A STUDY OF THE HETEROGENEOUS REDUCTION OF NO ON BITUMINOUS COAL CHARS

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The influence of char textural properties and coal rank on NO reduction was studied. A range of bituminous coals were pyrolyzed to obtain chars with different textural properties. A TG-MS was used to study the combustion behavior of the samples and the nitrogen compounds evolved. Experiments on the heterogeneous reduction of NO were carried out using chars with a different surface chemistry. The results show that NO-char interaction depends, to a large degree, on temperature. In the range of low temperatures (<750°C) surface complexes played an important role in the overall NO reduction. In the high-temperature range (>750°C), a different mechanism seems to be involved.

Keywords: char combustion; NO reduction; texture; coal rank

INTRODUCTION

The emission of nitrogen oxides from the combustion of coal remains a problem of considerable concern. Emissions of NO$_x$ into the atmosphere have detrimental effects on human health, vegetation, and ecological systems, and also contribute to smog and acid rain. Although there are important natural sources of NO$_x$, the greatest contributions come from fossil fuel combustion (Kramlich and Linak, 1994).

It is generally believed that the amount of NO and N$_2$O emitted from coal combustion is the result of homogeneous and heterogeneous formation and *in situ* destruction reactions. The main source of the final NO and N$_2$O emissions is fuel-bound nitrogen (Tullin et al., 1993). Figure 1 shows a schematic representation of the formation and reduction of nitrogen oxides during coal combustion.

Coal-N transformation during combustion can be divided into three main stages: coal devolatilization, where nitrogen in coal is split into char-N and volatile-N, the formation of nitrogen oxide in an oxidant atmosphere, and, finally, nitrogen oxide reduction. During devolatilization and further tar cracking, nitrogen compounds such as NH$_3$ or HCN, which are considered as NO$_x$ precursors, are formed (Thomas, 1997). This NO$_x$ formation goes through homogeneous gas-phase reactions.

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The heterogeneous oxidation of char-N constitutes an important source of nitrogen oxides during the overall combustion process. The NO and N₂O formed from volatile-N and char-N oxidation can be reduced in a number of ways: homogeneous gas-phase reaction with NH₃ and HCN; heterogeneous catalytic reduction by CO, HCN, and NH₃ with char or ash as catalysts (Johnsson, 1994); and heterogeneous reduction with char, which is considered the most important reaction in reducing both NO and N₂O (Pels, 1995). The reactions of NO with carbonaceous materials have been studied by other authors (Aarna and Suuberg, 1997; Chambrion et al., 1997; Thomas, 1997). However, these reactions are not as well understood as other gas-carbon reactions, such as CO₂ and steam with carbons. The overall reduction process can be expressed as in Eq. (1), but the detailed mechanism and certain aspects, such as the effect of char surface area, coal rank, and the role of some char surface compounds, are still being investigated.

\[
C(\cdot) + NO \rightarrow N_2 + CO_x \text{ and/or } N_2O + CO_x \quad (1)
\]

The reaction between nitrogen oxides and carbon generates nitrogen-containing complexes on the carbon surface. The use of X-ray photoelectron spectroscopy (Chambrion et al., 1997) has made the characterization of some of these surface complexes possible. It is generally agreed that the first step in the heterogeneous reduction of NO by carbon is the chemisorption of nitrogen oxide on the carbon surface, with the subsequent formation of nitrogen and oxygen surface complexes as is shown in Eq. (2).

\[
2C(\cdot) + NO \rightarrow C(N) + C(O) \quad (2)
\]

The initial adsorption appears to involve the addition of nitric oxide, some authors suggest an approach of NO in an "N-down" configuration (Teng and Suuberg, 1993), while others suggest an approach of NO parallel to the graphite layer (Kyotani and Tomita, 1999). Following the chemisorption step, a series of reactions occur where different surface compounds intervene to produce N₂, N₂O, CO, and CO₂. The nature of the surface compounds involved is still unclear.
Several mechanisms have been proposed to explain the heterogeneous reduction of NO. Some authors (Teng and Suuberg, 1993) suggest that NO is adsorbed on the char surface to form NO complexes, C(NO), which can be reversible or irreversible. Adsorption of NO onto carbon at high temperature is thought to be dissociative (Teng et al., 1992), resulting in the formation of surface complexes that desorb to form, primarily, N\(_2\) and CO\(_2\):

\[
4C() + 2\text{NO} \rightarrow 2\text{C(N)} + 2\text{C(O)} \rightarrow \text{N}_2 + \text{CO}_2 + 3\text{C()}
\]  

(3)

However, other authors (Jones et al., 1997) propose the associative adsorption of NO:

\[
\text{C(NO)} + \text{C(N)} \rightarrow \text{N}_2\text{O} + 2\text{C()}
\]  

(4)

\[
\text{C(NO)} + \text{C(NO)} \rightarrow \text{N}_2 + \text{CO}_2 + \text{C()}
\]  

(5)

Regarding the surface compounds involved in NO heterogeneous reduction, there are also different theories (Illán-Gómez et al., 1996; Miettinen and Abul-Milh, 1996; Suzuki et al., 1994) about whether oxygen or nitrogen surface complexes react heterogeneously with NO on the char surface. Carbon, therefore, has been recognized as playing a significant role in reducing NO during combustion, although different aspects of this reaction are still unclear. Other authors (Shimizu et al., 1992) have found that with increasing surface area, the conversion of char nitrogen to NO\(_x\) decreased due to increased reduction of NO. Another paper (Johnsson, 1994) indicates that it is the specific surface area, and not the surface reactivity, that determines the char reactivity to NO. Other studies (Illán-Gómez et al., 1993; Ruiz Machado and Hall, 1998; Calo et al., 1999) have raised more debate on the relationship between char surface area and NO reduction activity. A better understanding of these NO reduction reactions during coal combustion could be an important contribution to the diminution of the final NO\(_x\) emissions. Basic studies on these reactions, along with the assessment of the factors that affect these reactions in a greater extent, will be of paramount importance. The objective of this paper, as a first approach to the study of these reactions, is to investigate the role of char properties (i.e., surface area, surface compounds) in the NO heterogeneous reduction.

**EXPERIMENTAL**

**Materials**

The chars used throughout this study were prepared from a series of bituminous coals (W, T, and C), with low, medium, and high volatile matter content, respec-
tively. The main characteristics of these coals are shown in Table I. Pyrolysis chars were obtained in a quartz reactor (i.d. 30 mm), under nitrogen flow, up to a final temperature of 850°C and a soaking time of 1 hr. A series of heating rates (5, 50, and 150°C/min) were used during W pyrolysis in order to obtain chars with different textural properties, chars being denoted as W5, W50, and W150, respectively. The other two coals (T and C) were pyrolysed at 150°C/min, giving the chars denoted as T150 and C150. The char analyses are also presented in Table I.

Textural characterization of the samples was carried out by measuring true (He) and apparent (Hg) densities and mercury porosimetry. Adsorption isotherms in N2 at –196°C were also performed. Active surface area values (ASA) were determined by a gravimetric method based on methods described by Laine et al. (1963) and Rubiera et al. (1998).

**Procedure**

Temperature-programmed combustion experiments (TPC) were performed in a thermogravimetric analyzer (TGA). In order to compare the samples, factors, such as sample weight, heating rate, and gas flow rate, should be well established to ensure good repeatability between experimental runs. In all the experiments carried out in this work, 25 mg of sample ground to pass a 0.212 mm (70 mesh) sieve, a gas flow rate of 50 ml/min and a linear heating rate of 15°C/min were employed. In the temperature-programmed combustion experiments, the sample was placed in a platinum crucible and the temperature was raised to 1200°C in 20% oxygen in argon.

Temperature-programmed reduction experiments (TPR) were also performed. The sample (25 mg) was placed in an alumina crucible over a bed of powdered alumina in order to facilitate contact between the char and the reactive gas. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (wt% db)</th>
<th>Ultimate analysis (wt% daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile matter</td>
<td>Ash</td>
</tr>
<tr>
<td>W</td>
<td>17.0</td>
<td>6.2</td>
</tr>
<tr>
<td>T</td>
<td>25.1</td>
<td>6.8</td>
</tr>
<tr>
<td>C</td>
<td>36.7</td>
<td>7.1</td>
</tr>
<tr>
<td>W5</td>
<td>1.9</td>
<td>6.3</td>
</tr>
<tr>
<td>W50</td>
<td>2.4</td>
<td>7.2</td>
</tr>
<tr>
<td>W150</td>
<td>1.7</td>
<td>8.0</td>
</tr>
<tr>
<td>T150</td>
<td>2.3</td>
<td>9.3</td>
</tr>
<tr>
<td>C150</td>
<td>3.5</td>
<td>9.8</td>
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</tbody>
</table>

oaCalculated by difference.
temperature was raised from room temperature to 1400°C at 15°C/min under Ar flow with 400 ppm of NO (50 ml/min).

A quadrupole mass spectrometer (MS) linked to the thermobalance was used to record the gas-evolution profiles. To avoid undesirable secondary reactions, a probe was placed very close to the sample crucible of the thermobalance, in the gas flow direction. A normalized procedure was applied in order to make the results internally consistent. In this way it was possible to compare the same m/z (mass-to-charge ratio) signals for different samples. The optimization of the online TGA-MS equipment and the normalization procedure were described in a previous work (Arenillas et al., 1999). The species were monitored at m/z 14 (N₂⁺⁺), 27 (HCN⁺), 28 (N₂⁺ and ¹²CO⁺), 29 (¹³CO⁺), 30 (NO⁺ and ¹²C¹⁸O⁺), 44 (CO₂⁺ and N₂O⁺), and 46 (C¹⁶O¹⁸O⁺). The N₂⁺⁺ and NO⁺ profiles were corrected for contributions from CO⁺⁺ and ¹²C¹⁸O⁺, respectively, using the method described by Jones et al. (1995).

During temperature-programmed combustion tests, signal m/z 44 belongs to CO₂ formation, this being the main gaseous product due to the oxidant atmosphere. Other signals belonging to CO₂ were also detected, such as m/z 12 (C⁺), 28 (CO⁺), and they follow the same trend as the main signal m/z 44. Consequently, the reduced species formed in the reaction between NO and the char surface were monitored as m/z 14. This signal belongs to the species N₂⁺⁺, which comes from either N₂ or N₂O. For this reason the species N₂⁺⁺ was denoted as reduced species.

![Figure 2](image_url)

**FIGURE 2** MS evolution profiles of signals m/z 44 (N₂O⁺) and m/z 12 (C⁺) during the temperature-programmed reduction (TPR) experiment (400 ppm NO in Ar) and a blank experiment (Ar).
However, in the temperature-programmed reduction experiments, no oxygen was present in the reacting gases. At temperatures below 1000 oC, signal m/z 44 presents different peaks that do not appear in signal m/z 12. This is because m/z 44 belongs mainly to N$_2$O$^+$ and not CO$_2$$^+$. Figure 2 shows the N$_2$O$^+$ and C$^+$ profiles of a temperature-programmed reduction experiment (400 ppm NO in Ar) and a blank experiment (Ar).

As can be observed in Figure 2, signal m/z 44 presents different peaks, although the main peak appears at 800 oC. However, signal m/z 12 belonging to C$^+$ does not present any appreciable peak. This implies that signal m/z 44 can be assigned to N$_2$O as the main product, although some CO$_2$ and CO may be formed as subproducts of the heterogeneous reduction (Aarna and Suuberg, 1996; Chambrion, et al., 1997; Illán-Gómez et al., 1996).

The TPR experiments were concentrated in the temperature range of 20-1000 oC, because at higher temperatures gasification of the char was detected to some extent, as can be observed in Figure 2 where a high intensity of the signals m/z 12 and 44 was detected. In this study, special attention was paid to the formation of N$_2$O (i.e., influence of different char surface complexes). N$_2$O emission is especially important in the combustion of coal in fluidized bed reactors, mainly due to their relatively low operation temperatures (800–950 oC). As can be seen in Figure 2, the main peak temperature in the N$_2$O profile takes place at 800 oC.

Several researchers have reported that the presence of O$_2$ is essential for N$_2$O formation during coal char-NO reactions (Krammer and Sarofim, 1994; Tullin et al., 1993). This has been explained by assigning to oxygen the role of freeing the internal C(N) species so that it can react with NO to form N$_2$O. However, because of the molecular similarity between O$_2$ and NO, it is doubtful whether the ability to break up char structure can be attributed just to O$_2$ (Miettinen and Abul-Milh, 1996). The higher reactivity of O$_2$ in comparison to that of NO, is the reason why the reaction of coal char-NO is enhanced in the presence of oxygen. However, this reaction also occurs when there is no oxygen in the reactive gases, though to a lesser extent. The results obtained in this work support this theory.

RESULTS AND DISCUSSION

Textural Characterization of the Chars

After pyrolysis of the coals, the nitrogen was preferentially retained in the char, as can be observed in the analyses presented in Table I. The nitrogen content of the chars is similar in all cases, irrespective of the pyrolysis conditions (i.e., heat-
ing rate) or the nature of the parent coal. Only char C150 presents a higher nitrogen content. There is some difference in the ash content of the chars. For this reason the potential influence of the mineral matter in the combustion behavior of the chars was also taken into account, as is discussed later.

The heating rate used during the pyrolysis process had a marked effect on the texture of the resultant chars. Heating rate influenced the plastic behavior of the samples and, as a consequence, different char structures and textures were obtained between W5 and W150.

From the true and apparent densities, the total pore volume $V_T$, which includes pores with a radius of less than 14700 nm, can be obtained by

$$V_T = \left[ \frac{1}{\rho_{\text{Hg}}} - \frac{1}{\rho_{\text{He}}} \right]$$

As $V_T$ is the sum of micro-, meso-, and macropores, micropore volume can be calculated as

$$V_{\text{micro}} = V_T - (V_{\text{macro}} + V_{\text{meso}})$$

In this work the pore volume, which corresponds to the mercury volume intruded between the 3.7 and 25 nm pore radii, is considered as mesopores, and between the 25 and 14700 nm pore radii, as macropores. Both are determined by mercury porosimetry. Pores with a radius lower than 3.7 nm will be considered as micropores. Figure 3 shows the pore volume distribution and BET surface areas for the W chars.

Micropores are the main contributors to the surface area, and mesopores are very important in reactant diffusion. Thus, they are often called feeder pores. As the heating rate used during the pyrolysis process increases, macropore volume decreases (see Fig. 3); whereas micropore volume increases, giving rise to higher surface areas. The mesopore volume is almost constant. Thus, operating conditions during char obtention (i.e., heating rate) have a considerable influence on the resultant textural properties. The char obtained at the highest heating rate ($150^\circ$C/min) presents the highest values of micropore volume and surface area.

The other two bituminous coals (T and C) were pyrolysed at $150^\circ$C/min in order to compare the influence of coal rank on char textural properties. The results are shown in Figure 4.

As can be observed, the rank of the parent coal also plays an important role in the development of char texture. As the coal rank decreases (W > T > C), the char presents a lower macropore and higher micropore volume and, therefore, higher BET surface area values. It should also be noted that char T150 has developed a higher mesopore volume than the other two chars.
FIGURE 3 Pore volume distribution and BET surface areas for the W chars.

FIGURE 4 Pore volume distribution and BET surface areas for the chars obtained at 150°C/min.
The variation in char textural properties exerts a marked effect on the diffusion of reactants and products through the pores during reaction. Thus the operating conditions during pyrolysis (i.e., heating rate) will be determinant in the reactivity of the char obtained, whether oxygen or other reactive gases, such as NO.

**Temperature-Programmed Combustion Tests (TPC)**

The results of the TPC tests showed different NO\textsuperscript{+} profiles for the chars, which presented a variety of textural properties. As can be seen in Figures 5–7, the NO\textsuperscript{+} profiles underwent a bimodal evolution, probably due to the two main types of nitrogen functionality in the chars (Davison, 1994; Kelemen et al., 1998; Pels et al., 1995; Thomas et al., 1993).

The evolution of CO\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{+} during the TPC experiments is also shown in these figures, as they represent carbon evolution during the TPC test, and they are directly connected with NO homogeneous and heterogeneous reductions. Thus in the determination of the conversion of nitrogen, not only has the NO\textsuperscript{+} peak area been considered, but also the CO\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{+} peak areas, as suggested by other authors (Jones et al., 1995).

A comparison of the evolution profiles of the chars studied during the TPC tests (Figs. 5–7) shows that the combustion process and the emission of CO and CO\textsubscript{2} shift to a higher temperature as the rank of the parent coal increases. This is indicative of lower char reactivity due to lower char textural properties.

![Graph showing NO\textsuperscript{+}, CO\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{+} evolution profiles during the TPC test for char W150.](image)
FIGURE 6  NO+, CO+ and CO2+ evolution profiles during the TPC test for char T150.

FIGURE 7  NO+, CO+ and CO2+ evolution profiles during the TPC test for char C150.
As mentioned earlier, char textural properties increased with the heating rate used during pyrolysis and with the decrease in the parent coal rank. Higher textural properties imply higher accessibility to the active sites on the char surface. The influence of this reactivity on final NO emission during the TPC tests can be seen in Table II.

Table II shows the N/C atomic ratio for the parent coals and all the chars studied. It can be observed that the N/C atomic ratio is almost constant for all the chars (0.012–0.014), except for the C150 char, which presents a higher value due to the higher N content of the parent coal C. From the integrated peak areas of NO$^+$, CO$^+$, and CO$_2^+$ evolution profiles during the TPC tests, the conversion of nitrogen to NO can be calculated for all samples (Table II). It can be seen that the N conversion decreases as the heating rate used during pyrolysis increases, and the rank of the parent coal decreases. This means that NO emissions during combustion decrease, although the N/C ratio from the analyses is very similar. This is due to NO reduction on the char surface, which intensifies as the char textural properties increase (i.e., micropore volume and surface area). As a consequence, greater accessibility to the active sites over the char surface is attained. It also needs to be pointed out that char C150 presents the lowest N conversion to NO, even though its nitrogen content is the highest. This is due to the high textural properties developed and the higher availability of the char active sites, which play an important role in heterogeneous reactions. Active surface area (ASA) values give an idea of the amount and availability of these active sites. Figure 8 shows the relationship between ASA values and N conversion for the chars studied.

As the ASA values of the chars increase, nitrogen conversion to NO decreases and conversion to the reduced species N$_2^{++}$ increases. This implies that heterogeneous NO reduction takes place on the char surface, reducing NO formation and increasing the emission of the reduced species. Thus, operating condi-
tions during pyrolysis and coal rank play an important role in the final emissions of NO from char combustion.

The potential influence of char mineral matter content on NO emissions was also studied. Mineral cluster dispersion was observed by SEM-EDAX, which showed no significant differences between the samples studied. TPC tests on demineralized samples obtained from chars W5 and W150 were also performed. The results reflect the same trend: an increase in heating rate was accompanied by a corresponding intensification of NO reduction. Thus, for the samples studied here, mineral matter content does not play the main role in the heterogeneous reduction of NO. This role is performed by the textural properties of the chars.

**Temperature-Programmed Reduction Tests (TPR)**

During these experiments, special attention was paid to N\textsubscript{2}O evolution, even though the study of this signal is only qualitative because of the possibility of CO\textsubscript{2} interference.

Figure 9 shows the NO\textsuperscript{+} and N\textsubscript{2}O\textsuperscript{+} evolution profiles of a TPR experiment. The relative intensity (RI) indicates the formation or destruction of a gaseous compound from the initial reactive gas (400 ppm NO in Ar), which means that N\textsubscript{2}O is formed (RI positive) while NO disappears (RI negative).

It can be observed that the maximum peak temperatures for N\textsubscript{2}O emission are the same as the minimum peak temperatures for NO. This corroborates the
view that the main species of the signal m/z 44 is N₂O⁺. It can also be seen that the N₂O⁺ profile presents different peaks at around 400, 600, and 825°C, the latter being the main peak. The NO⁺ profile presents an extra minimum around 950°C, while no maximum was detected for N₂O⁺. It is possible for the reduction of NO to give other gaseous products different to N₂O (i.e., N₂). The NO profile also presents a peak at low temperature. This could be due to the reversible adsorption of NO at low temperature, which is possibly desorbed as the temperature increases and reaches a maximum at around 200°C.

In this work the influence of different surface complexes on the heterogeneous NO reduction was also studied. The W150 char was used to obtain different samples: char without surface complexes (W150*), char with oxygen surface complexes (W150-O), and char with free carbon active sites (W150-C).

Char W150* was obtained by heating the W150 char at 850°C for 6 hr under Ar flow in order to clean the char surface before performing the TPR test. Char W150-O was obtained by heating the initial W150 char at 850°C for 6 hr under Ar atmosphere. The temperature was then lowered to 150°C, and the char was exposed to oxygen for 17 hr in order to increase the amount of oxygen-surface complexes. The oxygen was swept from the chamber before the TPR test. Finally, char W150-C was obtained after cleaning the char surface (850°C and 6 hr under Ar flow), oxygen chemisorption (17 hr under O₂ flow at 150°C), and desorption of oxygen complexes formed by heating under Ar for 6 hr at 850°C.

![Graph showing NO⁺ and N₂O⁺ evolution profiles during a typical TPR experiment.](image.png)
N₂O evolution profiles during the TPR tests for these chars are presented in Figure 10. Figure 10 displays a shift to higher temperatures at the main maximum peak of the N₂O⁺ profiles of the modified chars (i.e., W150*, W150-O, and W150-C). This behavior could be due to the initial cleaning step performed in the modified chars production process. Surface complexes have a similar effect to ignition due to the presence of volatile matter in the combustion process. As can be seen in Figure 10, N₂O formation from the W150* char is much lower than in the case of the original W150 char. This implies the importance of surface complexes in the heterogeneous reduction of NO. The maximum peak, though to a lesser extent, appears at the same temperature as the other chars, possibly due to the same mechanism of formation.

The N₂O⁺ profile from the TPR test of the W150-O char presents formation at low temperature, though to a lower extent than the original char. This may be because W150-O has mainly oxygen surface complexes on its surface and they are part of the total number of complexes that take part in the NO heterogeneous reduction on the char surface. However, the main peak in N₂O formation appears around 900°C.

Char W150-C does not present N₂O formation at low temperature due to there being no surface complexes on it. There is only the main peak, which appears to a higher extent than in char W150-O. This could be due to the presence of free carbon sites in char W150-C.
Other authors (Aarna and Suuberg, 1997; Li et al., 1998) have suggested two different regimes in the NO heterogeneous-reduction process. A distinctive break in apparent activation energy has been found to occur around 700–750°C. This behavior does not seem to correspond to a simple case of transition from a chemical reaction rate control to a mass transfer control. This transition temperature range rather indicates a change in the mechanism of NO heterogeneous reduction. It seems that in the regime of low temperature (<750°C), the process is dominated by desorption of surface complexes (i.e., oxygen surface complexes), while at high temperature (>750°C) the process is controlled by other factors, as at this temperature all the surface complexes are practically desorbed. The results obtained in this study corroborate this theory because, at low temperatures, only the chars with surface complexes produce some NO heterogeneous reduction (W150 and W150-O), while at high temperatures all the chars present a main peak of N2O formation.

Figure 11 shows the evolution of reaction rate constants with temperature for chars W150-O and W150-C (obtained from TGA data during the TPR test), assuming a first-order reaction.

It can be observed in Figure 11 that the rate constant for the W150-C follows a linear trend with the inverse of temperature, indicating a first-order reaction and no change in the mechanism over the whole range. However, the rate constant for the W150-O decreases at higher temperatures, which is consistent with the desorption of surface complexes. The activation energies for the reactions are Ea = 80 kJ mol⁻¹ for W150-O and Ea = 14 kJ mol⁻¹ for W150-C.
constant for char W150-O shows a change in the mechanism at around 750°C due to the transition from surface complex desorption to another process at high temperature.

It is worth noting that the mechanisms of W150-O and W150-C at high temperature coincide, suggesting that only one mechanism is involved at high temperature. However, at low temperature the rates are totally different due to the presence of oxygen surface complexes in the W150-O char and the absence of complexes in the W150-C char.

CONCLUSIONS

In this work, the effect of varying bituminous coal char properties on NO emissions was studied by thermal-analysis mass spectrometry. It was found that an increase in heating rate and a decrease in coal rank produced chars with higher textural properties (i.e., higher values of micropores and surface area). These textural properties made active sites more accessible, exerting a big influence on final NO emissions because heterogeneous reduction on the char surface takes place to a greater extent.

Temperature also seemed to be of great importance in the coal char-NO reaction. Two main mechanisms could be distinguished, the transition temperature range occurring at around 750°C, as follows. At low temperature, the surface complexes were desorbed, producing free carbon sites in situ, which were very reactive toward NO. At high temperature, where no remaining surface complexes were left, the mechanism was totally different.

NOMENCLATURE

- C()  reactive carbon surface site
- CO\textsubscript{X}  CO or CO\textsubscript{2}
- C(N)  nitrogen surface complexes
- C(O)  oxygen surface complexes
- C(NO)  NO adsorbed group on carbon surface
- $\rho\textsubscript{Hg}$  apparent density, determined by mercury
- $\rho\textsubscript{He}$  true density, determined by helium

References


