Intensification of NO\textsubscript{x} Conversion over Activated Coke by Ozone Oxidation for Sintering Flue Gas at Low Temperatures

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ABSTRACT: Denitration (De-NO\textsubscript{x}) over activated cokes (ACs) for sintering flue gas needs intensification. Gaseous reactions in a gas mixture containing NO, NO\textsubscript{2}, and NH\textsubscript{3} with the effect of O\textsubscript{2} concentration and moisture, were taken into consideration in the study of NO\textsubscript{x} conversion over ACs. Experimental studies on NO\textsubscript{x} conversion with and without NH\textsubscript{3} over ACs were conducted using a fixed-bed reactor at 100 °C. The results demonstrated that moisture significantly affected NO\textsubscript{x} removal over ACs, especially the NO\textsubscript{2} conversion. Under dry conditions, a disproportionation reaction of NO\textsubscript{2} over ACs dominated NO\textsubscript{x} conversion with no NH\textsubscript{3}, whereas apparent fast selective catalytic reduction (SCR) over the ACs was observed in the presence of NH\textsubscript{3}. Regardless of the presence of absence of NH\textsubscript{3} in wet mixtures, NO\textsubscript{2} adsorption on ACs via the disproportionation route dominated the NO\textsubscript{x} conversion. Increasing the NO\textsubscript{2}/NO ratio in the simulated flue gas enhanced the NO\textsubscript{x} conversion rate over ACs. −C(ONO\textsubscript{2}) deposition on ACs generated by the disproportionation route inhibited NO\textsubscript{x} conversion with time. O\textsubscript{3} oxidation was found to be efficient in increasing the NO\textsubscript{2}/NO ratio and intensifying the NO\textsubscript{x} conversion compared with commercially direct NH\textsubscript{3}-SCR over ACs. Increasing the temperature and decreasing the gas hourly space velocity can promote NO\textsubscript{x} conversion over ACs after O\textsubscript{3} oxidation. NO oxidized with O\textsubscript{3} coupled with NH\textsubscript{3} spray and continuous regeneration of ACs is a potential method for removing NO\textsubscript{x} from sintering flue gas.

1. INTRODUCTION

SO\textsubscript{2}, NO\textsubscript{x}, and particulate matter are the dominant flue gas pollutants generated by coal combustion, which remains the leading primary energy supply process in China. After the successful application of pollution control technologies in coal-fired power plants, emissions from other industrial processes have been increasingly attracting attention.\textsuperscript{1−5} According to the latest China emission standard published in 2019, the emission limit of particulate matter, SO\textsubscript{2}, and NO\textsubscript{x} for the sintering flue gases is 10, 35, and 50 mg/Nm\textsuperscript{3}, respectively.\textsuperscript{6} To meet the emission standard, activated cokes (ACs) have been widely recognized as a potential candidate for SO\textsubscript{2} and NO\textsubscript{x} removal from sintering flue gas, and NH\textsubscript{3} has been commonly used as a reductant to react with NO\textsubscript{x} to form gaseous nitrogen. ACs act as not only the adsorbent but also a catalyst in the process of NO\textsubscript{x} removal. The adsorption properties of NO and NO\textsubscript{2} on ACs have been studied in the absence of NH\textsubscript{3}.\textsuperscript{13−17} Some researchers believed that NO was catalytically oxidized to NO\textsubscript{2} on the surface of ACs, and NO\textsubscript{2}...
was adsorbed and converted into HNO₃ in the presence of O₂ and moisture.¹³,¹⁸,¹⁹ When NH₃ was introduced into this process, ACs acted as a catalyst to convert NOₓ into nitrogen via the following selective catalytic reduction (SCR) reaction.²⁰

\[
\text{NO}_x + \text{NH}_3 \xrightarrow{\text{catalyst}} \text{N}_2 + \text{H}_2\text{O}
\]

Because the temperature for SO₂ adsorption at upstream must be controlled below 150 °C, the catalytic activity of ACs is limited for the NH₃-SCR reaction.²¹⁻²³ Low-temperature NH₃-SCR itself has been a research hotspot all over the world.²⁴ Development of a highly active catalyst at low temperatures in the presence of moisture and SO₂ is of interest. Numerous studies have demonstrated that the doping of transition metals such as vanadium,²¹,²⁵,²⁶ iron,²²,²⁷,²⁸ manganese,²⁹ and cerium³⁰,³¹ on ACs could effectively improve their catalytic activity at low temperatures. Although the NOₓ removal efficiency could reach as high as 40%, the modified ACs still suffered from low-moisture resistance at low temperatures, which limits their application in NOₓ removal. Besides, flue gas reheating by using a gas–gas heater fitted downstream of a flue-gas desulfurization (FGD) reactor has also been considered to improve the catalytic activity. In addition to improving the catalytic activity, previous works also demonstrated that the increase of the NO₂/NO molar ratio could enhance the NOₓ conversion using NH₃ as a reductant (NH₃-SCR). When the NO₂/NO molar ratio = 1, the denitration (De-NOₓ) rate was found to increase dramatically compared to the NO₂/NO molar ratio of 0.³¹⁻³³ This fast SCR method consists of the following reaction:

\[
\text{NO} + \text{NO}_2 + 2\text{NH}_3 \xrightarrow{\text{catalyst}} 2\text{N}_2 + 3\text{H}_2\text{O}
\]

Figure 2. Characteristics of NOₓ mixtures with the effect of O₂ and NH₃ (a) NO mixtures; (b) NO₂ mixtures.
To increase the NO\textsubscript{2}/NO molar ratio, lots of oxidizing regents have been utilized for oxidizing NO to NO\textsubscript{2}, such as ozone, hydrogen peroxide, chlorine hypochlorite, chlorine dioxide, etc.\textsuperscript{34} As the typical oxidizing regent, ozone attracts NO oxidized by ozone accompanied by a wet scrubber was the most popular technology. NO was oxidized to NO\textsubscript{2} or N\textsubscript{2}O\textsubscript{5}, which was more soluble in water than NO, and can be removed using the scrubber. Generally, N\textsubscript{2}O\textsubscript{5} was preferred when accompanying with a wet scrubber. NO oxidation efficiency reached higher than 90% with O\textsubscript{2}/NO \approx 1 at 100 °C\textsuperscript{35,36} No N\textsubscript{2}O\textsubscript{5} formed when O\textsubscript{2}/NO \ll 1.\textsuperscript{37} Increasing temperature also decreased N\textsubscript{2}O\textsubscript{5} yield when O\textsubscript{2}/NO > 1, due to the decomposition of N\textsubscript{2}O\textsubscript{5} to NO\textsubscript{2}.\textsuperscript{37} NO\textsubscript{2} was the mean oxidation product when O\textsubscript{2}/NO \ll 1 at low temperatures. NO\textsubscript{2} is more susceptible to be adsorbed than NO. When NO oxidation was accompanied by adsorption, most studies focused on NO\textsubscript{3} adsorption to the adsorbent.\textsuperscript{13,17} Studies on the fast SCR method have used TiO\textsubscript{2} or AC-supported metal oxide as a catalyst. As for sintering flue gas De-NO\textsubscript{x} over ACs, how the fast SCR reaction affects NO\textsubscript{2} conversion was rarely studied. Besides, NO adsorption on ACs is always accompanied by oxidation of NO to NO\textsubscript{2}.\textsuperscript{39} Furthermore, sintering flue gas is characterized by high O\textsubscript{2} and moisture concentrations. How NO\textsubscript{2} adsorption and NH\textsubscript{3}-SCR reaction affect NO\textsubscript{2} conversion on ACs in a sintering flue gas atmosphere was unknown. Ozone (O\textsubscript{3}) was introduced into gas mixtures for increasing the NO\textsubscript{2}/NO molar ratio in the experiment to study its effect on NO\textsubscript{2} removal.\textsuperscript{38} Feasibility of O\textsubscript{3} oxidation combined with NH\textsubscript{3} spray for NO\textsubscript{3} removal over ACs after FGD was also discussed.

2. RESULTS

2.1. Gaseous Characteristics of NO\textsubscript{2} and NH\textsubscript{3} with the Effect of O\textsubscript{2}. Simulated gas flow used in the experiment is a mixture of gases from a cylinder. This would result in difference from the real flue gas. A clear understanding of the gaseous reaction among the gases is fundamental for following studies. Figure 2 illustrates the effect of O\textsubscript{2} and NH\textsubscript{3} on the composition of a gas mixture containing NO and NO\textsubscript{2}. Experimental conditions for this study can be found in sets I and II of Table 2. As can be seen from Figure 3a, the NO\textsubscript{2} concentration slightly increased with the increase of O\textsubscript{2} concentration from 0 to 20%, while the NO concentration decreased continuously. It indicates that part of NO was oxidized to NO\textsubscript{2} in the presence of O\textsubscript{2}. However, no apparent difference in the NO concentration between the gas mixture with and without the addition of NH\textsubscript{3} was observed.


d| C | H | O | N | S |
---|---|---|---|---|---|
\textsuperscript{31}S | 83.76 | 1.32 | 0.89 | 0.76 | 0.3 |
\textsuperscript{32}pore texture | S\textsubscript{REF} (m\textsuperscript{2}/g) | V\textsubscript{total} (cm\textsuperscript{3}/g) | V\textsubscript{micro} (cm\textsuperscript{3}/g) | V\textsubscript{meso-macro} (cm\textsuperscript{3}/g) | D (nm) |
---|---|---|---|---|---|
| 192.26 | 0.109 | 0.054 | 0.055 | 2.28 |

“Air-dry; S\textsubscript{REF}: specific surface area; V\textsubscript{total}: total pore volume; V\textsubscript{micro}: micropore volume; V\textsubscript{meso-macro}: mesopore and macropore volume; and D: average pore size.”

According to the results reported in the literature, there are two main routes for NO\textsubscript{3} adsorption on ACs:

(i) NO\textsubscript{3} was adsorbed on −C(O) or −C(\*\*) complexes as −C(\textsubscript{O})\textsubscript{NO\textsubscript{2}} or −C(\textsubscript{O})\textsubscript{NO\textsubscript{2}}.

\[ −\text{C}(\*\*) + NO\textsubscript{2} \rightarrow −\text{C}(\textsubscript{O})\textsubscript{NO\textsubscript{2}} \]

(ii) A pair of adsorbed NO\textsubscript{3} (−C(\textsubscript{O})\textsubscript{NO\textsubscript{2}}) on one active site or two adjacent active sites reacts through the disproportionation route

\[ 2 \times NO\textsubscript{2} \rightarrow −\text{C}(\textsubscript{O})\textsubscript{NO\textsubscript{2}} + NO \]

When NO\textsubscript{2} was adsorbed through the disproportionation route, the adsorption of 2 M NO\textsubscript{2} will release 1 M NO and leave 1 mol of −C(\textsubscript{O})\textsubscript{NO\textsubscript{2}} on the AC surface. Operation conditions, such as temperature, O\textsubscript{2} concentration, and
moisture, play an important role in determining the fraction of NO\textsubscript{x} conversion via nondisproportionation and disproportionation routes. The increase of the NO concentration and the drop in the NO\textsubscript{2} concentration under wet conditions implied that NO\textsubscript{2} adsorption over ACs was dominated by the disproportionation route in the presence of H\textsubscript{2}O.

NO\textsubscript{x} conversion over ACs with NH\textsubscript{3} supposed to be derived from the complex interaction between NO\textsubscript{2} adsorption through the two routes and the NH\textsubscript{3}-SCR reaction. Transient reaction analyses were conducted under wet and dry conditions, respectively, to investigate the effect of those processes on NO\textsubscript{x} conversion.

Figure 3 shows the change in concentrations of NO and NO\textsubscript{2} along with the reaction time under dry conditions. When experiment was conducted without the addition of NH\textsubscript{3}, the NO\textsubscript{2} concentration sharply dropped to nearly zero at the initial state and then slowly increased to the initial NO\textsubscript{2} concentration in 294 min. A reverse trend was observed for the NO concentration, which rapidly increased to about 624 ppm that was higher than the initial NO concentration and then slowly dropped to the level equal to the initial concentration. In comparison, the decrease in the concentration of NO\textsubscript{2} is about twice the increase in the concentration of NO, indicating that the increase of the NO concentration is mainly attributable to the NO\textsubscript{2} adsorption on ACs via the disproportionation route. When NH\textsubscript{3} was introduced to the mixture at 294 min, the NO concentration sharply dropped within 20 min and remained stable at about 36 ppm, which was much lower than the initial NO concentration. Meanwhile, the NO\textsubscript{2} concentration rapidly dropped to near zero and then slowly increased, which was still much lower than the initial NO\textsubscript{2} concentration after 356 min.

NO\textsubscript{2} conversion in the presence of NH\textsubscript{3} could be divided into two parts: the reduction of NO\textsubscript{2} and NO to N\textsubscript{2} via fast NH\textsubscript{3}-SCR (blue area) and the adsorption of NO\textsubscript{2} through a nondisproportionation route (gray area). There was no significant increase of the NO concentration being found when NH\textsubscript{3} was introduced, which meant that the adsorption of NO\textsubscript{2} on ACs via a disproportionation route was limited in the presence of NH\textsubscript{3}.

### Table 2. Experimental Conditions

| sets     | carrier gas (500 mL/min)                          | descriptions                                      |
|----------|--------------------------------------------------|--------------------------------------------------|
| set I i: | N\textsubscript{2} + (0, 4, 8, 12, 16, 20%) O\textsubscript{2} + 900 ppm NO + 900 ppm NH\textsubscript{3} | gaseous reaction at 100 °C                        |
| set I ii: | N\textsubscript{2} + (0, 4, 8, 12, 16, 20%) O\textsubscript{2} + 900 ppm NO + 900 ppm NH\textsubscript{3} | gaseous reaction at 100 °C                        |
| set I iii: | N\textsubscript{2} + (0, 4, 8, 12, 16, 20%) O\textsubscript{2} + 900 ppm NO | gaseous reaction at 100 °C                        |
| set II i: | N\textsubscript{2} + 8% H\textsubscript{2}O + 700 ppm NO\textsubscript{2} + 900 ppm NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set II ii: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 700 ppm NO\textsubscript{2} + 900 ppm NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set III i: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 900 ppm NO + 900 ppm (if present) NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set III ii: | N\textsubscript{2} + 20% O\textsubscript{2} + 750 ppm NO + 150 ppm NO\textsubscript{2} + 900 ppm (if present) NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set IV i: | N\textsubscript{2} + 20% O\textsubscript{2} + 450 ppm NO + 450 ppm NO\textsubscript{2} + 900 ppm NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set IV ii: | N\textsubscript{2} + 20% O\textsubscript{2} + 700 ppm NO\textsubscript{2} + 900 ppm NH\textsubscript{3} | NO\textsubscript{2} conversion over 1 g ACs at 100 °C |
| set V i: | N\textsubscript{2} | regeneration of ACs (set IV:i) |
| set VI i: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 900 ppm NO + (0, 150, 300, 500, 700, 900, 1080, 1450 ppm) O\textsubscript{3} | gaseous reaction at 100 °C |
| set VI ii: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 900 ppm NO + 900 ppm NH\textsubscript{3} | gaseous reaction at 100 °C |
| set VII i: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 900 ppm NO + 900 ppm NH\textsubscript{3} + 500 ppm O\textsubscript{3} | NO\textsubscript{2} conversion over ACs at 100, 180, 250 °C |
| set VIII i: | N\textsubscript{2} + 20% O\textsubscript{2} + 8% H\textsubscript{2}O + 900 ppm NO + (0, 900, 1800 ppm) NH\textsubscript{3} + 500 ppm O\textsubscript{3} | NO\textsubscript{2} conversion over 4 g ACs at 100 °C |
addition of NH₃, NO₂ adsorption on ACs via a disproportionation route played the dominant role in NO₂ removal.

Figure 6 shows the effect of NH₃ on NOₓ conversion over ACs under wet conditions. When NH₃ flow was turned off, no significant change in the NO₂ concentration was observed, whereas the NO concentration slightly increased. When NH₃ flow was turned on again, the NO concentration decreased by 12 ppm, while it was still higher than the initial NO concentration, which means that the addition of NH₃ partially inhibited the NO₂ conversion via a disproportionation route under wet conditions. However, the NO₂ concentration remained unchanged, indicating that the addition of NH₃ had no contribution to NO₂ removal under wet conditions. Hence, it can be concluded that increasing the NO₂/NO ratio supposed to enhance the NOₓ conversion ratio.

Figure 7 illustrates the NOₓ conversion rate along with reaction time with different NO₂/NO ratios. NOₓ conversion was only about 12% and remained stable during the experiment period when the NO₂/NO ratio was 0.25. When the NO₂/NO ratio increased to 1.21, the NOₓ conversion rate was about 30% at the initial stage and decreased linearly to about 3% after 300 min. With a further increase of the NO₂/NO ratio to 24, the NOₓ conversion ratio reached 46% at the initial stage and then linearly decreased to about 20% and maintained at about 20% after 250 min. The above results confirmed that increasing the NO₂/NO ratio could effectively improve the NOₓ conversion rate, while further investigation is required to explain why the NOₓ conversion rate decreased along with reaction time at a NO₂/NO ratio higher than 0.25.

Figure 8 shows the breakthrough curves of NO₂ conversion over ACs at a NO₂/NO ratio of 1.21 and 24 under wet conditions. A significant decrease of the NO₂ concentration and an increase of the NO concentration were observed, indicating that the disproportionation route of NO₂ adsorption is dominant in NO₂ conversion at NO₂/NO = 24 and 1.21. Different from the

Figure 4. NOₓ transient conversion over ACs with the effect of NH₃ in dry mixtures.

Figure 5. NOₓ transient conversion over ACs with the effect of NH₃ under wet conditions.
stable NO and NO\textsubscript{2} outlet concentrations in the ratio NO\textsubscript{2}/NO = 0.25, the NO\textsubscript{2} concentration increased slightly after reaching nearly zero and the NO concentration decreased slightly after cresting. The adsorbed NO\textsubscript{2} in the form of −C(ONO\textsubscript{2}) occupied the active sites on the AC surface. The active sites were reduced with the increase of the adsorbed NO\textsubscript{2} molecules, which resulted in the breakthrough of NO\textsubscript{2}. The initial NO\textsubscript{2} concentration of the gas mixture with a NO\textsubscript{2}/NO ratio of 0.25 is too low, and the adsorption time was not long enough to achieve the breakthrough of NO\textsubscript{2}.

Figure 9 shows the reduction percentage of NO\textsubscript{2}, calculated based on the production of NO (gray shadow in Figure 8), and the adsorption percentage of NO\textsubscript{2}, calculated by subtracting the reduced NO\textsubscript{2} from the total NO\textsubscript{2} conversion (red shadow in Figure 8), along with reaction time, within the first 150 min, the NO\textsubscript{2} reduction rate was almost equal to the NO\textsubscript{2} adsorption rate. This was consistent with the disproportionation route. After 150 min, NO\textsubscript{2} reduction was getting higher than NO\textsubscript{2} adsorption and the difference increased along with reaction time. The decrease of NO\textsubscript{2} reduction and adsorption was due to the reducing active sites on ACs for the formation of −C(ONO\textsubscript{2}) along with reaction time. The production of NO did not follow the production of −C(ONO\textsubscript{2}). This means that the direct reduction of NO\textsubscript{2} to NO occurs, which might not make any contribution to final NO\textsubscript{x} conversion.

According to Gao\textsuperscript{15} and Jeguirim,\textsuperscript{40} the adsorbed NO\textsubscript{2} would release NO and leave −C(O) on the surface of ACs. Generally, −C(O) would further react with NO\textsubscript{2} to form −C(ONO\textsubscript{2}), which follows the disproportionation route. With the increase of the adsorption time, not every −C(O) would react with NO\textsubscript{2}, which resulted in a higher NO\textsubscript{2} reduction rate than the adsorption rate as shown in Figure 9.

2.3. NO\textsubscript{x} Conversion over ACs with Ozone Oxidation. As discussed above, a higher NO\textsubscript{2}/NO ratio could improve the
NOx conversion. Ozone oxidation has been considered as a common method for NOx removal. The effect of O3 on NO oxidation, especially in the presence of NH3, was studied before the mixture went through the fixed-bed reactor containing ACs, and the results are shown in Figure 10.

It can be seen that with the increase of the O3 concentration from 0 to 900 ppm (O3/NO ≪ 1), the NO concentration sharply dropped, whereas the NO2 concentration increased rapidly whether with or without NH3. With a further increase of the O3 concentration to higher than 900 ppm (O3/NO > 1), the NO concentration dropped to zero for both with and without NH3. The NO2 concentration stabilized at about 650 ppm in the absence of NH3 in the gas mixture. As for gas mixtures with NH3, the NO2 concentration dropped to about 166 ppm at an O3/NO ratio of 1.5. The NH3 conversion rate was 10−20% at O3/NO ≪ 1, and sharply increased to 67% at O3/NO = 1.5. Furthermore, white crystals were found on the inside wall of the tubes after NH3 addition. The produced crystalline solids were collected and characterized by infrared spectroscopy (IR) using a Fourier-transform infrared spectroscopy (FTIR) spectrometer (Thermo Scientific Nicolet 6700). The sample was mixed with KBr at a weight ratio of 1:200 and milled before being flaked. The IR spectra of the white crystals are shown in Figure 11. According to literature,41,42 the solid is identified as ammonium nitrate (NH4NO3). The utilization rate of O3 was around 80% at O3/NO ≪ 1, which dropped upon further increasing the O3/NO ratio. When O3/NO > 1, N2O5 was generated in the gas mixture,37 which resulted in the decrease of the O3 utilization rate. N2O5 further reacts with NH3 and produced NH4NO3,43 which caused the decrease of the NO2 concentration and the increase of the NH3 conversion rate.

Transient experiments were conducted over ACs in a wet mixture consisting of 900 ppm NO, 500 ppm O3, and the results are in Figure 12. At 100 °C, NOx conversion after O3 oxidation exhibits a similar trend compared to directly mixing of NO and NO2 at a ratio of 1.21. The produced NO decreased along with NO2 breakthrough. This indicates that
the existence of O₃ in the gas mixture exhibits hardly any impact on NOₓ conversion over AC when O₃/NOₓ ≈ 1. When the experimental temperature increased to 180 °C, the NO concentration dropped to 413 ppm following a crest. The NO₂ concentration stabilized at about 28 ppm after the crest. With the increase of experimental temperature to 250 °C, the NO concentration further decreased to 385 ppm after a crest. The NO₂ concentration dropped to nearly zero. The decrease of NO and NO₂ concentrations with increasing temperature was attributed to the weakening NO₂ adsorption via a disproportionation route and the strengthening fast SCR reaction. The crests of NO and NO₂ concentrations at 180 °C and the NO concentration at 250 °C were resulted from the decomposition of deposited NH₄NO₃ in the ACs. The results can prove that higher operation temperature can promote total NOₓ conversion.

Although increasing the operation temperature is an effective method to enhance NOₓ conversion, it is difficult to be achieved in practical applications. Increasing the gas hourly space velocity (GHSV) and the NH₃/NOₓ ratio is also believed to be beneficial for NOₓ conversion. The NOₓ conversion of the gas mixture with different NH₃/NOₓ ratios at a low GHSV of only 4500 was studied and the results are shown in Figure 13. Compared with the breakthrough of NO₂ in Figures 8 and 12, the NO₂ concentration stabilized at near zero for 350 min after putting more ACs in the reactor. This means lower GHSV can contribute to stable NOₓ conversion for a longer reaction time. Transient change of NH₃ in mixtures effected the NO concentration at the outlet of the reactor. When the NH₃/NOₓ ratio was 1 in the gas mixture, the NO concentration stabilized at about 500 ppm, which was approximately 170 ppm higher than the initial NO concentration. Taking NH₃ away from mixtures resulted in the increasing of the NO concentration. The NO concentration resumed after NH₃ reloaded as NH₃/NOₓ = 1. A further increase of the NH₃/NOₓ ratio to 2 led to a slight decrease of the NO concentration through the ACs. The NO concentration stabilized at around 490 ppm (10 ppm lower than NH₃/NOₓ = 1). The amounts of NO production and NO₂ reduction approximately meet the disproportionation route molar ratio. This has demonstrated the domination of the disproportionation route in the process.

3. DISCUSSION

3.1. Reaction Mechanism over ACs. NOₓ conversion mechanisms are summarized in Figure 14. Oxidation of NO by O₂ or O₃ under both wet and dry conditions as well as in the presence of NH₃ was studied before the gas mixture was sent to the fixed bed containing ACs. O₂ can oxidize NO with low efficiency, while O₃ is more efficient. A slight reduction of NO and NO₂ by NH₃ was observed. If the O₃ concentration was higher than the NO concentration, NH₄NO₃ crystals were formed in the gas mixture containing NH₃. Moisture plays an important role in determining the conversion routes of NOₓ over ACs. Under dry conditions, NOₓ conversion was dominated by the disproportionation route if there was no NH₃ in the mixture. Obvious fast SCR reaction as well as direct adsorption of NO₂ to ACs were found after NH₃ was added to gas mixtures. As for wet mixtures, the fast SCR reaction was too weak to be observed under most operating conditions, especially for the gas mixture containing a higher NO₂ concentration at 100 °C. The disproportionation reaction dominated under most operation conditions and under wet conditions. Because of the deposition of (ONO₂) on the ACs, the disproportionation reaction was inhibited, which has resulted in the increase of the outlet NO₂ concentration and the decrease of NOₓ removal with time. With the breakthrough
of NO$_2$, the NO$_2$ conversion gradually shifted from adsorption via the disproportionation route to direct reduction to NO. Increasing operation temperature can strengthen the fast SCR reaction over ACs, which has become quite important at 250 °C under wet conditions.

### 3.2. Method of NO$_x$ Removal with ACs in a Highly Oxidizing Atmosphere

According to the analysis discussed in section 3, increasing the NO$_2$/NO molar ratio by O$_3$ oxidation can promote NO$_x$ conversion over ACs at 100 °C with moisture in flue gas. The NO$_x$ conversion cannot exceed 50% ($C_{NOx} = C_{NO2}$) due to the dominant disproportionation reaction of NO$_2$ over ACs with one-time oxidation. Increasing operation temperature is an efficient method to break the conversion limit, while energy consumption created difficulties. NH$_3$ is essential in NO$_x$ conversion. Lack of NH$_3$ will result in the increase of direct reduction of NO$_2$ to NO over ACs, which is negative for total NO$_x$ conversion. Further study is required to optimize the amount of NH$_3$ added into the flue gas.

![Figure 13. NO$_x$ conversion mechanisms in the gaseous phase and over ACs in a highly oxidizing atmosphere.](image)

![Figure 14. Regeneration curves of ACs after the reaction under the conditions of set IV-i.](image)

![Figure 15. Schematic diagram of the fixed-bed experiment system.](image)
When temperature increased to 150°C, replacement of AC regeneration can be coupled with SO2 conversion over ACS both with or without NH3 in the gas mixtures. Increasing temperature and decreasing GHSV can promote NOx oxidation by O3 coupled with NH3 and continuous regeneration after NOx saturated ACS in the regenerator in Figure 1. Products of AC regeneration are expected to be further converted into N2 or acid liquor. The temperature, low moisture, and low flow rate were utilized in the study. The ACs received are columnar with a diameter of 9 mm, and were crushed and sieved into particles with a size of 0.15–0.3 mm. The commercial coal-based AC specialized for desulfurization and denitrification was utilized in the study. The ACs received are columnar with a diameter of 9 mm, and were crushed and sieved into particles with a size of 0.15–0.3 mm. The chemical composition of the sample was determined using an elemental analyzer (Vario EL). The textural properties of the sample were characterized by an automatic surface analyzer (Quantachrome Autosorb 1C) as N2 adsorption/desorption isotherms at 77 K. The specific surface area was calculated by the Brunauer–Emmett–Teller method using the N2 adsorption isotherm. The single-point adsorption method was employed to calculate the total pore volume of the sample. The micropore volume was calculated using the t-plot method. The chemical composition and textural properties of the sample are shown in Table 1.

### 5.2. NOx Adsorption, Reduction, and Desorption Tests

The NOx conversion (adsorption and reduction) and desorption tests were carried out using a 500 mm long quartz fixed-bed tube reactor (17 mm i.d.), as shown in Figure 15. All flue gas components except ozone (O3) and water vapor were supplied in cylinders and were mixed in a gas mixer to simulate the flue gas. The flow rate was precisely controlled using mass flow controllers. O3 was made of pure O2 using an ozonator, and water vapor was generated using a heated water bubbler. All the tubes, valves, and joints in contact with SO2 were constructed from either quartz or polytetrafluoroethylene. Moreover, electric-heating tape (Thermolyne) embedded with temperature controllers was used to heat the transport line both upstream and downstream of the fixed-bed reactor to preheat the simulated flue gas and prevent any possible condensation before analysis. The NO, NO2, and NH3 concentrations were monitored and recorded continuously every 5 s using an on-line FTIR spectroscopy gas analyzer (DX4000, Gasmet Company, Finland). The O3 concentration was analyzed using an ozone monitor (GF-Z-3-S0, Shenzhen).

The experimental conditions are summarized in Table 2. In each typical conversion experiment operation, ACSs (if required) were put into the glass reactor. Before each experiment, the gas mixtures compositions were measured by FTIR spectroscopy through the bypass of the reactor. When the desired value was reached and stabilized, the gas flow was switched to the glass reactor to start the NOx conversion and desorption experiments. NOx conversion, NO2 adsorption, NO2 reduction, NH3 conversion, and O3 utilization were calculated according to the following equations:

\[
\text{NOx conversion} = \frac{C_{\text{NOx,inlet}} + C_{\text{NOx,outlet}} - C_{\text{NOx,inlet}} - C_{\text{NOx,outlet}}}{C_{\text{NOx,inlet}}} \times 100\%
\]

\[
\text{NO2 adsorption} = \frac{C_{\text{NO2,inlet}} - C_{\text{NO2,outlet}} - (C_{\text{NO2,inlet}} - C_{\text{NO2,outlet}})}{C_{\text{NO2,inlet}}} \times 100\%
\]

\[
\text{NO2 reduction} = \frac{C_{\text{NO2,inlet}} - C_{\text{NO2,outlet}}}{C_{\text{NO2,inlet}}} \times 100\%
\]

\[
\text{NH3 conversion} = \frac{C_{\text{NH3,inlet}} - C_{\text{NH3,outlet}}}{C_{\text{NH3,inlet}}} \times 100\%
\]

\[
\text{O3 utilization} = \frac{C_{\text{O3,inlet}} - C_{\text{O3,outlet}}}{C_{\text{O3,inlet}}} \times 100\%
\]

where, \(C_{\text{NH3,inlet}}\) and \(C_{\text{NH3,outlet}}\) represent the NH3 concentration (ppm) in the gas mixture at the inlet and outlet of the reactor, respectively, while \(C_{\text{NO2,inlet}}\) and \(C_{\text{NO2,outlet}}\) represent the NO concentration (ppm) in the gas mixture at the inlet and outlet of the reactor, respectively. \(C_{\text{O3,inlet}}\) is the O3 concentration (ppm) at the inlet of the reactor.

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Notes
The authors declare no competing financial interest.

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