Experimental and DFT research for the effects of sodium on the heterogeneous reaction between NO and semichar derived from O₂/CO₂ pretreatments

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Abstract. The excessive emission of NO is endangering the ecological environment and the health of humans. In-depth research on the reduction mechanisms of NO is crucial to regulating NO emissions. In this research, the influence of sodium on the heterogeneous reaction of NO by semichar derived from O₂/CO₂ pretreatments were investigated through the experimental and density functional theory (DFT) method. According to the results of atomic dipole corrected Hirshfeld atomic charge (ADCH), the additional Na and oxygen-containing compound altered the semichar's charge distribution of. The additional Na weakened the positive effects of the marginal hydrogen. And the charge of the carbon, which was attached to the phenol group, changed from negative to positive due to the strong electron-trapping ability of the phenol group. The energy potential diagrams between NO and semichars derived from O₂/CO₂ pretreatments without/with sodium addition reflected that sodium was beneficial to reduce NO. Compared with pure O₂/CO₂ pretreatments, the additional sodium decreased the energy gap of the NO reduction by 144.68 kJ/mol. On the other hand, the temperature-programmed reduction (TPR) results were performed to identify the accuracy of the calculation results. The experimental results illustrated that adding sodium enhanced the NO reducibility of semichar, expressing great consistency with the theoretical results.

1 Introduction

[1, 2] the desertification, global-warming effects, and acid rain [3]. To face the challenge of global climate change and focus on the issue of resource and environmental constraints, the preheating combustion technology was gradually proposed [4, 5]. In this technology, the pulverized coal samples were preheated in a circulating fluidized bed (CFB). Then, the char particles and the resulting fuel gaseous agents were burned out in the down-fired combustor (DFC) [6]. The preheating treatment under oxygen-deficient atmospheres effectively decreased NOx emissions. Man al. [4] have investigated the combustion performance of coal samples preheated in the CFB. They found that the combustion efficiency of the whole process reached 98% after the preheating treatment. And the conversion of fuel-N to NOx lowered below 10%. The influence of O₂/CO₂ ratios on the NO conversion during char combustion was revealed by Ding et al. [7]. They found that the preheating process was beneficial to the emissions of fuel-N thorough affecting the fragmentation of pulverized coal. The NO emission characteristics during the combustion of char preheated in O₂/CO₂/H₂O were discussed by Zhu et al. [8]. The experimental results illustrated that O₂/CO₂/H₂O pretreatment enhanced the combustion efficiency of coal particles, and all the efficiencies were above 99.0%. Compared with O₂/N₂ pretreatment, the additional H₂O further hindered the reduction of nitrogen. According to these investigations, it can be determined that the reduction of NO can be controlled by adjusting the preheating conditions.

The alkali/alkaline metals (AAEMs) are considered the main factors affecting the pyrolysis, oxidation, and gasification process of carbonaceous materials [9-11]. Jeong et al. [12] found the AAEMs could affect the gasification of biomass-coal blended char through the solid-solid interface and intercalation compounds. The generation of intercalation compounds enhanced the layer spacing and weakened the strength of C-C covalent bond, resulting in the reactivity enhancement of the blended char. Marsha et al. [13] demonstrated that the isotropic parts were much susceptible to gasification. And the anisotropic components were more sensitive to the catalyzed gasification. Masnadi et al. [14] found that the alkali constituents could catalyze the reaction at the edge of the crystal, leading to the formation of the channeling effect. The channeling development positively affected the oxidization or gasification of carbonaceous materials. The research performed by Suzuki et al. [15] reported that the catalytic effects of AAEMs was the generations of catalytic active centers, such as C₃N and C-Oₓ-N (N=Na, K, etc.). These vibrant centers were essential to the oxidization, gasification, and reduction mechanisms of coal-based fuels.
Recently, molecular simulation, especially the quantum chemistry method, has been widely employed in the combustion, gasification, and reduction research of hydrocarbon materials [16-18]. Zhao et al. [19] investigated the interaction of char(N)-CO₂ through the DFT method. They found that CO₂ tended to attract the electrons from char(N) surface, and the adsorption of CO₂ was considered an exothermic reaction, which took place when the core temperature of O₂/CO₂ combustion lowered by 1700 K. The effect of sodium on carbon-CO₂ was determined by Zhao et al. [20]. The results explicated that Na weakened the conjugate structure of aromatic rings and promoted the CO emissions. Yang et al. [21] have revealed the effects of Na on NO adsorption performance. They found that the NO adsorption performance was altered by sodium, changing from physisorption to chemisorption. Although many scholars have investigated the influence of CO₂ or sodium on the NO reduction, the heterogenous reduction between NO and semichar prepared from oxidizing pretreatments still lacks investigations, which needs further exploration.

In this research, the influence of sodium on the NO heterogenous reduction by semichar derived from O₂/CO₂ pretreatment were determined through the DFT and TPR experiments. Based on the ADCH and IRI analysis, the electron migration characteristics and weak interaction in semichar particles were determined. And the energy potential diagrams of the heterogeneous reductions were obtained to assess the effects of sodium on the reducibility of semichar. And the TPR experiments were employed to identify the reliability of calculation results.

## 2 Experimental and calculations

### 2.1 Preparation of preheated semichars

The HCl (6 mol/L, 500 mL, 4 h, 333 K) - HF (22.4 mol/L, 500 mL, 4 h, 333 K) - HCl (6 mol/L, 500 mL, 3 h, 333 K) deashing method was employed in this research to eliminate the effects of metal species and other impurities. Zhun Dong bituminous coal (RZD) was choose as the raw samples. The corresponding proximate and ultimate results for raw and deashing coal particles (DZD) are summarized in Table 1. The previous investigation demonstrated that NaCl was the primary form in coal particles [22, 23]. Therefore, NaCl was used to investigate the influence of Na on NO-semichar heterogeneous reaction. According to our previous investigation, 2.0 wt% was the appropriate concentration for the attachment of sodium [24]. The detailed attachment procedures can also be found in that research [24]. The DZD with sodium attachment was recorded as DZDNa. The preheating treatments of DZD and DZDNa were performed in the horizontal tubular furnace. The corresponding diagrammatic sketch is shown in Figure 1. 1173 K and 12 s were considered the appropriate parameters for the preheating experiments [24]. The preheating conditions in this research are shown in Table 2.

### Table 1. Ultimate and proximate analysis of RZD and DZD.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ultimate analysis (dry and ash-free)</th>
<th>Proximate analysis (as received)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (wt%)</td>
<td>H (wt%)</td>
</tr>
<tr>
<td>RZD</td>
<td>81.36</td>
<td>4.21</td>
</tr>
<tr>
<td>DZD</td>
<td>81.95</td>
<td>4.80</td>
</tr>
</tbody>
</table>

* Determined by difference

### Figure 1. Schematic diagram of the high-temperature horizontal tubular furnace.

### Table 2. Pretreatment conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atmospheres</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>6 vol.% O₂ + 10 vol.% CO₂</td>
<td>Without Na participation</td>
</tr>
<tr>
<td>S2</td>
<td>6 vol.% O₂ + 20 vol.% CO₂</td>
<td>Without Na participation</td>
</tr>
</tbody>
</table>
Preheating temperature: 1723 K; Duration Time: 12 s

2.2 Temperature-programmed reduction

In this research, the TPR experiments of D ZD and D ZD Na were conducted to quantitatively determine the reducibility of semichar derived from O₂/CO₂ pretreatments without/with sodium salt addition. During each TPR experiment, 50 mg of samples are placed in the corundum boat. Then, the corundum boat is pushed into the constant temperature region of the tubular furnace. The furnace is further heated from 0 ℃ to 1450 ℃. The heating rate of the reactor is 5 K/min. And the reaction gas is NO (1000 ppm + Ar). The gas rate is 0.8 L/min. The NO reducibility can be obtained based on the employment of an IR gas analyzer.

2.3 Calculation details

Previous investigations have identified that the hydrocarbon materials, such as coal and char, consisted of numerous aromatic ring structures [25-27]. According to the nuclear magnetic resonance, the graphite was composed of 3~7 aromatic rings [28]. Therefore, the graphite surface consisting of seven aromatic rings was used to simulate the surface of semichar (as shown in Figure 2 (a)). Pels et al. [29] reported that N-6 was the major nitrogen-containing compound in semichar after the pyrolysis treatment. Thence, the char surface was further optimized. The new configuration of semichar is shown in Figure 2 (b). The charN surface containing one sodium atom was conducted to estimate the effects of sodium. The configuration of each carbonaceous surface is shown in Figure 2 (c). The calculation level for the optimized and transition states is M062X/6-31G(d,p). Then, the vibration and intrinsic reaction coordinate calculation are employed to guarantee the correct connection among the reactant, intermediate, and product. All the calculation was performed on Gaussian09 [30]. And the wave function of each structure is analyzed through Multiwfn [31].

3 Results and Discussions

3.1 The ADCH charge distribution of semichar

It is pointed out by Nzihou et al. [32] that the reaction rate of carbon-O₂ was three orders of magnitude higher than that of carbon-CO₂. During the O₂/CO₂ preheating treatment, the oxidization of carbon by O₂ occurred before CO₂. Therefore, in the model construction of the semichar, the adsorption of O₂ and CO₂ on the surface of semichar should be separated. Our previous investigation demonstrated that many oxygen-containing functional groups were formed during the oxidizing pretreatment [33]. These groups included phenol, quinone, lactone, carboxyl, ether, and anhydride. Among them, the phenol group was considered the major group in semichar particles. Therefore, the charN model decorated with one phenol group without or with sodium addition was conducted. The corresponding configurations are shown in Figure 3.
characteristics. The ADCH results are summarized in Figure 4. It illustrated that the additional sodium and phenol effectively altered the electron distribution of semichar particle. According to the RAL colour card, the ADCH colours of marginal hydrogen atoms in charN and charN\textsubscript{OH}\textsubscript{Na} were all in beige red. However, these hydrogen atoms in charN and charN\textsubscript{OH} were expressed in red colours. It demonstrated that the additional sodium weakened the positive influence of marginal hydrogen atoms. For charN structure, the charge for atoms C\textsubscript{3}, C\textsubscript{6}, and C\textsubscript{8} were 0.18, 0.18, and -0.25, respectively. These values changed to 0.10, -0.37, and -0.03, respectively, for charN\textsubscript{Na}; 0.14, -0.12, and 0.13, respectively, for charN\textsubscript{OH}\textsubscript{Na}; and 0.10, -0.36, and 0.07, respectively for charN\textsubscript{OH}\textsubscript{Na}. This meant that when the phenol was attached to the semichar, the charge characteristic of the connecting carbon altered from negative to positive. The reason for it was the strong electron-trapping ability of the phenol group [35]. And the addition of sodium altered C\textsubscript{6}'s charge from positive to negative charge, the reason for this phenomenon was the strong positive charge of the alkali metal [36]. The variation of charge characteristics resulted in the different physicochemical performance of semichar, resulting in the different reducibility of NO.

3.2 The effects of sodium on the reaction between NO and semichar prepared from O\textsubscript{2}/CO\textsubscript{2}

Robert et al. [37-39] reported that the initial step for the reaction between the hydrocarbon material and CO\textsubscript{2} was the direct adsorption of CO\textsubscript{2}. Based on these investigations, the heterogeneous reaction mechanisms between NO and semichar preheated in O\textsubscript{2}/CO\textsubscript{2} atmosphere are determined. The optimized and transition states are shown in Figure 5. The energy barrier sketch is shown in Figure 6. On the basis of our previous investigation [39], the adsorptive site of CO\textsubscript{2} on semichar are atoms C\textsubscript{4} and C\textsubscript{6}. It meant that when CO\textsubscript{2} molecule approached to the semichar, the CO\textsubscript{2} adsorption on the surface of semichar occurred. The barrier value of this step was only 10.27 kJ/mol. Then, the molecule of CO was immediately decomposed. This process was a high-energy barrier and endothermic step, and the barrier and endothermic values were 235.08 and 220.6 kJ/mol. After the desorption of CO, an oxygen was remained on the surface of semichar in the form of quinone group. Subsequently, the NO adsorption on semichar occurred through the process of IM\textsubscript{2} \textsubscript{TS3} IM\textsubscript{3}. The generation of IM\textsubscript{3} was a low-energy barrier process, and the value was 27.38 kJ/mol. Then, the aromatic ring in semichar particle was dissociated due to the crack of C\textsubscript{6}-C\textsubscript{7}. The fracture of C\textsubscript{6}-C\textsubscript{7} promoted the decomposition of secondary CO. The energy gap between pre-lowest and post-highest energy points was widely used to reflect the occurrence difficulty of the multi-step reaction. Therefore, the generation of IM\textsubscript{4} was credited with the rate-determining step. The gap value of this process was 558.05 kJ/mol. Then, the covalent bond N\textsubscript{NO}-O\textsubscript{NO} cracked, and IM\textsubscript{5} was formed through TS\textsubscript{5}. The fraction of N\textsubscript{NO}-O\textsubscript{NO} weakened the strength of covalent bond (C\textsubscript{1}-N\textsubscript{2}), therefore, the fraction of C\textsubscript{1}-N\textsubscript{2} occurred. The structure of C-N-N in IM\textsubscript{6} was unstable, which could decompose from the surface semichar in the form of N\textsubscript{2}. The energy barrier for the desorption of N\textsubscript{2} was 136.77 kJ/mol. According to the reaction pathway, it could be determined that the reduction between NO and semichar prepared from O\textsubscript{2}/CO\textsubscript{2} included the adsorption of CO\textsubscript{2} and NO molecules and the successive desorption of CO and N\textsubscript{2}.
Figure 5. The stable structures for the reactant, intermediate states, transition states, and product for the heterogeneous reaction of NO by semichar prepared from O2/CO2 pretreatments without Na participation.

Figure 6. The energy barrier diagram for the heterogeneous reaction of NO by semichar prepared from O2/CO2 pretreatment without Na participation.

For the heterogeneous reduction between NO and semichar derived from O2/CO2 pretreatments with Na participation, the stable structures of the optimized and transition states are shown in Figure 7. Figure 8 is used to describe the energy barrier of each elementary reaction. As shown in Figure 7, the first step of this reaction was similar to Path 1. The IRI analysis was used to further compare the influence of Na on CO2 adsorption. The IRI results are shown in Figure 9. For the semichar prepared without sodium addition, there were a blue and two green-golden yellow discs between CO2 and semichar. The blue disc between atoms OCO2 and C6 corresponded to the chemical bond (Figure 9 (b)). It meant that the CO2 adsorption on the semichar was chemisorption. And this result was irrelevant with sodium. The green-golden yellow between -0.015 and 0.015 a.u. corresponded to the vdW interaction and notable repulsion. The red spikes at about 0.02 a.u. corresponded to the steric effect within the benzene ring structures. Moreover, it could be found from Figure 9 (a), Figure 9 (c), and Figure 10 that the additional sodium had little effect on the chemisorption of CO2.
Once IM1 was formed, the atom O₂ migrated from C\textsubscript{CO₂} to C\textsubscript{6} through the structure of C-O-Na. This process was an exothermic step (176.66 kJ/mol) accompanied by 60.77 kJ/mol barrier. Then, the dissociation of aromatic rings occurred after the transformation of atoms H\textsubscript{1} to C\textsubscript{6}. The energy barrier of this process was much higher (270.70 kJ/mol), illustrating that the dissociation of the aromatic ring generally required considerable energy. Subsequently, the desorption of first CO occurred through the step of IM4 \textrightarrow\textsubscript{TS5} IM5. Once IM5 was formed, the fragmented aromatic rings were reconstituted, and the cyclization reaction began. After the cyclization, the decomposition of secondary CO happened. Next, the NO molecule was adsorbed on semichar surface through the process of IM7 \textrightarrow\textsubscript{TS8} IM8. Then, the crack of the covalent bond N\textsubscript{NO}-ONO promoted the secondary dissociation of aromatic rings through the process of IM9 \textrightarrow\textsubscript{TS10} IM10. The barrier of IM9 \textrightarrow\textsubscript{TS10} IM10 was much higher (203.85 kJ/mol). It was noticed that the N\textsubscript{2} was not directly desorption from the surface of semichar. The C-N-N structure rotated around atom C\textsubscript{1}. This process was the rate-determining step in Path 2. The gap value of IM9 \textrightarrow\textsubscript{TS10} IM10 was 413.37 kJ/mol.
Finally, the cyclization of new five-membered rings promoted the decomposition of N\textsubscript{2}. Compared with Path 1, the energy gap decreased by 144.68 kJ/mol, illustrating that the additional sodium enhanced the reducibility of semichar.

![Reaction Process](image)

**Figure 8.** The energy barrier diagram for the heterogeneous reaction of NO and by semichar prepared from O\textsubscript{2}/CO\textsubscript{2} pretreatment with Na participation.

![TS1, IM1, TS2, IM2, TS3, IM3](image)

**Figure 9.** The transition for the CO\textsubscript{2} adsorption

### 3.3 The verification of the calculated results

The TPR experiment of each semichar was conducted to verify the calculated results derived from the DFT method. The TPR results are summarized in **Figure 10**. It can be found that the semichars obtained with sodium addition obviously enhanced the NO reducibility, expressing excellent consistent to the calculated results. Moreover, the sub-figure in **Figure 10** was used to discuss the NO reduction characteristics. It is confirmed from the TPR curve that the NO decrease can be approximately divided to four sections: NO reversible adsorption, NO primarily declined, NO rebounded, and NO rapidly reduced. When the reduction temperature lower than 670 K (section a), the NO concentration had a negligible variation, representing the NO reversible adsorption stage. In this section, the NO molecule was directly adsorbed on the semichar and primarily converted into C(NO) structures [40, 41]. C(NO) was a metastable structure with poor thermal stability, which could release from semichar in the...
form of NO again. Therefore, the NO reversible physical adsorption dominated this process, and all the samples exerted identical tendencies. This phenomenon implied that the physical adsorption of NO was irrelevant to the preheating atmospheres. When the reduction temperature further increased (670 K - 1000 K), the NO molecules experienced a preferential declined (section b) and rebounded process (section c). In section b, the volatile matters remaining in semichar participated in the NO reduction, resulting in the preferential decline of NO concentration. On the other hand, the C(O) compounds with poor thermal stability (carboxyl and lactone groups) started to decompose from the surface of semichars in the form of CO [42-44], promoting the homogeneous reaction of NO and enhancing the NO reducibility of semichars. Owing to the continuous consumption of volatile matter and oxygen-containing functional groups with poor thermal stability, the homogeneous reduction of NO was gradually weakened, leading to the rebound of NO in section c. In this section, C(O) on the surface of semichar started to dominate the consumption of NO, and the reaction mechanisms varied from pure homogeneous reduction to homogeneous-heterogeneous reduction. In section d (T>1000K), the concentration of NO significantly decreased. The reason for this was the formation of CO molecules and new reactive sites by decomposing C(O) compounds with high thermal stability (hydroxyl, anhydride, ether, and quinone) [43]. The additional sodium in the O2/CO2 preheating treatments expressed more tremendous advantages in the reducibility of NO than pure O2/CO2 pretreatment. Based on the results of this investigation, the optimal preheating condition for reducing NO emission was 6 vol.% O2 + 30 vol.% CO2 with sodium addition.

4 Conclusion

On the basis of the results and discussions presented above, the conclusions were summarized as follows:

1. Sodium addition in O2/CO2 pretreatments weakened the positive effects of marginal hydrogen atoms, and C6 altered from positive charge to negative charge.

2. The charge characteristic of the carbon connecting to the phenol group varied from negative to positive due to the strong electron-trapping ability of the phenol group.

3. For the heterogeneous reaction between NO and semichar prepared from pure O2/CO2 pretreatments, the energy gap was 558.05 kJ/mol, which decreased to 413.37 kJ/mol when Na was added in the pretreatments.

4. The TPR results illustrated that the Na enhanced the NO reducibility of semichar derived from O2/CO2 pretreatments, which had excellent consistence to the calculated results.

Acknowledgments

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References


