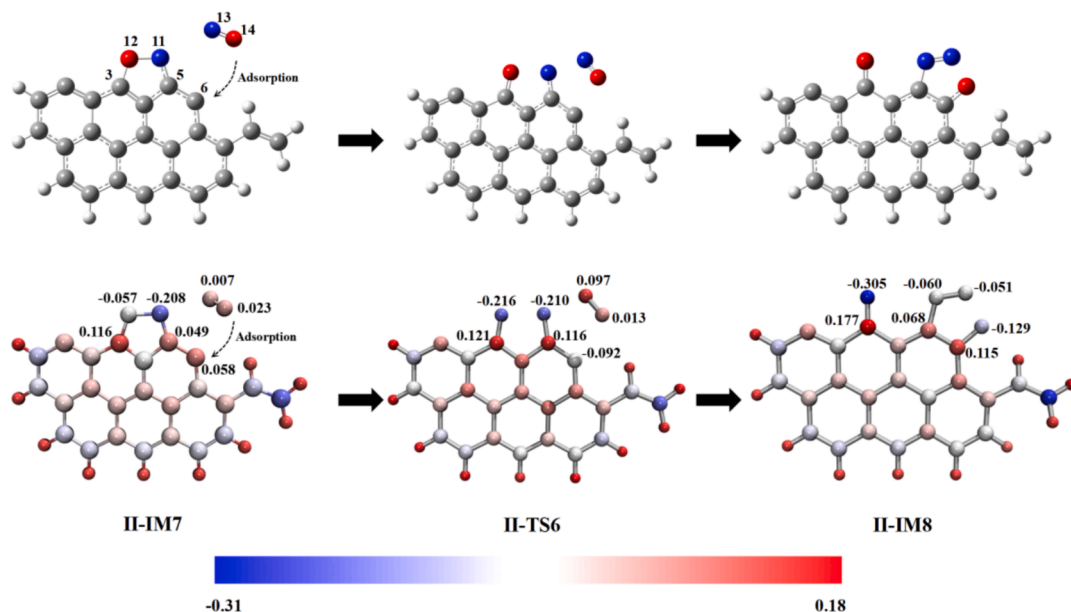


Fig. 12. ADCH atomic charge of II-IM7, II-TS6, and II-IM8.

have contrasting effects on the chemical reaction. The detailed conclusions of this research are summarized as follows:

1. Hydroxyl groups in the reaction atmosphere can affect the NO heterogeneous reduction by two different mechanisms. The first mechanism is named the “Adsorption-only” mechanism, in which the hydroxyl groups are adsorbed on the char surface only as surface functional groups. The second mechanism is called the “Modification” mechanism, in which the hydroxyl group reacts with the char, and new active sites are released on the char surface.
2. Kinetics analysis shows that the “Adsorption-only” mechanism not only fails to promote the NO heterogeneous reduction on char but also has an inhibitory effect, while the “Modification” mechanism significantly promotes the heterogeneous reduction of NO by char.
3. The “Modification” mechanism significantly shortens the chemical reaction pathway. From the adsorption of NO to the formation of the N-N structure is the critical process in the NO heterogeneous reduction on the char surface, and three elementary reactions are required to complete this process in other mechanisms. In the “Modification” mechanism, however, the electron distribution is changed, and only one elementary reaction is required to complete the above process.
4. The “Modification” mechanism significantly reduces the chemical reaction energy barrier. From the process of NO being adsorbed to the formation of the N-N structure on the surface of char, there is Coulomb repulsion between the breaking atoms mechanism and Coulomb attraction between the bonding atoms in the “Modification”. This phenomenon reduces the energy required for bond breaking and bonding, thus favoring the lowering of the chemical reaction energy barrier.

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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Novelty and Significance Statement

Based on density functional theory, the study investigated the impact of the hydroxyl group on NO heterogeneous reduction over char. It was proposed that the hydroxyl group could affect the chemical reaction through two different mechanisms, and the chemical reaction paths for both mechanisms were provided. Kinetic analysis indicated that these two mechanisms have opposite effects on the chemical reaction. Furthermore, the reasons behind the differing effects of these mechanisms on the chemical reaction were elucidated through methods such as wave function analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2024.120796>.

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