Synthetic coal chars for the elucidation of NO heterogeneous reduction mechanisms

C. Pevida, A. Arenillas*, F. Rubiera, J.J. Pis

Instituto Nacional del Carbón, CSIC. Apartado 73. 33080 Oviedo, Spain.

Abstract

In the present work, the mechanisms involved in NO-char heterogeneous reduction have been studied using a synthetic coal char (SC char) as carbon source. Another synthetic char (SN char) without nitrogen in its composition has also been employed in these studies. Isothermal reduction tests at different temperatures have been carried out. Two temperature regimes were considered: low temperature ($T < 250\text{ }^{\circ}\text{C}$) where NO chemisorption takes place and high temperature ($T > 250\text{ }^{\circ}\text{C}$) where NO-C reaction occurs. Step response experiments combining consecutive reaction stages with NO and ^{15}NO were performed in order to determine the role of nitrogen surface complexes, C(N), in the reduction process. The results revealed N_2 and CO_2 to be the main reduction products under the experimental conditions employed in this work. NO chemisorption at lower temperatures results in N_2 emission and surface complexes (mainly oxygenated) formation, while char gasification by NO involves a direct NO attack on the char surface to form surface complexes. As a consequence of desorption of these complexes new sites of reaction are created.

Keywords: NO heterogeneous reduction, coal char, isotopically labelled NO

1. INTRODUCTION

Among all the reactions that occur in coal-fired combustion systems, the least understood are the char-related reactions; for instance, the formation of NO_x from the char and the reduction of NO_x on the char surface [1-3]. Regulations for NO_x and N_2O

are expected to become more and more stringent in the near future, but without a detailed knowledge of the mechanisms of the reactions that occur during coal combustion, it will be difficult to meet such regulations.

Even though the global NO heterogeneous reduction can be schematised as:

where C_{ac} represents an active site on the char surface, the mechanisms involved in the process are not yet fully understood. Published works on this subject agree that reduction goes through two stages: NO adsorption, reversibly and/or irreversibly, at low temperatures, and NO-char reaction at higher temperatures. However, it is important to take into account that neither stage is independent, as NO adsorption influences the NO-char gasification process.

Coal has a very complex and heterogeneous structure which makes it difficult to isolate the factors influencing NO_x released during coal combustion. Moreover a deeper knowledge of the chemistry involved in the formation and the reduction of NO_x is required. Many authors have performed NO heterogeneous reduction studies on carbonaceous materials using, mainly, chars from phenol-formaldehyde resins [4-9], graphites [10] and activated carbons [11-13]. The use of model compounds, with controlled heteroatom content and well defined functionalities, is a useful approach that has been used by other authors [14, 15] to study the release of nitrogen compounds from char combustion. However, this picture leaves out important aspects such as coal structure, interactions between different surface groups and cross-linking reactions.

In the present work a char produced from the pyrolysis of a synthetic coal (SC) was used as carbon source in the NO-char heterogeneous reduction studies. The synthetic coal not only represents a carbonaceous matrix –nitrogen functionalities included- but also has the same type of active sites as those of a high volatile bituminous coal [16-18]. The synthetic coal was prepared by mixing and curing a series of model compounds (phenol-formaldehyde resin, PFR, perilentetracarboxylic-acid-dianhydride, PTC) and by incorporating nitrogen functionalities commonly present in coal (polyvinylpyrrolidone, PVP, and poly-4-vinylpyridine, p4VP) [19].

Previous studies in our group have validated the use of synthetic coal chars –with and without nitrogen in their composition- as well as isotopically labelled NO in the study of NO heterogeneous reduction [20]. Nevertheless, in order to attain a step further in the understanding of the mechanisms involved, the role of oxygen surface complexes and mainly of the nitrogen complexes formed need to be clarified. In this sense, the performing of isothermal and transient kinetics experiments, presented in this work, had revealed complementary and relevant information about the insight of the NO heterogeneous reaction mechanisms.

2. METHOD

The NO-C reaction was studied using a char produced from the pyrolysis of the synthetic coal (SC char). Pyrolysis was performed in a horizontal quartz reactor (i.d. 30 mm), under He flow, at a heating rate of 15 °C min⁻¹ to a maximum temperature of 850 °C. Another synthetic char (SN char) without nitrogen in its composition was also employed in these studies [17]. The chemical analyses of these chars are presented in Table 1.

A thermogravimetric analyser (Setaram TGA 92) linked to a gas analysis system -MS (Balzers MSC 200) and FTIR (Nicolet Nexus, DTGS detector and KBr windows)

mounted in parallel- was the experimental set-up used to study the evolution of the gases during the experiments. Samples ($\sim 2\text{mg}$, particle size $< 150\ \mu\text{m}$) were heated at atmospheric pressure in a flow ($50\ \text{cm}^3\ \text{min}^{-1}$) of the corresponding gas, according to the type of experiment.

One of the main factors influencing the NO-char reaction is temperature. Previous studies developed in our group had confirmed the differences in the behaviour of the chars towards NO reduction over the $20\text{-}1000\ ^\circ\text{C}$ temperature range [20]. For the present work, isothermal reduction studies at different temperatures were carried out in order to establish the different mechanisms influencing the reduction process. Two main regimes, NO chemisorption above ambient temperature ($<250\ ^\circ\text{C}$) and NO-char gasification reaction at higher temperatures ($>250\ ^\circ\text{C}$), were considered. With the aim of determining the role of nitrogenous complexes generated during the chemisorption stage in the heterogeneous NO reduction, step response experiments using NO and ^{15}NO (isotopically labelled NO) were performed. One important point of this type of experiment is that the switching of feed gas does not disturb the reaction and therefore it is monitored under steady-state conditions.

3. RESULTS AND DISCUSSION

3.1. Experimental studies of NO heterogeneous reduction

NO heterogeneous reduction involves a first step where NO is adsorbed on the carbonaceous surface. While chemisorption or irreversible adsorption takes place at temperatures above ambient and is followed by the formation of N_2 and surface oxides, it is physisorption or reversible adsorption that prevails at temperatures below ambient [21-23].

The calibration methods employed for quantification of the gases evolved during the different experiments have been described in detail elsewhere [19]. Moreover, consistency of the concentration values obtained with both gas analysers, MS and FTIR mounted in parallel [19, 20], supports the accuracy of the calibration methods used and the results presented below.

3.1.1. Low temperature ($T < 250^{\circ}\text{C}$) chemisorption experiments

In this work, previously to the chemisorption experiments, the chars (i.e., SC and SN) were subjected to a cleaning step under Ar flow and heating up to 1000°C . Afterwards, the temperature was lowered to 200°C . The temperature at which the chemisorption experiments were carried out (200°C) is high enough to ensure that chemisorption prevails over physisorption but it is low enough to minimise gasification of the char. A reactive gas mixture of 400 ppm NO in Ar was used and the chemisorption step was pursued for two hours. Finally, the samples were subjected to TPD tests under Ar, at a heating rate of $15^{\circ}\text{C min}^{-1}$ to a maximum temperature of 1000°C , this temperature being maintained for 30 minutes.

An analysis of the gases evolved during the TPD tests allowed the identification of the surface compounds generated during the chemisorption step. Although there is not much literature on this field, most published works agree that NO chemisorption at temperatures above ambient implies the dissociation of the molecule, with the subsequent formation of oxygen and nitrogen surface complexes that would evolve afterwards as CO, CO₂ and N₂ during the thermal treatment. However, other authors [23] have proposed dimerisation –associative chemisorption– as the first step towards the formation of surface complexes during chemisorption. The exact nature of these complexes and their contribution to the overall NO-C reaction is not known for certain. The results presented in this work will provide valuable information in this respect.

Figure 1 shows the evolution of NO and N₂ during the NO chemisorption step at 200 °C for the synthetic chars (i.e., SC and SN). Both chars behaved similarly and only small differences were observed during the first hour (due to the stabilisation of the system). Neither CO nor CO₂ was detected, suggesting that at the selected temperature, 200 °C, gasification of the chars does not take place. However, the NO profile in Figure 1 clearly shows that NO chemisorbs on the chars -NO concentration is reduced by 3%, with respect to the feeding gas, after two hours-. Likewise, N₂ is also detected. Taking into account the similarity in the behaviour of the chars, with and without nitrogen in their compositions, the possibility that the detected N₂ may be originated from the nitrogen inside the char can be discarded.

From the experimental results presented here, the NO chemisorption mechanism can be explained by a reaction between two neighbouring C(N) complexes formed by the dissociation of a NO molecule (dissociative chemisorption) and/or by the formation of a dimer, (NO)₂, giving rise to the formation of N₂ (associative chemisorption) and oxygen complexes on the char surfaces. A gas analysis of the emissions during the TPD test performed after the NO chemisorption step would provide valuable information in this respect. The evolution of the main desorption products, CO₂ and N₂, detected by MS and FTIR analysis is presented in Figure 2. CO desorption was not detected at all in the TPD test. NO desorption was not detected either indicating that physisorption does not take place at 200 °C.

The CO₂ desorbed during the TPD tests comes from the oxygen surface complexes, designated here as C(O₂), which are generated during the chemisorption stage. According to the CO₂ profiles presented in Figure 2, it seems clear that the source of these oxygenated precursors is not unique. The detection of N₂ during the TPD tests indicates the formation of nitrogen surface complexes, designated here as C(N), during

the NO chemisorption stage. The SN char has no nitrogen in its composition and desorption takes place in an inert atmosphere (Ar), so the N₂ must come from previously chemisorbed nitrogen.

The fact that the concentrations of N₂ are similar during the chemisorption step but quite different during the TPD tests for both synthetic chars, indicates that the most probable mechanism for N₂ formation would not involve two adjacent C(N) complexes, as they are thermally stable and would not evolve at the chemisorption temperature (200 °C). Furthermore, 200 °C is a temperature low enough to avoid gasification of the char, so the N₂ formed during the chemisorption stage cannot be a product of the reaction of NO with the nitrogen in the char surface [C(N) or composition nitrogen]. The source of the N₂, therefore, must be NO dimerisation –an associative mechanism– as a previous step to the breakage of the NO molecule. This mechanism will be described in detailed below.

From the results presented in Figures 1 and 2, it can be concluded that during NO chemisorption the formation of oxygen surface complexes together with N₂ emission takes place. However, to a lesser extent, the process also involves the formation of nitrogen surface complexes, C(N), which are thermally more stable and do not desorb at the chemisorption temperature (200 °C). During the subsequent TPD tests at higher temperatures, these complexes evolve as N₂.

3.1.2. High temperature ($T > 250^{\circ}\text{C}$) chemisorption experiments

Isothermal reduction experiments in the high temperature regime ($>250^{\circ}\text{C}$) were also performed. First, the influence of temperature was tested through NO reduction experiments at different temperatures (600 °C, 700 °C, 850 °C and 1000 °C). Figure 3 shows NO profiles for the SC char during the reduction experiments at the above mentioned temperatures. NO reduction increases exponentially with temperature, from

3% at 600°C to 39% at 1000°C. Nevertheless, after two hours at 1000°C complete reduction had still not been achieved.

The main reduction products were N₂ and CO₂, as in the non-isothermal experiments that had been previously performed [20]. At 600°C, NO reduction accounts for 3%, a similar percentage to that obtained during the chemisorption experiments at 200°C. Furthermore, no CO₂ was detected, indicating that at 600°C char gasification by NO is not significant. For the experiments at 750, 850 and 1000°C, a NO-char reaction takes place and CO₂ is generated. N₂ and CO₂ concentrations increase with temperature, in accordance with NO evolution during the isothermal reduction experiments at these temperatures (Figure 3). From a comparison of the N₂ and CO₂ profiles at the different temperatures a change in the reduction mechanisms can be inferred. Above 750°C the differences between the N₂ and CO₂ concentrations become significant, indicating that char gasification prevails over the formation of oxygen surface complexes. NO attacks the char surface, creating oxygen complexes that rapidly desorb instead of stabilising on the char surface.

Other authors have observed a change in the activation energy between 600 and 750°C [8, 24, 25], reported also in previous works by our research group [26, 27]. This change in activation energy could be related to a change in the reduction mechanism.

NO heterogeneous reduction on the carbonaceous surface generates N₂, both in the low temperature regime –where NO chemisorption takes place- and in the high temperature regime –where char gasification prevails- as was inferred from the isothermal reduction experiments. However, little information is available in the literature about the N₂ formation mechanism or about the role of the nitrogen surface complexes, C(N), in the reduction process. In order to study these topics, the gas feed was changed from NO to ¹⁵NO after 60 min of reaction and step response experiments were carried out. Pursuit of

m/z signals 28 ($^{14}\text{N}_2$), 29 ($^{14}\text{N}^{15}\text{N}$) and 30 ($^{15}\text{N}_2$) by means of the MS, clarifies the role of the nitrogen surface complexes in the reduction process. Switching on the feed gas does not disturb the reaction which can be monitored under steady-state conditions.

The temperatures selected for the step response experiments were 750, 850 and 1000°C. Figure 4 shows the evolution of nitrogen - $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$, $^{15}\text{N}_2$ - during the step response experiments of the SC char. During the first step of the reaction with NO, signal m/z 30 corresponds to the evolution of NO because ^{15}N has not yet been introduced. $^{14}\text{N}_2$ is the only nitrogenous product during this reaction step and its concentration increases with temperature, which means that the reduction of NO increases with temperature. Although C(^{14}N) formation is expected at this stage, no clear evidence of this is obtained as the SC char contains ^{14}N that could contribute to $^{14}\text{N}_2$ formation.

After switching to ^{15}NO a change in the reduction products is observed. $^{15}\text{N}_2$, instead of $^{14}\text{N}_2$, becomes the main reduction product. However, the most outstanding feature about this reaction stage is the $^{14}\text{N}^{15}\text{N}$ formation which clearly shows that there is a reaction between the ^{15}N from the reactive gas and the ^{14}N in the carbonaceous material. Likewise, the $^{15}\text{N}_2$ (m/z 30) and $^{14}\text{N}^{15}\text{N}$ (m/z 29) intensities increase with temperature. In the last stage in an Ar atmosphere, no nitrogenous products were detected.

The same experimental protocol was followed for the SN char. Figure 5 shows the nitrogen evolution - $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$, $^{15}\text{N}_2$ - during the step response experiments of the SN char. Although the behaviour observed is similar to that of the SC char, this time new conclusions about the role of C(N) complexes can be established. During the second stage of the reaction with ^{15}NO , the generation of $^{14}\text{N}^{15}\text{N}$ is clear evidence not only of the formation of C(^{14}N) complexes during the stage of reaction with ^{14}NO , but also of the participation of these complexes in the NO-C reaction. In fact, ^{14}N chemisorbs on the char surface forming C(^{14}N) complexes that afterwards react with the ^{15}N from the

reactive gas. The intensity signal m/z 29 ($^{14}\text{N}^{15}\text{N}$) increases with temperature, indicating that $\text{C}(^{14}\text{N})$ formation also increases with temperature during the first stage of the reaction with ^{14}NO . Finally, during the last stage under an Ar atmosphere no nitrogenous product was detected.

By performing a nitrogen mass balance in the step response experiments for the synthetic char without nitrogen in its composition -SN char-, the concentration of the nitrogen surface complexes formed by reaction with NO can be determined. Because of the steady state conditions, the nitrogen concentration is calculated as follows:

$$[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} = 2 [^{14}\text{N}_2] + [\text{C}(^{14}\text{N})]$$

During the second stage of reaction with ^{15}NO , the concentration of nitrogen surface complexes - $\text{C}(^{14}\text{N})$ and $\text{C}(^{15}\text{N})$ - can be evaluated according to:

$$[\text{C}(^{14}\text{N})] = [\text{C}(^{14}\text{N})]_{\text{initial}} - 2 [^{14}\text{N}_2] - [^{14}\text{N}^{15}\text{N}]$$

$$[\text{C}(^{15}\text{N})] = [^{15}\text{NO}]_{\text{in}} - [^{15}\text{NO}]_{\text{out}} - 2 [^{15}\text{N}_2] - [^{14}\text{N}^{15}\text{N}]$$

where $[\text{C}(^{14}\text{N})]_{\text{initial}}$ represents the amount (mol) of nitrogen surface complexes at the beginning of the second reaction stage.

^{14}NO and ^{15}NO were quantified throughout the experiment. However, the lack of a $^{15}\text{N}_2$ standard prevented the quantification of $\text{C}(^{15}\text{N})$ generated during the stage of reaction with ^{15}NO . The above equation system would therefore give the total amount of ^{15}N that reacted, i.e., $[\text{C}(^{15}\text{N})] + [^{14}\text{N}^{15}\text{N}] + 2 [^{15}\text{N}_2]$.

Figure 6 shows the results of the nitrogen mass balance for the SN char during the step response experiments in NO and ^{15}NO . During the first step of reaction with NO, nitrogen complexes - $\text{C}(^{14}\text{N})$ - are formed on the SN char surface. Temperature plays an important role in their formation; at 850°C and above there is an increase in the formation of $\text{C}(^{14}\text{N})$ with time. Nevertheless, the quantities of $\text{C}(^{14}\text{N})$ formed at 850°C

and at 1000°C are more or less similar. During the second step of reaction with ^{15}NO similar tendencies were observed. The increase in temperature results in an increase in the amount of ^{15}NO reduced, here represented by $[\text{C}(^{15}\text{N})] + [^{14}\text{N}^{15}\text{N}] + 2 [^{15}\text{N}_2]$. In the step response experiments for the SN char (Figure 5) $^{14}\text{N}^{15}\text{N}$ was the gas compound predominantly generated during the initial moments of the reaction with ^{15}NO , whereas from the mass balance it can be inferred that the formation of nitrogen surface complexes, $\text{C}(^{15}\text{N})$, would prevail at the end of the reaction with ^{15}NO .

3.2. Reduction mechanisms

The results presented in this work provide valuable information about the mechanisms involved in NO heterogeneous reduction on carbonaceous materials. The global reaction is complex and temperature plays a determining role in the reaction mechanism.

In the experimental conditions used in this work, N_2 and CO_2 are the main reduction products. Therefore the global NO-C reaction may be schematised as:

where C_{ac} represents active centres on the char surface.

However, the formation of CO, as an intermediate of reaction, would also be possible according to,

where the char surface would catalyse CO oxidation to CO_2 by NO.

In the previous section, a quantitative change was observed in the behaviour towards reduction from 750°C that could be related to a change in the reaction mechanism. Therefore, for the analysis of the NO heterogeneous reduction mechanisms three

different temperature ranges will be considered: one at low temperature ($T < 250^{\circ}\text{C}$) and two at high temperature ($250-750^{\circ}\text{C}$ and $750-1000^{\circ}\text{C}$). The different stages of reaction are not independent and clear evidence of the influence of the adsorption (chemisorption) process on the subsequent gasification reaction has been found.

3.2.1. Low temperature ($T < 250^{\circ}\text{C}$) reduction mechanisms

NO chemisorption experiments at 200°C revealed that in this temperature range there is no char gasification by NO. The main reduction product was N_2 and during the following thermal treatment in an Ar atmosphere, N_2 and CO_2 are desorbed. It was therefore concluded that NO chemisorption on the char surface generates N_2 together with the formation of oxygen surface complexes and, to a lesser extent, nitrogen surface complexes on the char surface.

Thus, the chemisorption process may be schematised by the following sequence of reactions:

where the first reaction suggests that N_2 formation is linked to the formation of oxygen surface complexes on the char surface. However, other authors [8] have proposed the formation of a dimer, $(\text{NO})_2$, as a previous step to NO dissociative chemisorption. Then, the previous sequence of reactions would be:

where the formation of C(O₂) would proceed as follows:

NO dimer formation is thermodynamically favoured, so the most probable mechanism for NO chemisorption on the char surface would be this last sequence, where N₂ formation is linked to the formation of oxygen surface complexes -C(O₂) in this work- which are precursors of CO₂ generation.

The formation of nitrogen surface complexes, C(N), due to NO chemisorption on the char surface indicates that the N-N bond in the dimer has been broken. Experimental results at 200°C suggest little C(N) concentration on the char surface, whereas no NO reversible adsorption was observed on the char surface at 200°C.

NO chemisorption at low temperature therefore implies two processes with a common beginning and the association of two NO molecules to form a dimer. This dimer evolves, generating N₂ and forming C(O₂) complexes on the char surface, while NO dimer dissociation forms surface complexes, C(N) and C(O₂) on the char.

The formation of nitrogen and oxygen surface complexes during the NO chemisorption stage at low temperature clearly influences the succeeding gasification reaction at higher temperatures.

3.2.2. High temperature ($T > 250^{\circ}\text{C}$) reduction mechanisms

Most of the published literature on NO heterogeneous reduction on carbonaceous materials considers two characteristic temperature ranges: low temperature ($T < 250^{\circ}\text{C}$) where NO chemisorption prevails and high temperature ($T > 250^{\circ}\text{C}$) where NO-char gasification reaction takes place.

However, kinetic studies in the high temperature range have shown that there is a change in the activation energy around 750°C that probably corresponds to a change in the reaction mechanism [7, 23-26]. Although this work does not include kinetic studies, it was observed that from 750°C a significant change in NO reduction took place. Therefore, two temperature ranges will be considered for the analysis of the reaction mechanisms in the high temperature range.

i) Temperatures between 250 and 750°C

In this temperature range NO chemisorption coexists with char gasification by NO. As the temperature increases, gasification becomes more relevant than NO chemisorption.

Oxygen complexes on the char surface desorb as CO_2 creating new sites for reaction with NO. However, the lower the temperature is, the lower the extent of desorption of these complexes takes place and thus they can block the NO attack to the char surface. The mechanism in this temperature range is therefore controlled by desorption of the oxygen surface complexes:

Nitrogen surface complexes are thermally more stable than oxygen surface complexes and so they should not desorb as N₂ in this temperature range. N₂ formation in this temperature range will proceed by an analogous mechanism to that described for NO chemisorption at T<250°C.

A comparison of the isothermal NO reduction experiment at 600°C with the NO chemisorption experiments at 200°C leads to the conclusion that the higher the temperature, the greater the number of sites susceptible to NO chemisorption and therefore to C(N) formation.

ii) Temperatures between 750 and 1000°C

As the temperature increases char gasification by NO starts to control the process and N₂ and CO₂ are the main reduction products.

Step response experiments between 750 and 1000°C presented in section 3.1.2 have shown that nitrogen surface complexes, C(N), are formed and that these are the real intermediates in the NO-C reaction. Therefore N₂ formation in this temperature range can be explained as follows:

The direct reaction of two C(N) groups forming N₂ is not very probable in the light of our experiment results, there being only a small content of these complexes on the char surface.

The global NO heterogeneous reduction mechanism in the high temperature range (750-1000°C) could be explained by a combination of NO attack on the char forming surface complexes and the desorption of these complexes, mainly those that are oxygenated, leading to new sites of reaction. The following sequence of reactions summarises the process:

where the role of nitrogen and oxygen surface complexes as the real reaction intermediates is shown.

4. CONCLUSIONS

The combined use of a synthetic char, with a known and controlled composition but resembling very well a coal char, and isotopically labelled NO allowed a more accurate study of the nitrogen evolution during NO heterogeneous reaction. The role of nitrogen both in the carbonaceous material and in the reactive gas was elucidated using synthetic chars with and without nitrogen in their composition. Therefore, based on the experimental data of this work, mechanisms for NO heterogeneous reduction on carbonaceous materials in the absence of catalytic effects were ascertained.

Temperature and surface chemistry play a determining role in the reduction process. NO chemisorption at low temperatures implies the previous formation of a dimer, $(\text{NO})_2$, which later evolves, generating N_2 and oxygen surface complexes, $\text{C}(\text{O}_2)$, and to a much lesser extent, nitrogen surface complexes, $\text{C}(\text{N})$. These nitrogen surface complexes, $\text{C}(\text{N})$, are the real intermediates in the NO-C reaction. As temperature increases, NO char gasification takes place in a larger extent, that implies the attack of NO on the char surface forming surface complexes (mainly those that are oxygenated). These complexes desorb creating new sites for reaction with more NO.

ACKNOWLEDGEMENTS

CP gratefully acknowledges CSIC I3P Programme, co-financed by the European Social Fund, for financial support.

REFERENCES

- [1] Harding AW, Brown SD, Thomas KM. Combust Flame 1996;107:336.
- [2] Thomas KM. Fuel 1997;76:457.
- [3] Molina A, Eddings EG, Pershing DW, Sarofim AF. Prog Energy Combust Sci 2000;26:507.
- [4] Chambrion Ph, Orikasa H, Kyotani T, Tomita A. Prep Am Chem Soc, Div Fuel Chem 1996;41:170.
- [5] Chambrion Ph, Orikasa H, Suzuki T, Kyotani T, Tomita A. Fuel 1997;76:493.
- [6] Chambrion Ph, Suzuki T, Zhang Z-G, Kyotani T, Tomita A. Energy and Fuels 1997;11:681.
- [7] Chambrion Ph, Kyotani T, Tomita A. Energy and Fuels 1998;12:416.
- [8] Teng H, Suuberg EM, Calo JM. Energy and Fuels 1992;6:398.
- [9] Teng H, Suuberg EM. J Phys Chem 1993;97:478.
- [10] de Soete GG. 23rd Symposium (International) on Combustion, The Combustion Institute, Pittsburg; 1990 p. 1257.
- [11] Furusawa T, Kunii D, Osuma A, Yamada N. Int Chem Eng 1980;20:239.
- [12] Illán-Gómez MJ, Linares-Solano A, Salinas-Martínez de Lecea C. Energy and Fuels 1993;7:146.
- [13] Illán-Gómez MJ, Linares-Solano A, Radovic LR, Salinas-Martínez de Lecea C. Energy and Fuels 1996;10:158.

- [14] Jones JM, Zhu Q, Thomas KM. Carbon 1999;37:1123.
- [15] Xiao B, Boudou JP, Thomas KM. Langmuir 2005;21:3400.
- [16] Arenillas A, Pevida C, Rubiera F, García R, Pis JJ. J Anal Appl Pyrol 2004;71:747.
- [17] Arenillas A, Pevida C, Rubiera F, Pis JJ. Fuel 2003;82:2001.
- [18] Arenillas A, Pevida C, Rubiera F, Palacios JM, Navarrete R, Denoyel R, Rouquerol J, Pis JJ. Carbon 2004;42:1345.
- [19] Pevida C. PhD Thesis, University of Oviedo; 2004.
- [20] Pevida C, Arenillas A, Rubiera F, Pis JJ. Fuel 2005;84:2275.
- [21] Brown CE, Hall PG. Transactions of the Faraday Society 1971;67:3558.
- [22] Smith RN, Lesnini D, Mooi J. J Phys Chem 1956;60:1063.
- [23] Teng H, Suuberg EM. Ind Eng Chem Res 1993;32:416.
- [24] Aarna I., Suuberg EM. Fuel 1997;76:475.
- [25] Li YH, Lu GQ, Rudolph V. Chem Eng Sci 1998;53:1.
- [26] Arenillas A. PhD Thesis, University of Oviedo; 1998.
- [27] Arenillas A, Rubiera F, Pis JJ. Environ Sci Technol 2002;36:5498.

Table 1. Proximate and ultimate analyses of the chars

	Proximate analysis (wt%, db)		Ultimate analysis (wt%, daf)				
	Volatile matter	Ash	C	H	N	S	O
SC char	11.3	0.0	95.5	1.2	1.6	0.0	1.7
SN char	9.8	0.0	94.7	1.5	0.0	0.0	3.8

Figure 1. NO and N₂ evolution during NO chemisorption at 200°C (reactive gas mixture 400 ppm NO in Ar; isothermal step pursued for two hours) for the synthetic chars.

Figure 2. CO₂ and N₂ evolution during the TPD tests performed after the NO chemisorption step (heating rate of 15 °C min⁻¹ under 50 cm³ min⁻¹ of Ar flow from 20 °C up to 1000 °C, maintaining at 1000 °C for half an hour) for the SC and SN chars.

Figure 3. NO, CO₂ and N₂ evolution during the isothermal reduction experiments at 600, 750, 850 and 1000°C for the SC char.

Figure 4. Nitrogen evolution during the step response experiments for the SC char.

Figure 5. Nitrogen evolution during the step response experiments for the SN char.

Figure 6. Nitrogen mass balance during the step response experiments for the SN char.