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# Catalytic oxidation of NO to $NO_2$ on N-doped activated carbons

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ABSTRACT

The catalytic oxidation of NO on N-doped activated carbons provides a promising alternative for the control of emissions of this air pollutant. Materials with different contents of nitrogen were obtained from an activated carbon precursor modified by different treatments. The presence of nitrogen-containing surface groups was shown to favour the oxidation of NO to $NO_2$. The oxygen concentration in the gas phase strongly influenced the oxidation of NO.

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## 1. Introduction

Contamination of the atmosphere is one of the most important environmental problems caused by the progressive industrialization of the planet. Nitrogen oxides ($NO_x$) are considered to be the most toxic gases emitted into the atmosphere during the combustion of fossil fuels in the industry and transport sectors [1].

The conventional method used for the reduction of $NO_x$ emissions is the selective catalytic reduction (SCR) with ammonia as the reduction agent. The use of ammonia causes additional environmental problems, mainly due to ammonia slip [2,3].

One alternative to this process is the oxidation of NO into $NO_2$ [4]. This process can be carried out at room temperature using an appropriate catalyst, the $NO_2$ produced being captured in water as nitric acid [5]. Activated carbon has been recognized as an effective catalyst for this reaction, as well as for $SO_2$ oxidation [6].

The presence of nitrogen atoms in the carbon matrix was shown to enhance the catalytic activity of carbon materials in oxidation reactions and to increase the ability to adsorb acidic gases [7,8]. The effect of nitrogen doping of carbons on their catalytic properties might be due to two overlapping effects, catalysis by basic surface sites and by electron donation [9].

Nitrogen can be introduced into the structure of the activated carbon following different approaches, such as treatment with ammonia [10] and preparation of the material from N-containing polymers [11].

The goal of the present study was to prepare activated carbons with a high density of surface nitrogen Lewis basic sites, and to test them in the oxidation of NO.

## 2. Experimental

### 2.1. Sample preparation

A Norit RX 3 Extra activated carbon was used, as supplied (sample AC), as the starting material for subsequent treatments: oxidation in the liquid phase with 5 M nitric acid at boiling temperature for 6 h (sample AC-$HNO_3$); oxidation in the gaseous phase with 5% $O_2$ for 3 h at 500 °C (sample AC-O); thermal treatment, by heating sample AC to 1100 °C at 10 °C $min^{-1}$ under a flow of $N_2$ (100 $Ncm^3\,min^{-1}$) and keeping it at this temperature for 1 h (sample AC-1100 °C); treatment with urea at room temperature, by dipping AC into aqueous urea solution 1 M for 24 h (sample AC-U); treatment with urea at high temperature, by reaction with urea solution (0.1 M, 1 M) in the autoclave at 200 °C during 2 h under a pressure of 20 bar (samples AC-U-0.1 M-T-P and AC-U-1 M-T-P). The samples treated with urea were stabilized by heat treatment at 600 °C under $N_2$ because it is known [12] that at moderate temperatures N5 nitrogen is converted to pyridine (N6), which is a stronger Lewis base (pyridine $K_b$ is $2.3 \times 10^{-9}$) than the five-membered N species (pyrrole $K_b$ is $2.5 \times 10^{-14}$).

### 2.2. Characterization of the carbon samples

The textural characterization of the materials was based on the $N_2$ adsorption isotherms, determined at −196 °C in a Quantachrom NOVA 4200e analyzer.

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**Table 1**
Chemical and textural properties of materials used.

| Sample | $S_{BET}$ [$m^2\,g^{-1}$] | $S_m$ [$m^2\,g^{-1}$][a] | $V_\mu$ [$cm^3\,g^{-1}$][a] | $CO/CO_2$[b] | $N_{CHNO}$ [%][c] | $N_{XPS}$ [%][d] | $pH_{pzc}$ |
|---|---|---|---|---|---|---|---|
| AC | 1357 | 116 | 0.52 | 2.1 | 0.4 | 0.48 | 7.0 |
| AC-$HNO_3$ | 1450 | 219 | 0.53 | 2.1 | 0.6 | 0.97 | 5.5 |
| AC-O | 1468 | 219 | 0.49 | 14.3 | 0.5 | 0.60 | 8.0 |
| AC-U | 1174 | 125 | 0.43 | 2.0 | 1.3 | 1.65 | 8.6 |
| AC-U-0.1 M-T-P | 1259 | 91 | 0.52 | 2.9 | 0.8 | 0.90 | 7.6 |
| AC-U-1 M-T-P | 1312 | 83 | 0.53 | 2.0 | 1 | 0.82 | 8.4 |
| AC-1100 °C | 1726 | 156 | 0.70 | 1.3 | 0.1 | 0.35 | 8.5 |

[a] Micropore volume ($V_\mu$) and mesopore surface area ($S_m$) calculated by the *t*-method.
[b] Calculated by TPD spectra integration.
[c] Nitrogen content obtained from elemental analysis.
[d] Nitrogen content obtained from XPS analysis

The surface chemistry was characterized by temperature programmed desorption (TPD), $pH_{pzc}$, elemental analysis, as described elsewhere [13,14]; and by XPS analysis, with a VG Scientific ESCALAB 200A spectrometer utilizing a non-monochromatized Mg Kα radiation (1253.6 eV). The vacuum in the analysis chamber was always less than $10^{-7}$ Pa. The values of binding energies were calibrated with respect to C1s peak at 285.0 eV.

### 2.3. Oxidation of NO

Oxidation of NO was performed in a fixed-bed, U-shaped flow reactor. The mass of the sample was 0.2 g, the flow rate was 100 $Ncm^3\,min^{-1}$, the concentration of NO in He containing 2–20% $O_2$ was 1000 ppm and the reaction temperature was 25 °C.

The concentrations of NO, $NO_2$ and $NO_x$ were determined with a high level NO–$NO_2$–$NO_x$ analyzer (Model 42i-HL Thermo Scientific).

## 3. Results and discussion

### 3.1. Characterization of the activated carbons

Table 1 summarizes the chemical and textural properties of the activated carbons used.

The surface area slightly decreases for the sample treated with urea at room temperature; this may be due to the presence of numerous groups on the activated carbon surface, which may partially block the access of $N_2$ molecules to the micropores. The increase of the surface area after the thermal treatment can be explained by the decomposition of the oxygenated groups present in the surface of activated carbons.

The thermal treatment of AC removes the oxygen groups almost completely. The basic characteristics of the sample AC-1100 °C ($pH_{pzc}$ 8.5) are mainly associated with the electron-rich oxygen-free sites located on the carbon basal planes (Lewis basicity). Sample AC-$HNO_3$ has an acid character, while the sample AC-U has the highest basic character due to the presence of nitrogen groups. Table 1 shows the $CO/CO_2$ ratio; the amounts of CO and $CO_2$ released were obtained by integration of the areas under the TPD peaks [15]. This ratio increases significantly after the treatment with oxygen, due to the introduction of large amounts of oxygenated groups such as phenols, carbonyls and quinones, and decreases slightly after heat treatment, which almost completely removes the oxygenated groups.

Elemental analysis yields the bulk composition of the materials. Table 1 shows the elemental analysis of the samples prepared. Even the original activated carbon contains a small amount of nitrogen. Significant amounts of nitrogen were introduced on the surface of the carbon materials after the treatments. The sample that was treated with urea at room temperature presents the largest amount of nitrogen. In order to obtain additional information about the nature of the N bonding, XPS analyses were performed on the carbon materials. It is well-known that the XPS technique only gives the composition of the surface of a solid at a maximum depth of 2–3 nm. However, for most samples, the amount of nitrogen determined by XPS is larger than that determined by elemental analysis. The XPS N1s spectra of the carbons were decomposed into five peaks (Fig. 1) based in the previous literature data [14,16–18].

The results from deconvolution of the N1s spectra are shown in Table 2. The first peak identified at around 398 eV, designated as N6, is attributed to pyridinic-N. The second peak, situated between 400.0 and 400.9 eV, is ascribed to pyrrolic-N, and will be referred as N5. The next peak identified at 401.4–401.7 eV is attributed to quaternary nitrogen (N-Q). The peak observed between 402.4 and 403.0 eV represents certain forms of oxidized nitrogen (N-X). The last peak is observed at higher binding energy and it is attributed to nitro-type complexes (–$NO_2$). Pyridinic and quaternary nitrogen are present in the starting material (AC) and in the activated carbon treated at 1100 °C. Only the sample AC-U-1 M-T-P has N-X complexes. The treatments with nitric acid and with urea originated nitro-type complexes on the surface of the activated carbon. N5 was originated on the surface of the activated carbons by elimination of CO from pyridones, and apparently increases by formation of NH groups at the edges of the graphene layers [19]. Pyridinic nitrogen confers greater basicity to the surface; sample AC-U is the most basic sample, and presents the largest content of N6.

### 3.2. Oxidation of NO

Fig. 2a shows the typical breakthrough curves of NO oxidation on the activated carbons. This figure illustrates the evolution of NO oxidation at room temperature over AC-U, where NO and $O_2$ concentrations were 1000 ppm and 20%, respectively.

No $NO_2$ is detected at the reactor outlet during the initial stage of the experiment. $NO_2$ is adsorbed on the carbon surface until saturation of the adsorption sites; then a sharp increase of $NO_2$ in the gas phase is observed. The decrease in the NO concentration to the stationary concentration after the peak maximum is ascribed to the rapid increase of $NO_2$ desorption and NO oxidation which appears to take place when the coverage of $NO_2$ adsorbed reaches a level of almost saturation. It is noted that a small amount of NO is converted to $N_2$, besides the conversion of $NO_2$ for all the samples.

The $N_2$ conversion was obtained by molar balance after reaching steady state. In this condition, it was assumed that adsorption is negligible and that NO is only producing $NO_2$ or $N_2$.

To make sure that the $NO_2$ produced was captured by water, the same experiment was carried out with a washing bottle after the reactor and before the analyzer. Fig. 2b illustrates the extended capture of $NO_2$ at the outlet of the reactor after the catalytic oxidation of NO over AC-U. Water in the washing bottle was found to capture all $NO_2$ produced, and some unreacted NO.

Table 3 summarizes the influence of $O_2$ on NO adsorption, on the amount of $NO_2$ released and on the conversion of NO into $NO_2$

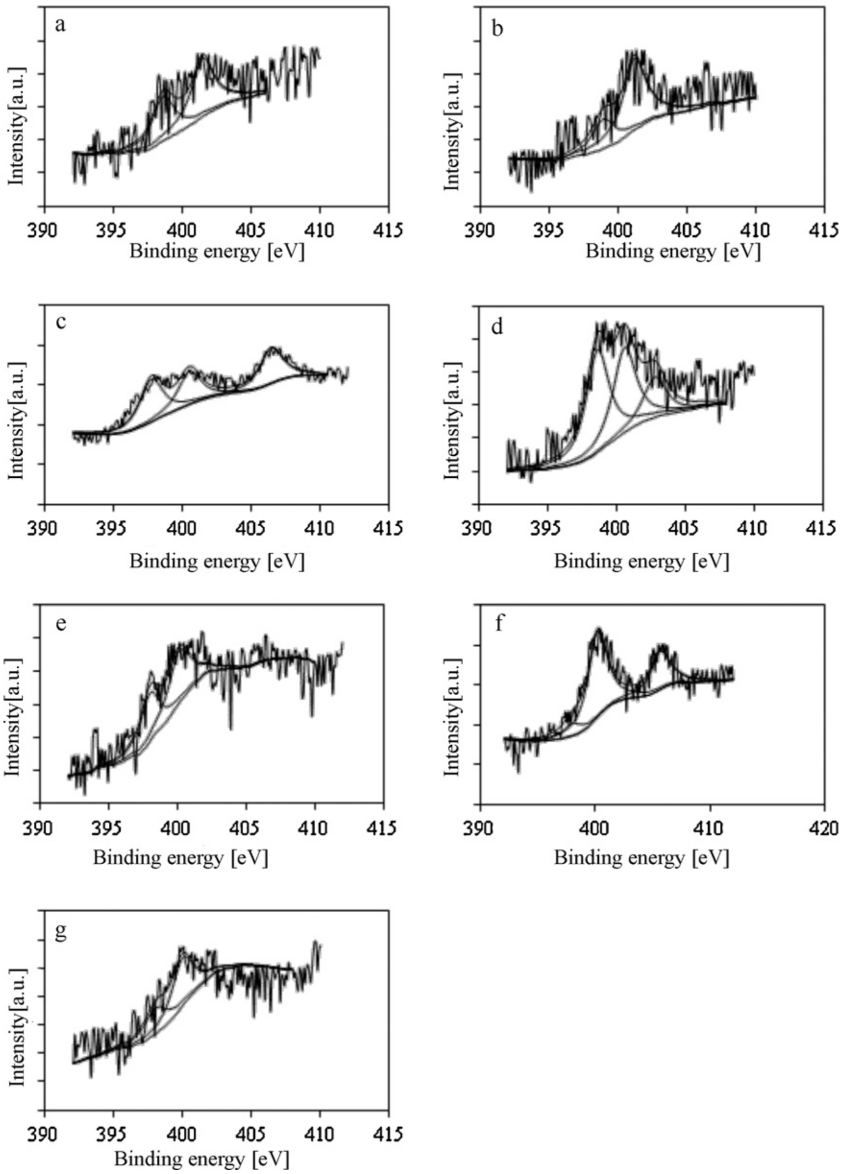

**Fig. 1.** Deconvoluted XPS spectra of nitrogen groups on (a) AC-1100, (b) AC, (c) AC-U, (d) AC-1 M-U-T-P, (e) AC-0.1 M-U-T-P, (f) AC-$HNO_3$ and (g) AC-O.

at steady state, for all samples. The oxygen concentration strongly influenced these reaction parameters. Both adsorption and oxidation are strongly affected by $O_2$ concentration. When oxygen is absent, there is no NO removal.

These experiments show that larger $O_2$ concentration decreases the time needed to achieve stationary NO and $NO_2$ concentrations. The oxidation of NO to $NO_2$ increases with larger oxygen concentrations. The conversion of NO increases greatly when the concentration of $O_2$ changes from of 2% to 5%; but raising the $O_2$ concentration from 10% to 20% practically does not affect the NO conversion. NO conversion can reach 68% with AC-U in the presence of only 2% oxygen. The largest conversions of NO were obtained when 20% of $O_2$ was used. However, the amount of $NO_2$ released is smaller than that obtained with 5% of $O_2$, which means that more NO is converted to $N_2$.

**Table 2**
Binding energies and relative surface concentrations of nitrogen species obtained by fitting the N1s core level XPS spectra.

| Sample | N6 groups | | N5 groups | | N-Q groups | | N-X groups | | –$NO_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | B.E. [eV] | % | B.E. [eV] | % | B.E. [eV] | % | B.E. [eV] | % | B.E. [eV] | % |
| AC | 398.9 | 0.13 | – | – | 401.2 | 0.35 | – | – | – | – |
| AC-$HNO_3$ | 398.0 | 0.09 | 400.2 | 0.60 | – | – | – | – | 405.7 | 0.28 |
| AC-O | 398.0 | 0.38 | 400.0 | 0.22 | – | – | – | – | – | – |
| AC-U | 398.0 | 0.47 | 400.8 | 0.60 | – | – | – | – | 406.6 | 0.58 |
| AC-U-0.1 M-T-P | 398.0 | 0.40 | 400.2 | 0.50 | – | | – | – | – | – |
| AC-U-1 M-T-P | 398.7 | 0.37 | 400.6 | 0.30 | – | | 402.8 | 0.15 | – | – |
| AC-1100 °C | 398.6 | 0.15 | – | – | 401.5 | 0.20 | – | – | – | – |

**Table 3**
Influence of $O_2$ concentration on NO conversion, on the amount of $NO_2$ released and on NO adsorption.

| Sample | $O_2$ concentration [%] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | | | 5 | | | 10 | | | 20 | | |
| | $X_{NO}$ [%] | $NO_{ads}$ [mmol] | $NO_2$ [mmol] | $X_{NO}$ [%] | $NO_{ads}$ [mmol] | $NO_2$ [mmol] | $X_{NO}$ [%] | $NO_{ads}$ [mmol] | $NO_2$ [mmol] | $X_{NO}$ [%] | $NO_{ads}$ [mmol] | $NO_2$ [mmol] |
| AC | 49 | 1.58 | 0.58 | 72 | 1.68 | 3.56 | 78 | 3.21 | 1.92 | 82 | 1.88 | 2.15 |
| AC-$HNO_3$ | 59 | 1.55 | 3.38 | 83 | 1.70 | 4.46 | 83 | 1.80 | 4.13 | 88 | 1.92 | 2.93 |
| AC-O | 67 | 1.60 | 3.49 | 83 | 1.81 | 4.07 | 85 | 2.12 | 3.87 | 86 | 1.08 | 2.33 |
| AC-U | 68 | 1.84 | 3.40 | 72 | 1.96 | 4.22 | 82 | 1.89 | 2.70 | 87 | 1.83 | 2.41 |
| AC-U-0.1 M-T-P | 58 | 1.78 | 2.86 | 72 | 0.13 | 4.27 | 79 | 2.01 | 2.70 | 80 | 1.76 | 2.46 |
| AC-U-1 M-T-P | 47 | 0.72 | 1.96 | 73 | 1.78 | 4.49 | 86 | 1.96 | 3.51 | 87 | 1.19 | 2.97 |
| AC-1100 °C | 70 | 1.82 | 3.35 | 76 | 1.93 | 4.18 | 78 | 2.09 | 3.16 | 89 | 1.41 | 2.42 |

The reaction of NO oxidation over carbon materials suggests that oxygen is first chemisorbed on the surface (Eq. (1)) and then NO reacts with surface oxygen to form $NO_2$ adsorbed on the carbon surface (Eq. (2)).

Oxygen favours the formation of new active sites on the surface of the carbon material for NO adsorption. Formation of a NO dimer $(NO)_2$ has been proposed as a possible mechanism to explain the reduction of NO to $N_2$ at low temperatures (Eq. (3)). The formation of $(NO)_2$ occurs when the concentration of strongly adsorbed NO is high and there is a higher probability that two NO molecules could be located adjacently to form a $(NO)_2$ dimer.

$$2C_f + O_2 \rightarrow 2C\text{–}O \qquad (1)$$

$$C\text{–}O + NO \rightarrow C\text{–}NO_2 \qquad (2)$$

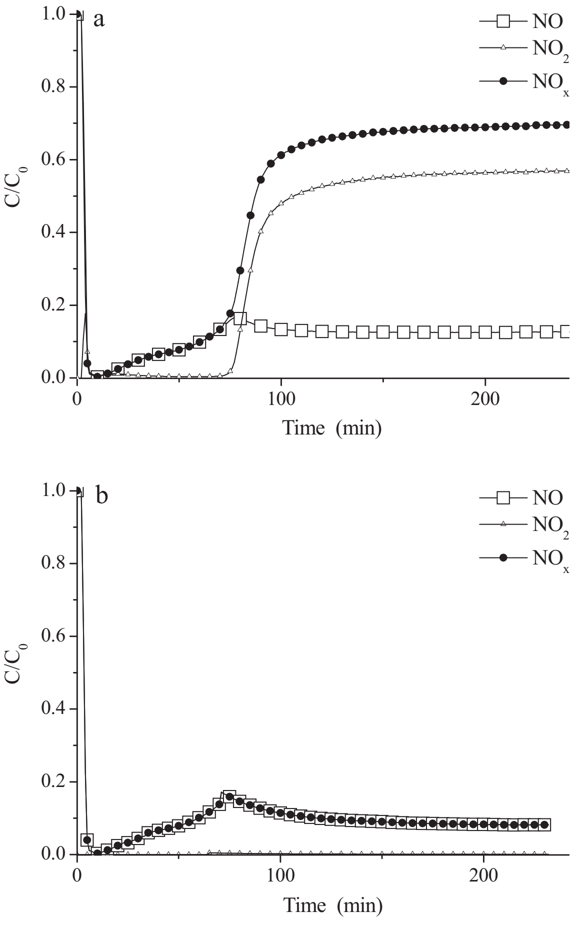

**Fig. 2.** Oxidation of NO into $NO_2$ over AC-U: (a) outlet gas passed directly to NO analyzer and (b) outlet gas passed through washing bottle.

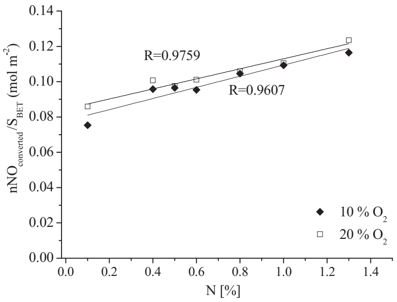

**Fig. 3.** Amount of NO converted per unit surface area versus nitrogen content of the activated carbons.

$$(NO)_2 + 2C_f \rightarrow N_2 + 2C_f\text{–}O \qquad (3)$$

The formation of molecular nitrogen implies a concerted reaction with the formation of N–N and C–O bonds, followed by splitting of the N–O bonds to produce a $N_2$ molecule. These reactions are exothermal, which means that they are favoured at lower temperatures.

In order to assess the influence of the nitrogen groups, the amount of NO converted, normalized by the surface area, was plotted against the nitrogen content of the activated carbons, as shown in Fig. 3.

A strong correlation was obtained. It can be concluded that the presence of nitrogen groups enhances the oxidation of NO to $NO_2$. The extra electrons resulting from the substitution of C for N in the aromatic ring are delocalised and can be transferred to adsorbing species to form reactive surface intermediates [19].

Carbons with pyridine nitrogen-containing groups at the edge of graphene layers have the lowest bandgap, thus they should present the highest catalytic activity. This is generally observed when the amount of NO converted, normalized by the surface area, is plotted against the N6 content (determined by XPS), although the correlation is not as good as that shown in Fig. 3.

## 4. Conclusions

A range of activated carbons with different N contents have been prepared.

The removal of NO by catalytic oxidation of NO to $NO_2$ on N-doped activated carbons is possible at low temperatures. NO conversion increases with the gas phase oxygen concentration. The presence of nitrogen-containing surface groups favours the oxidation of NO to $NO_2$. All the produced $NO_2$ could be captured by water to form nitric acid.

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