Low-Temperature Catalytic Adsorption of NO on Activated Carbon Materials

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The catalytic adsorption of NO on activated carbon materials provides an appropriated alternative for the control of low-concentration emissions of this air pollutant. The surface complexes formed upon NO adsorption at 30 °C were studied by X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). The effects of the addition of O_2 and the presence of copper as a catalyst were studied. Copper assisted the oxygen transfer to the carbon matrix. For the Cu-impregnated carbon sample, the presence of O_2 favored NO adsorption by increasing the breakthrough time, the adsorption capacity, and the formation of nitrogen and oxygen complexes of higher thermal stabilities, which mainly desorbed as NO and CO_2.

Introduction

Nitrogen oxides (NO_x) are considered to be among the most toxic gases emitted into the atmosphere during the combustion of fossil fuels in the sectors of industry and transport. As a consequence, the laws that regulate the emissions of these pollutants have become more drastic and have encouraged research toward the development of immediate solutions. These solutions may include substantial variations of the actual combustion processes, the redesign of equipment, and the application of new technologies leading to a decrease in the emission of pollutants into the atmosphere.[1,2]

For NO_x, the most common commercial techniques are selective catalytic reduction (SCR) by NH_3 and selective noncatalytic reduction (SNCR). However, these processes have several problems. On one hand, the SCR technique suffers from catalytic deactivation caused by SO_2 poisoning as well as high maintenance costs.[3,4] On the other hand, SNCR requires high temperatures.

NO_x removal by adsorption provides an appropriate alternative for the control of low-concentration NO_x emission. Several potential adsorbents have been investigated, including metal oxides[5,6] and FeOOH and Fe_2O_3 dispersed on activated carbon fibers (ACF)[7,8] and activated carbon.[9−11] Activated carbon is an amorphous material used industrially as an adsorbent for the control of environmental pollution because of its high porosity and extensive surface area. It is obtained by pyrolysis, gasification, or chemical oxidation of any substance rich in organic carbon, with the objective of increasing the volume and diameter of pores that were created during the carbonization process.

Adsorption on activated carbons is one of the most investigated methodologies; besides its capability for regeneration, it allows the removal of most of the impurities found in effluents, such as SO_2, NO_x, particles, mercury, dioxins, furans, VOC, and heavy metals.[12,13] Additionally, activated carbon has been used as a catalyst as well as a catalyst support,[14−17] although it is necessary to minimize its tendency to behave as a reactant, especially in the presence of oxygen. Metals with catalytic activity can be exploited to reduce reaction temperatures and to minimize carbon loss by gasification.[18] Previous studies have demonstrated that when activated carbon is used as a catalyst support the adsorption capacity increases considerably.[16] In particular, copper has been reported to be a good catalyst for the adsorption of NO_x at low temperatures, whereas very low adsorption capacities have been reported in the absence of copper using zeolites as the adsorbent.[5] However, in the above-mentioned research there is a lack of information concerning the interactions of the NO_x molecules with the surface functional groups on activated carbon, as well as with the metal supported on the carbon material.[19]

To obtain a kinetics description of the gas-phase catalytic process, it is necessary to determine the nature of the interaction between the gaseous molecules and the catalyst/carbon surface, thus helping to understand the elemental reactions that describe the process. The objective of this work was to study the adsorption of NO on activated carbon, the catalytic effect of copper supported on this material, and the effect of the addition of oxygen to the gas stream.

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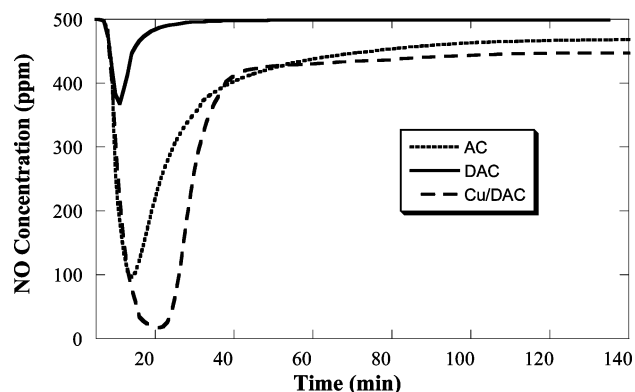(14) Radovic, L. R.; Rodriguiez-Reinoso, F. *Chem. Phys. Carbon* **1997**, *25*, 243−248.
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Figure 1. NO outlet concentration profiles for the adsorption of NO at 30 °C on three different samples.

Figure 2. Schematic representation of common nitrogen surface complexes found on carbon.

Experimental Section

Sub-bituminous coal (mesh 100/200) was pyrolyzed at 900 °C for 1 h in a N_2 atmosphere to produce the char that was subsequent activated with steam at 850 °C for 3 h. The activated carbon (AC) contains 7 wt % mineral matter (ash), mainly composed of Na, K, Ca, and Fe, which could have a catalytic effect on the NO adsorption reaction. Thus, part of the activated carbon was demineralized with HCl−HF−HCl−HNO$_3$ solutions using a technique adapted from Bishop and Ward.[20] The demineralized activated carbon (DAC) was loaded with copper by immersion in an aqueous solution of Cu-(NO$_3$)$_2$·3H$_2$O in an appropriate concentration to obtain approximately 10 wt % Cu (Cu/DAC) using the method of incipient wetness.

The NO$_x$ adsorption experiments were carried out in a fixed bed reactor using 0.100 g of sample. The temperature was monitored with a thermocouple attached to the reactor's external wall, close to the sample bed. Before each experiment, the sample was heat treated at 500 °C under a helium flow of 100 mL/min for 30 min to partially clean the surface oxides that may be formed during the exposure of the sample to air while handling. The reactor was then cooled to 30 °C, and He was switched to the reaction mixture (NO or NO/O$_2$) at a flow of 100 mL/min until saturation of the activated carbon was achieved. The gas concentrations used in these experiments were NO, 500 ppm; O$_2$, 5%; and He, the balance. The NO concentration was continuously monitored by an NO$_x$ chemiluminescence analyzer (Thermo Environmental Instruments, model 42C).

After the adsorption experiment, the samples were subjected to XPS analysis with a VG-Microtech Multilab Electron apparatus equipped with Mg Kα radiation (15 kV, 20 mA). The C 1s binding energy at 284.6 eV was taken as the reference. To obtain a reference point for a comparison of the results, an activated carbon sample without Cu was heat treated at 500 °C in He, and then the surface complexes were characterized by XPS.

To establish the effects of the reversible chemisorption reactions of NO and the formation of oxygen complexes, the adsorption experiments were run for 2 h and then flushed with He for 30 min to remove the NO remaining on the reactor or weakly adsorbed on the surface. After that, the samples were subsequently subjected to temperature-programmed desorption (TPD) under He flow, with a heating rate of 15 °C/min up to 900 °C. The evolved gases (NO, N$_2$O, NO$_2$, CO, and CO$_2$) were monitored with a quadrupole mass spectrometer and a chemiluminescence analyzer.

Results and Discussion

NO Adsorption. Figure 1 shows the profiles for the NO concentration at the reactor exit (flow of 100 mL/min containing 500 ppm NO in He at 30 °C) on the different samples as a function of time. All of the adsorption profiles show similar behavior in which three stages of adsorption are clearly differentiated. In the first stage, the diffusion and adsorption of
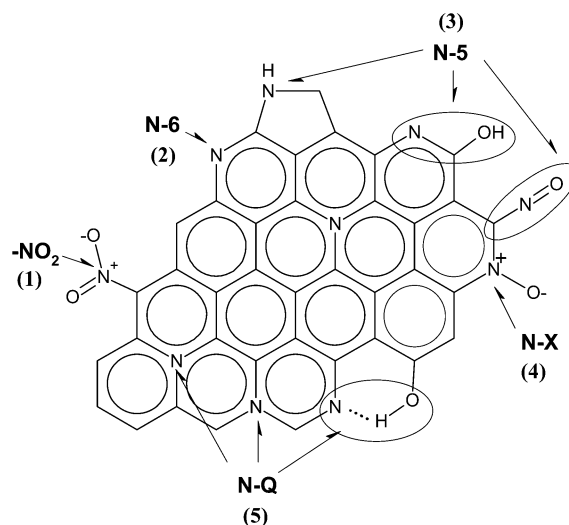
NO mainly occur on the internal surface of the activated carbons; in the second stage, just after the breakthrough point, adsorption takes place at the active sites of the surface; and, finally, the outlet concentration of NO reaches a value close to the initial one for the DAC sample, indicating that active sites for adsorption have been saturated. However, for the AC and Cu/DAC samples the NO adsorption continues after 140 min.

It can be observed that the demineralized activated carbon (DAC) exhibited very little adsorption capacity in the first 30 min whereas the parent activated carbon (AC) and the impregnated activated carbon (Cu/DAC) showed a much higher adsorption capacity, which can be attributed to the catalytic effect of the mineral matter and copper, respectively, present in these materials. It has been reported in the literature that metals such as Na, K, Ca, and Fe show good catalytic activity for both the NO adsorption and NO dissociation reactions.[21−23] The Cu-impregnated activated carbon exhibited the highest adsorption capacity and also the lowest outlet concentration at the end of the process, which indicates that there is a favorable effect of Cu catalyzing the adsorption of NO on the carbonaceous material.

After NO adsorption, activated carbons were analyzed by XPS in order to study the nitrogen and oxygen complexes that could be formed during the reaction. Figure 2 shows the most important nitrogen complexes observed on a carbon surface by XPS.[24] They are (1) nitro-type complexes (NO$_2^−$), (2) the pyridinic complex (N-6), (3) N-5 complexes (e.g., pyrrolic, pyridone, and nitroso), (4) pyridine-N-oxide complexes (N−X), and (5) quaternary-N complexes (N−Q). Among these, pyridinic and pyrrolic complexes are the most abundant. The nitrate complexes (−NO$_3^−$) are not shown in this Figure since they have been considered to constitute part of the mineral matter present in the carbon.[25,26]

Figure 3 presents the deconvoluted XPS spectra of nitrogen complexes formed during the NO adsorption on the activated carbon (AC) and the demineralized activated carbon (DAC).

The usual method for quantitative analysis in XPS is to determine the area of each photoelectronic signal, which is then

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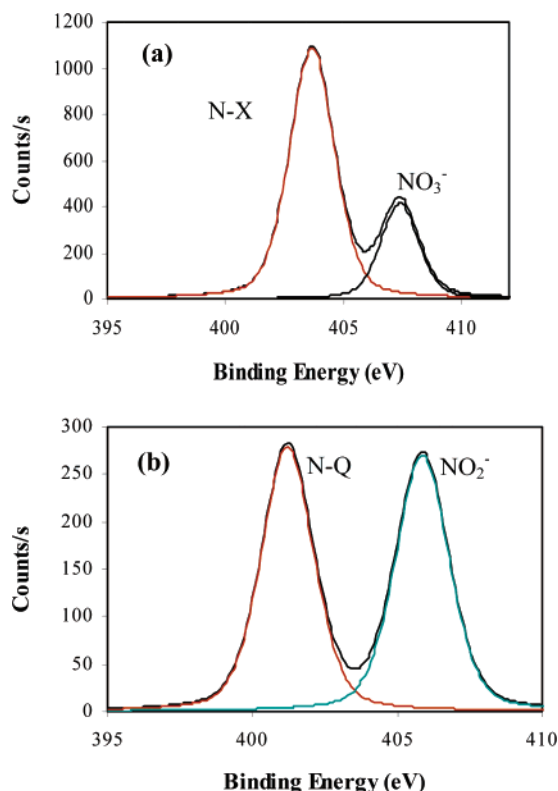(22) Chang, H.; Li, B.; Li, W.; Chen, H. *Fuel* **2004**, *83*, 679−683.
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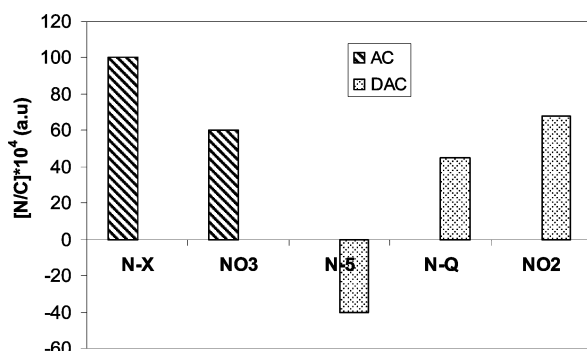(24) Suzuki, T.; Kyotani, T.; Tomita, A. *Ind. Eng. Chem. Res* **1994**, *33*, 2840−2845.
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Figure 3. Deconvoluted XPS spectra of nitrogen complexes formed during NO adsorption on (a) activated carbon (AC) and (b) demineralized activated carbon (DAC).

Figure 4. Nitrogen complexes formed during NO adsorption, represented as XPS data referenced to the initial carbon.

corrected by the atomic sensibility factor. For carbon surfaces, the signal intensities are normalized with respect to the corresponding area below the C 1s signal. To determine the relative changes in N and O complexes due to the reaction, the value of the ratio of the intensity of the peak corresponding to each heteroatom (N or O) and the C 1s peak intensity (i.e., N/C and O/C) was subtracted from the ratio in the heat-treated sample used as a reference.

Figure 4 presents the total number of nitrogen complexes formed during NO adsorption for both samples. The values on the *y* axis (in arbitrary units) correspond to the subtraction of the N complexes/C ratio of the heat-treated activated carbon from the corresponding ratio for the activated carbon after reaction. The *x* axis shows the complexes changing concentration after NO adsorption. The nitrogen complexes formed on the activated carbon (AC) surface were pyridine-N-oxide (N−X) and nitrate (NO$_3^-$) complexes, and the later probably formed on the mineral matter. It has been reported that catalytically active components
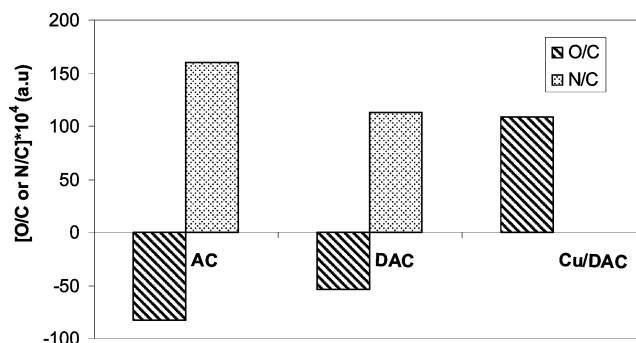
Figure 5. Nitrogen and oxygen complexes formed during NO adsorption on the different samples.

in mineral matter such as Fe, Ca, K, and Na may have a potential synergistic activity in the NO−carbon reaction.[21−23,27]

Pyridinic (N-6) complexes present in the starting activated carbon (AC), heat-treated under helium at 500 °C, did not suffer any transformation after NO adsorption. Therefore, the significant increment in the production of N−X complexes could be due to nitrogen incorporation onto the carbon structure by reaction with the active sites generated during the thermal decomposition of surface groups leading to CO desorption, as shown in the following reactions that have been proposed in the literature:[28−30]
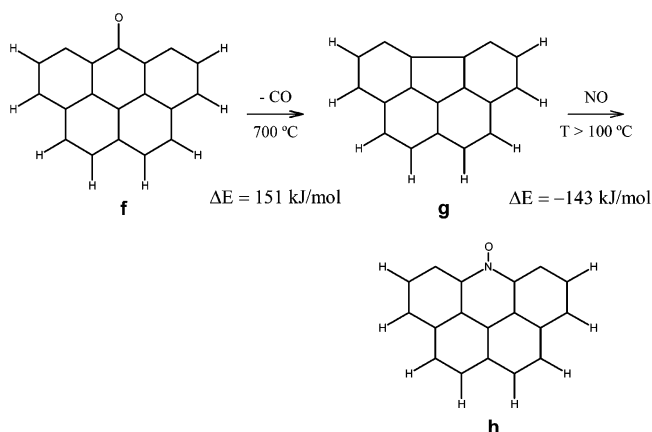

CO evolution seems to produce five-membered ring structures during the carbonization process, which are sites where the NO molecule can be chemisorbed at low temperatures to give N-oxide complexes.

The demineralized activated carbon (DAC) showed the formation of only nitro (NO$_2^-$) and quaternary-N (N−Q) complexes, with the latter probably formed through the trans-formation of the N-5 complexes from the initial activated carbon upon NO adsorption.

Figure 5 presents the nitrogen and oxygen surface complexes formed after NO adsorption on the different samples. Activated carbon (AC) exhibits the largest number of nitrogen complexes formed on the surface. Nitrogen complexes were not detected on the impregnated sample (Cu/DAC), probably because they have been transferred to internal sites in the carbon support where the XPS technique cannot detect them. Another possibility is that surface complexes such as C(N) could be formed on the
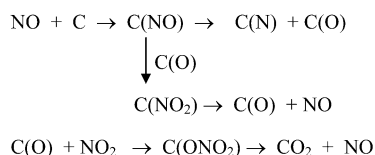
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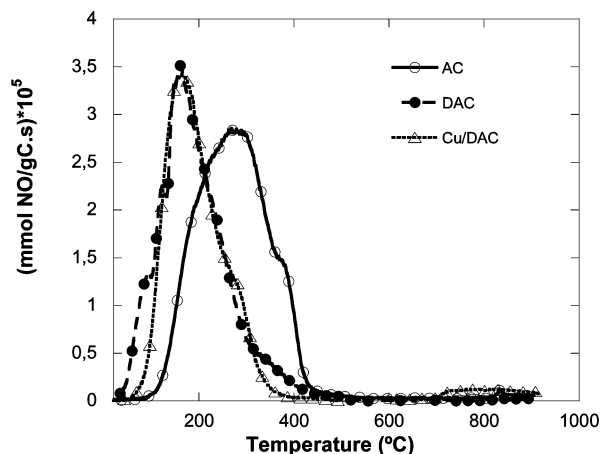
Figure 6. NO desorption profile for the different samples after the adsorption of 500 ppm of NO.

surface and they were removed by vacuum treatment previous to the XPS analysis producing N_2. To verify this possibility, a DRIFT analysis was performed; however, the complexes could not be clearly observed. The observed decrease in the number of surface oxygen groups on the activated carbon and the demineralized activated carbon indicates that gasification of the carbon material takes place and oxygen from NO is removed in the form of CO or CO_2.[28,31] The CO/CO_2 product ratio from TPD after the adsorption of NO on the activated carbon was lower than the CO/CO_2 product ratio obtained from the TPD after He treatment for the same sample. Moreover, XPS analysis showed the decrease in the intensity of the O 1s signal with a binding energy between 532 and 534.8 eV, which corresponds to oxygen complexes such as C—O, C=O, and —COO— formed after NO adsorption on both samples. However, Cu/DAC showed a considerable increase in oxygen surface complexes, which can be explained by the dissociative NO chemisorption on the catalyst, with the oxygen and nitrogen atoms being transferred to the carbon support by a spillover mechanism. These oxygen surface complexes desorbed mainly as CO_2 during the TPD. The following mechanism, already proposed in the literature, could explain the formation of these complexes:[32,33]

$$NO + C \rightarrow C(NO) \rightarrow C(N) + C(O)$$
$$\downarrow C(O)$$
$$C(NO_2) \rightarrow C(O) + NO$$
$$C(O) + NO_2 \rightarrow C(ONO_2) \rightarrow CO_2 + NO$$

Before the adsorption process, only Cu^{2+} was detected by XPS, but after the reaction, a mixture of Cu^{2+} and Cu^+ was observed. X-ray diffraction analysis confirmed the formation of CuO and Cu_2O, thus suggesting the redox role of the catalyst during the adsorption of NO.

A comparison of the NO—TPD spectra from AC, DAC, and Cu/DAC following the adsorption of 500 ppm of NO is presented in Figure 6. The spectra are predominantly monomodal profiles, with small distribution shoulders at slightly higher temperatures. In the case of DAC and Cu/DAC, the NO desorption peak is narrower and is centered at 180 °C, whereas the corresponding peak for AC is centered at about 300 °C. This shows that the active sites are very different and nitrogen complexes with

different thermal stabilities are formed on the carbon matrix. Although nitrogen complexes were not observed by XPS for the Cu/DAC sample, NO was desorbed during the TPD (Figure 6). The XPS technique can analyze only the most external surface, whereas the TPD analysis involves data from the external surface as well as from the inner pore surface.

The amounts of NO desorbed from the DAC and the Cu-impregnated carbons were almost the same even though the NO adsorptions from Figure 1 were different. However, just before the TPD the samples were flushed with He; therefore, the weakly adsorbed NO could be removed during the flushing time, which could imply that copper has a catalytic effect for this reaction forming NO complexes and some of these complexes are weakly adsorbed and desorb at room temperature. However, the number of oxygen complexes drastically increased for Cu/DAC as observed by XPS and TPD analysis, where a large evolution of CO and CO_2 was observed for this sample compared to the CO/CO_2 product ratio for the same sample just after the helium heat treatment and before the NO adsorption. This could mean that copper is catalyzing the reaction by transferring oxygen to the carbonaceous matrix and nitrogen is likely incorporated into the carbon structure as N-Q and N-6 complexes, as observed in previous work.[34]

NO desorption begins at temperatures as low as 50 °C and is completed at temperatures around 400 °C. This means that several complexes of low thermal stability are being formed on the carbon material and that Cu is catalyzing their decomposition.[26,35,36] However, NO was the only desorbed species during the TPD experiment for all carbon samples, thus suggesting that the nitrogen complexes are of the same nature but are located on different reactive sites of the graphene layers and therefore have different desorption activation energies. As observed in Figure 6, NO desorption for the AC sample presented NO complexes of higher thermal stability, for example, nitrate and nitrite complexes that decompose to NO_2 with further transformation to NO and an oxygen surface complex that can desorb as CO_2. This behavior could be due to a catalytic effect of the mineral matter present in the activated carbon. Fluorescence X-ray analysis of the mineral matter in the char used in the present research showed that the main inorganic compounds were CaO (25.2%) and Fe_2O_3 (11.1%), which have been reported to have catalytic activity in the reduction of NO.[37,38] It has also been reported that the reductive carbon surface captures oxygen from NO_2^- and NO_3^- to form oxygen functional groups that give CO and CO_2 in TPD and release NO.[28,32,33]

Effect of the Addition of O_2. It has been reported that the addition of oxygen during the adsorption of NO favors the formation of new active sites on the surface of the carbon material. Suzuki et al.[24] observed an increase in the adsorption of NO when oxygen was added to the reaction mixture or when the material was pretreated with oxygen. Oxygen complexes formed on the surface act as active sites during the reaction of nitrogen oxides with carbon material. Zhu et al.[39] reported that the addition of O_2 resulted in a large number of reactive carbon—oxygen complexes and that the decomposition of these complexes produced more active sites.

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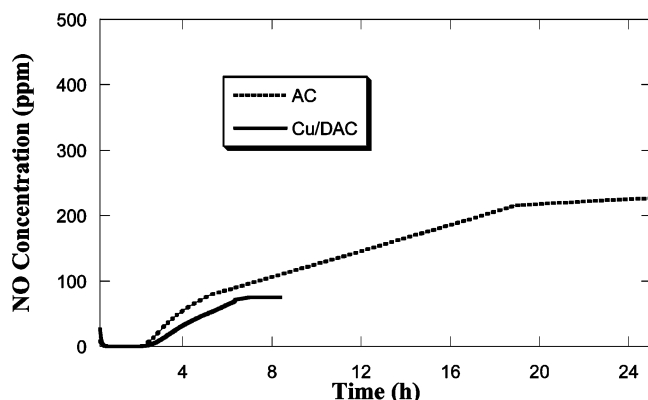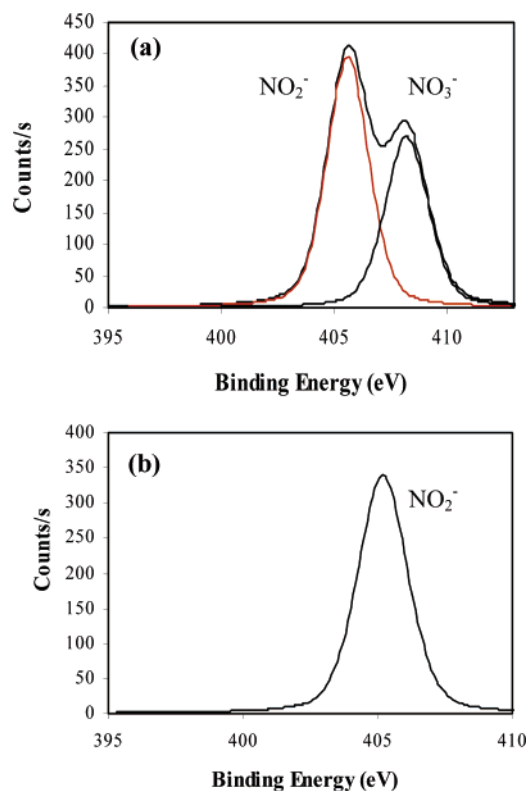
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Figure 7. NO outlet concentration profiles during the adsorption of NO/O_2 at 30 °C on the activated carbon and Cu-impregnated demineralized activated carbon samples.

Figure 7 shows the NO outlet concentration profiles for the adsorption reaction of NO/O_2 at 30 °C as a function of time for the AC and Cu/DAC samples. The adsorption profiles exhibit similar behavior in which two stages of adsorption are clearly differentiated. In the first stage, NO adsorption takes place mainly on the internal surface of the activated carbons; in the second stage, just after the breakthrough (approximately at 5 h), the adsorption takes place on the active sites of the surface, with oxygen providing new active sites for further adsorption. The addition of oxygen favored NO adsorption for both samples in comparison to adsorption obtained in the absence of O_2, as shown in Figure 1, where the carbon samples reached the saturation of the active sites at ca. 40 min and the adsorption percentage was close to 22%. The presence of copper catalyzes NO adsorption in the presence of O_2, increasing the breakthrough time and the adsorption capacity of this material; approximately 94% of the initial NO was adsorbed. The DAC carbon presented a very low adsorption capacity in the presence of O_2, which was probably due to the blockage of the active sites on the surface.

Figure 8 presents the deconvoluted XPS spectra of nitrogen complexes formed during the NO/O_2 adsorption on the activated carbon (AC) and the demineralized activated carbon (DAC).

Figure 9 presents the number of nitrogen complexes formed on the surface during NO/O_2 adsorption on the activated carbon (AC) and the demineralized activated carbon (DAC). The nitrogen complexes formed on the AC surface were nitro (NO_2^-) and nitrate (NO_3^-) complexes. The N–X complexes observed in the absence of O_2 are not present now, which can be explained by assuming that oxygen is first chemisorbed on the surface and then NO reacts with adsorbed oxygen to form NO_2 complexes. It is important to mention that stable oxygen complexes such as semiquinone have been suggested to form in the NO–carbon reaction at low temperatures either in the absence or presence of O_2.[40,41] For the demineralized carbon, only NO_2^- complexes were observed. Once again, no nitrogen complexes were observed in the Cu-impregnated activated carbon.

Table 1 summarizes the relative numbers of nitrogen and oxygen surface complexes formed during NO adsorption in either the absence or presence of oxygen. It can be observed from these results that in the presence of molecular oxygen the number of nitrogen surface complexes significantly increased for the AC carbon and decreased for the demineralized carbon, possibly because of a blocking effect of oxygen in the active sites where NO was first adsorbed. However, the number of oxygen surface

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Figure 8. Deconvoluted XPS spectra of nitrogen complexes formed during NO/O_2 adsorption on (a) activated carbon (AC) and (b) demineralized activated carbon (DAC).
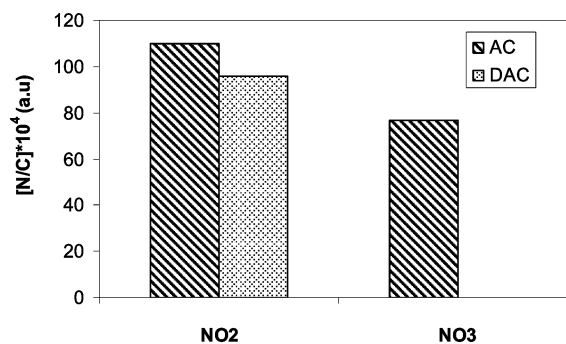
Figure 9. Nitrogen complexes formed during NO/O_2 adsorption at 30 °C on the activated carbon and demineralized activated carbon samples.

Table 1. Summary of the Total Amount of Each Complex Formed during the Adsorption of NO in Both the Absence and Presence of O_2
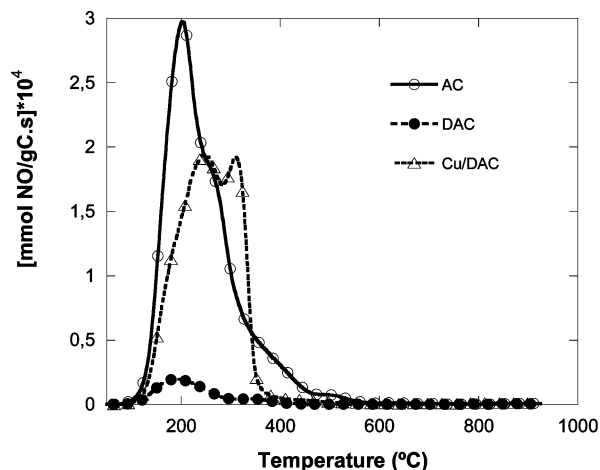
carbon sample	NO adsorption		NO/O_2 adsorption	
	N/C	O/C	N/C	O/C
AC	160	−83	187	216
DAC	164	−54	96	494
Cu/DAC		109		939

complexes increased for all of the samples, with this effect being more drastic for the impregnated activated carbon, thus suggesting that copper catalyzes the dissociative chemisorption of O_2 on the carbon material.

A comparison between the NO TPD spectra obtained from the different activated carbons following the adsorption of NO in the presence of O_2 is presented in Figure 10. The NO profile for the impregnated carbon (Cu/DAC) is bimodal, indicating that at least two different types of adsorption sites exist with higher

Figure 10. NO desorption profile for the different samples after the adsorption of NO/O_2.

Table 2. Total Amount of Each Desorbed Complex from Cu-Impregnated Activated Carbon (Cu/DAC) after the Adsorption of NO and NO/O_2

adsorption	NO (μmol/gC)	CO (μmol/gC)	CO_2 (μmol/gC)
NO	19.8	1470	1069
NO/O_2	129.4	843	1676

thermal stabilities than those appearing in the NO profile obtained in the absence of O_2. These adsorption sites could be related to strongly adsorbed NO or oxidized to NO_2^- or NO_3^-, thus indicating that copper has a catalytic effect on the transformation of NO into other species that are strongly adsorbed on the carbon support. As previously mentioned, nitrogen complexes were not observed by XPS in the Cu/DAC sample, although a significant amount of NO was desorbed during the TPD.
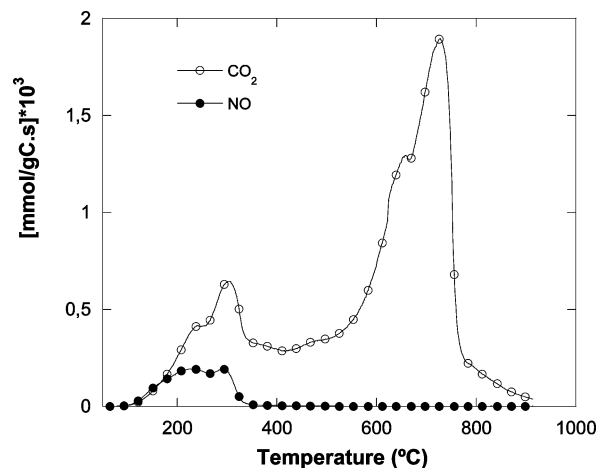
NO was the only desorbed species during the TPD in both the activated carbon and the impregnated activated carbon. Therefore, the nitrite or nitrate complexes could be decomposed to NO and oxygen surface complexes that desorb as CO_2 and CO. In the case of the AC and DAC carbon samples, the low-temperature desorption of weakly adsorbed NO is predominant.

Figure 11 presents the NO and CO_2 desorption spectra obtained after the adsorption of NO/O_2 on the impregnated Cu/DAC activated carbon. NO desorbs at low temperature, between 100 and 300 °C, where the evolution of a given amount of CO_2 is also observed. This can be explained assuming that NO_2^- complexes decompose as in the following reaction, which has been proposed in the literature:[42,43]

$$C + NO_2(ads) \rightarrow C(O) + NO$$

$$C(O) + NO_2(ads) \rightarrow CO_2 + NO$$
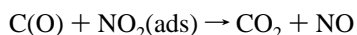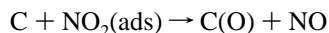
For the AC and DAC carbon samples, the CO_2 evolution took place at approximately 600 °C. However, for the impregnated sample, CO_2 was desorbed in two stages, and the last one occurred at temperatures higher than 600 °C, which could mean that copper catalyzes the chemisorption of oxygen-forming complexes of higher stability that decompose, evolving as CO_2.

Table 2 summarizes the total number of desorbed complexes from the impregnated demineralized activated carbon after the adsorption of NO and NO/O_2. The presence of O_2 has an important effect on both the formation of nitrogen complexes that desorb

(42) Yang, J.; Mestl, G.; Herein, D.; Schlogl, R.; Find, J. *Carbon* **2000**, 38, 729−740.
(43) Klose, W.; Rincon, S. *Fuel* **2007**, *86*, 203−209.

Figure 11. NO and CO_2 desorption spectra after the adsorption of NO/O_2 on the Cu/DAC catalyst.
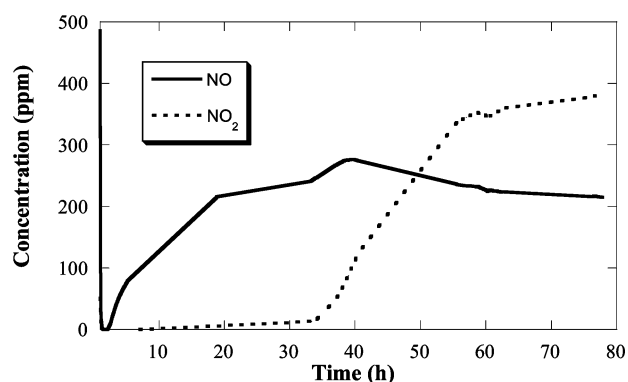
Figure 12. NO and NO_2 concentrations after the adsorption of NO/O_2 on Cu-impregnated activated carbon (Cu/DAC).

as NO, by providing more active sites for NO adsorption, and the formation of oxygen complexes that desorbed mainly as CO_2, especially CO_2 complexes of higher thermal stability as observed in Figure 11. The adsorption of NO in the absence of O_2 mainly favored the formation of CO complexes of high thermal stability; similar results were observed for the other carbon samples, but in smaller amounts.

To evaluate the stability of the impregnated activated carbon, the adsorption of NO/O_2 was carried out for a longer period of time. Figure 12 presents the NO and NO_2 concentrations at the exit of the reactor during the adsorption of NO/O_2. It shows that the material reaches slight stability after 20 h of reaction. Then the NO concentration continuously increases until reaching a maximum value near 40 h, and there it begins to decay at the same time that the NO_2 concentration begins to increase, thus indicating that there is a balance between the NO adsorption and oxidation of the material and the amount of NO_2 that evolves from the oxidation of NO with the oxygen complexes formed on the surface. Similar results were reported by Mochida.[44] After 75 h, this material still shows great stability with reaction time.

Possible Mechanistic Routes. Different reaction mechanisms have been proposed in the literature for the adsorption of NO. They mainly coincide in the formation of an oxygenated nitrogen

(44) Mochida, I.; Korai, Y.; Shirahama, M.; Kawano, S.; Hada, T.; Seo, Y.; Yoshikawa, M.; Yasutake, A. *Carbon* **2000**, *38*, 227−239.

complex (for example, an NO_2 complex) in the presence of O_2, suggesting that the oxygen surface groups improve the adsorption of NO.[44-47]

In previous work, García et al.[19,28] observed by XPS the formation of pyridine-N (N-6) and nitro (NO_2^-) complexes during the adsorption of NO at 100 °C on a coal-based char. The NO_2^- complexes were possibly formed from the dissociative chemisorption of NO on a surface with oxygen complexes.

In this investigation, it has been found that the nitrogen species formed during the adsorption of NO at 30 °C on activated carbon (AC) correspond to pyridine-N-oxide (N−X) and nitrate (NO_3^-) complexes, with the last one possibly formed on the mineral matter. For the carbon-supported copper catalyst (Cu/DAC), a considerable increase in the number of oxygen complexes was observed, thus suggesting that NO is dissociatively chemisorbed on the catalyst and oxygen is being transferred to the carbon surface.

There is evidence from TPD results of the formation of at least three types of complexes that desorb as NO. One of them is evident at temperatures below 200 °C, corresponding to NO weakly adsorbed on Cu/DAC and demineralized activated carbon. The activated carbon shows evidence of the second one, which is a strongly adsorbed complex, and of the third one, which appears as a shoulder around 400 °C. This last type could correspond to the decomposition of the nitrates formed on the

mineral matter. In the presence of oxygen, nitrogen complexes with a higher thermal stability as well as oxygen complexes that desorbed mainly as CO_2 were formed in the impregnated demineralized activated carbon (Cu/DAC).•

Conclusions

• Copper catalyzes the adsorption of NO, thus increasing the breakthrough time and decreasing the outlet NO concentration.

• Pyridine-N-oxide (N−X), nitro (NO_2^-), and nitrate (NO_3^-) complexes are formed upon NO and NO/O_2 adsorption onto the different activated carbons.

• For NO adsorption, the Cu-impregnated demineralized activated carbon exhibited the larger number of oxygen complexes, with this possibly indicating that NO is being dissociatively chemisorbed and copper is transferring the oxygen to the carbon matrix.

• For the Cu/DAC catalyst, the presence of O_2 favored NO adsorption, and this increased the breakthrough time, the adsorption capacity, and the formation of nitrogen and oxygen complexes of higher thermal stabilities that mainly desorb as NO and CO_2.

(45) Wilde, J. D.; Marin, G. B. *Catal. Today* **2000**, *62*, 319−328.
(46) Mochida, I.; Kawano, S.; Yatsunami, S.; Hironaka, M.; Matsumura, Y.; Yoshikawa, M. *Carbon* **1994**, *32*, 175−177.
(47) Mochida, I.; Kawano, S.; Yatsunami, S.; Hironaka, M.; Matsumura, Y.; Yoshikawa, M. *Energy Fuels* **1995**, *9*, 659−664.