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Catalytic wet air oxidation of aqueous ammonia with activated carbon

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Abstract

The oxidation of aqueous ammonia to nitrogen by the catalytic wet air oxidation (CWAO) process with activated carbon as catalyst was studied. A commercial activated carbon CUDU1000 chemically modified by oxidation with HNO_3 and/or reduction with H_2 was used. The characterization of the activated carbons was carried out by N_2 adsorption, thermal programmed decomposition (TPD), Fourier transformed infrared (FTIR) spectroscopy, Boehm titration and zero point charge (ZPC) techniques. Studies of aqueous ammonia adsorption on the activated carbons under atmospheric conditions showed that carboxylic, lactonic and anhydride surface groups increase both the rate and capacity of adsorption. The oxidized carbons had lower activity towards selective aqueous ammonia oxidation in CWAO process because of a strong ammonia adsorption. However, hydrogenated activated carbons had higher activity for selective aqueous ammonia oxidation. It is establish that a strong ammonia adsorption takes place onto carboxylic, lactonic and/or anhydride surface groups while the quinonic surface groups are responsible of the catalytic activity shown by these carbons.

Keywords: CWAO process; Activated carbon; Ammonia oxidation (aqueous)

1. Introduction

Aqueous ammonia ($NH_{3(aq)}$) is highly hazardous to aquatic life and produces the eutrophication into receptor bodies like lakes and rivers. Its toxicity occurs at very low concentrations [1,2]. Waste waters that contain aqueous ammonia come from different sources, such as, petrochemical plants, sewage sludge residential wastes and coal gas plants [3,4]. In order to reduce aqueous ammonia in waste water, several methods have been used: biological processes [5–7], adsorption processes [8,9], and supercritical wet oxidation [10]. However, the actual trend is to use mild operative conditions in a highly selective one-stage process, to obtain friendly or biodegradable products. Catalytic wet air oxidation (CWAO) is an alternative method, which fulfills these conditions by selective ammonia oxidation to nitrogen [11,12]. Metals like Pt, Ru, Pd, Ir, Mn, Co supported over CeO_2, TiO_2, Al_2O_3, graphite, ZSM-5 [11–14] have been used in this process.

Activated carbons are widely used as adsorbents or catalytic supports because of their high surface area, tailored pore distribution, and the presence of several oxygenated groups. They are relatively inexpensive and stable both in acidic and alkaline environments [15,16]. The different oxygenated functions present onto activated carbons surface provide the means for ammonia and oxygen adsorption [17–21]. No reports

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have been found on CWAO transformation of ammonia using activated carbon, thus it was of interest to learn about its transformation to nitrogen. The aim of this study was to understand the role of surface oxygenated groups of activated carbons on the CWAO of ammonia. A commercial activated carbon chemically modified by nitric acid oxidation and/or hydrogen reduction was used. The influence of the surface groups on activated carbons both on $NH_{3(aq)}$ adsorption under environmental conditions, together with adsorption and catalytic activity under CWAO conditions were studied. Textural and chemical properties of activated carbons are related to $NH_{3(aq)}$ adsorption and catalytic activity for selective ammonia oxidation.

2. Experimental

2.1. Activated carbons

A commercial activated carbon CUDU1000 manufactured by Petrochil S.A. was used. This adsorbent is obtained from lignocellulosic material (peach stones) by steam activation. The CUDU1000 was chemically modified by oxidation and/or reduction. The oxidation was carried out in 6 M HNO_3 at 80 °C using 1 g carbon/10 ml solution during 1 h. The treated carbon was thoroughly washed until complete elimination of residual HNO_3. The reduction was carried out at 400 °C for 10.5 h with a hydrogen flow of 50 ml/min. The modified activated carbons were kept under nitrogen for later use. Table 1 presents a summary of the modification conditions together with the nomenclature of activated carbons.

2.2. Adsorption of aqueous ammonia under environmental conditions

Studies of $NH_{3(aq)}$ adsorption versus time, and ammonia concentration were carried out at 30 °C and atmospheric pressure. 1 g of dry activated carbon was contacted with 50 ml of 1000 ppm ammonia solution in an isothermal shaker. Samples of 1 ml were withdrawn at different times for ammonia analysis. Equilibrium adsorption studies of $NH_{3(aq)}$ were carried out varying $NH_{3(aq)}$ concentration from 50 to 3000 ppm. After 24 h, the solution was separated from the activated carbon, and the residual ammonia analyzed.

Table 1
Modification conditions and nomenclature of activated carbons

Activated carbon	Modification process		Name
	Oxidation	Hydrogenation	
CUDU1000	No	No	C
Oxidized activated carbon	Yes	No	COX
Hydrogenated activated carbon	No	Yes	CH
First hydrogenated and later oxidized activated carbon	Yes	Yes	CHO
First oxidized and later hydrogenated activated carbon	Yes	Yes	COH
Oxidized activated carbon treatment at 400 °C in N_2 atmosphere	Yes	–	CO400

2.3. Catalytic decomposition of aqueous ammonia

Table 2 presents the experimental conditions used in ammonia CWAO studies. The reactions were carried out in a pressurized Parr reactor of 300 ml capacity.

2.4. Chemical analysis

$NH_{3(aq)}$ concentrations were determined using the Merck ammonia test (1.14752.001). Aqueous ammonia conversions to nitrogen were followed by gas chromatography (molecular sieve 13X, 60/80 mesh, Supelco) using He as carrier gas. Oxidation products, nitrate and nitrite were analyzed by colorimetric methods [22].

2.5. Activated carbon characterization

Nitrogen adsorption isotherms at 77 K was obtained using a sorptometer Micromeritics Gemini 2370. BET

Table 2
Conditions of aqueous ammonia decomposition by CWAO process

Temperature (°C)	130–190
Pressure (atm)	7.5–16
Time (h)	1–12
Ratio[a]	0.67/100 to 1.68/250
Particle size (mm)	2–0.6
Ammonia concentration (ppm)	1000–2600
Atmosphere	O_2

[a] Ratio: activated carbon mass (g)/solution volume (ml).

(S_{BET}) apparent surface areas were evaluated, and micropore volumes were determined from Dubinin–Radushkevich (DR) equation. Mesopore volumes (V_P) were calculated as the difference between total pore volume and micropore volume (V_O) [23].

Chemical characterization of the activated carbons surface was obtained from the following techniques: (i) thermal programmed decomposition (TPD) carried out under He flow of 50 ml/min from 383 to 1400 K; (ii) carboxylic, lactonic and phenolic groups were estimated by Boehm method [24,25]; (iii) Fourier transformed infrared (FTIR) spectra were recorded on a Magna IR 550 Nicolet, using KBr pellets (0.1% activated carbon); (iv) zero point charge (ZPC) was measured with a Zeta Meter (ZM-77) [26]; (v) pH_{slurry} was measured from a suspension of 1 g of carbon into 20 cm^3 water CO_2 free, after 48 h equilibrium [27].

3. Results and discussion

3.1. Activated carbons aqueous ammonia adsorption

Fig. 1a shows $NH_{3(aq)}$ adsorption as time function. Three hours time were enough to achieve equilibrium. Adsorption rates obtained from the initial slopes of these curves showed that COX gives the highest rate; similar rates to those of CH and COX were found for COH and CHO, respectively. Fig. 2 shows textural properties of activated carbons, no significant changes were observed after the modifications. This behavior is similar to that observed in previous work [28], which showed that oxidation and reduction under moderate conditions did not change the carbon textures [29,30]. Thus, the differences for ammonia adsorption shown in Fig. 1a are mainly a consequence of chemically controlled ammonia adsorption rates. The different nature and concentration of functional groups at the activated carbons surface explains this behavior. Fig. 1b shows adsorption isotherms of ammonia at 30 °C. According to Giles et al. classification [31] these isotherms could be L-type. This implies that there is not a strong competition between solvent and adsorbate molecules for the adsorbent surface sites. CHO and COH presented the same trends as those of COX and CH, respectively. Fig. 1b shows that for ammonia equilibrium concentrations of up to 1000 ppm the oxidized

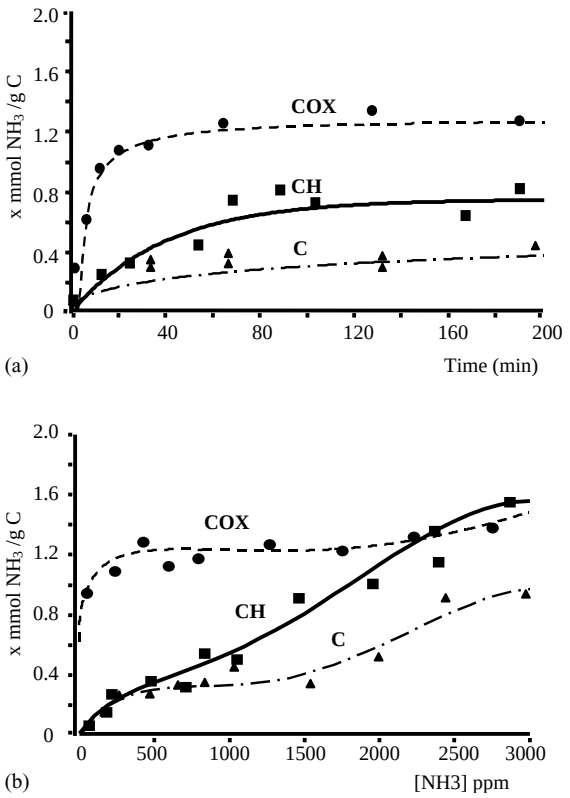

Fig. 1. Aqueous ammonia adsorption at 30 °C and atmospheric pressure: (a) as time function; (b) as function of aqueous ammonia concentration (isotherm).

activated carbon presents very high $NH_{3(aq)}$ adsorption, and the hydrogenated carbon adsorbs more than the original activated carbon C. However for $NH_{3(aq)}$ concentrations higher than 1000 ppm, the $NH_{3(aq)}$ adsorption capacity of the hydrogenated activated carbon increases showing $NH_{3(aq)}$ values similar to those observed on COX at higher $NH_{3(aq)}$ concentrations. As already mentioned, the textural properties shown by these activated carbons do not explain the observed behavior of $NH_{3(aq)}$ adsorption. Therefore the difference in chemical properties of activated carbons must be considered.

TPD profiles (Figs. 3 and 4) show that important surface changes were introduced by chemical modifications. As expected, upon oxidation, a significant increase in the nature and concentration of oxygenated surface groups, which decompose as CO_2 and CO is observed. In contrast, the reduction treatment

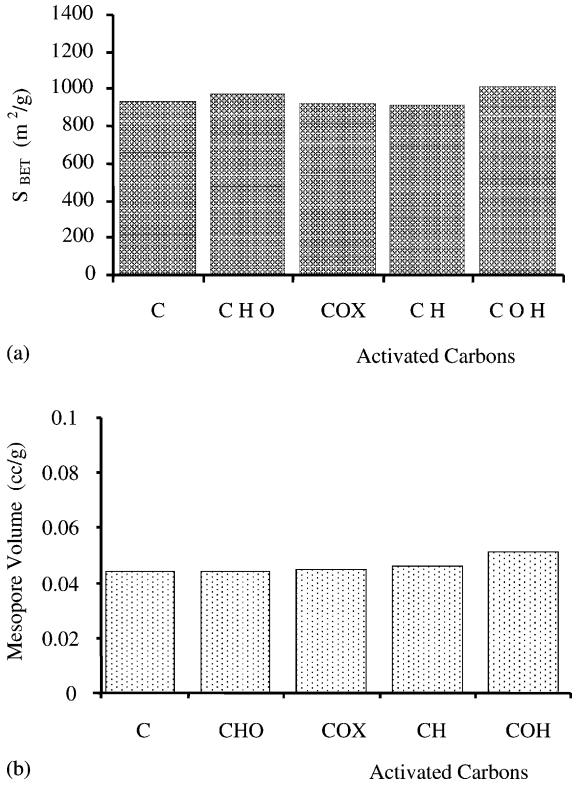

Fig. 2. Textural characterization of activated carbons: (a) BET apparent surface area (m^2/g); (b) mesopore volume (cm^3/g).

decreases the amount of functional groups, mainly those decomposing in the lower temperature range (Fig. 4). COX and CHO activated carbons show surface functional groups decomposing from 125 to 500 °C (low-temperature). They are mainly assigned as carboxylic (200–300 °C) [32,33], lactonic (190–650 °C) [29,33,34,36] and low-temperature anhydride groups (350–657 °C) [29,32–34,37]. Others groups that decompose from 600 to 900 °C (high-temperature) are assigned to phenol (600–700 °C) [29,33,35,37], carbonyl (800–980 °C) [29,33,36], high-temperature anhydride (800–900 °C) [33] and a shoulder at 900 °C assigned to quinone [33,36]. On the other hand, TPD analysis of CH and COH activated carbons presented mainly surface groups that decompose at high-temperatures as phenolic, carbonyl, high-temperature anhydride and quinonic surface groups.

Fig. 5 shows FTIR spectra of activated carbons. The most significant bands are in the regions of 3400, 2900, 1731, 1569 and 1165 cm^{-1}. The band around 3420 cm^{-1} is mainly associated with –OH stretches in hydroxyl, carboxylic and phenolic groups [33,38]. This band in COX is intense and broad and according to its TPD profile could be indicative of a greater amount of carboxylic and/or phenolic groups than in C and COH. The bands in the region 2800–3000 cm^{-1} are assigned to C–H stretching modes of aliphatic

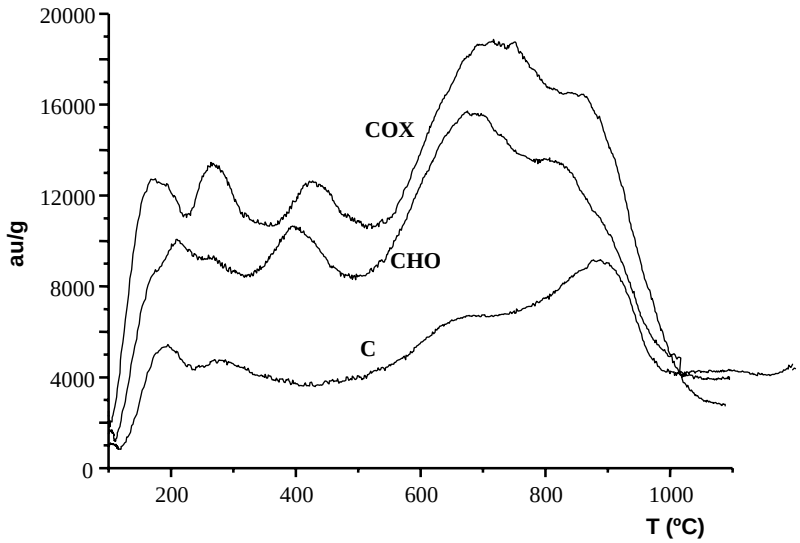

Fig. 3. TPD spectra of oxidized activated carbons COX, CHO and original activated carbon C.

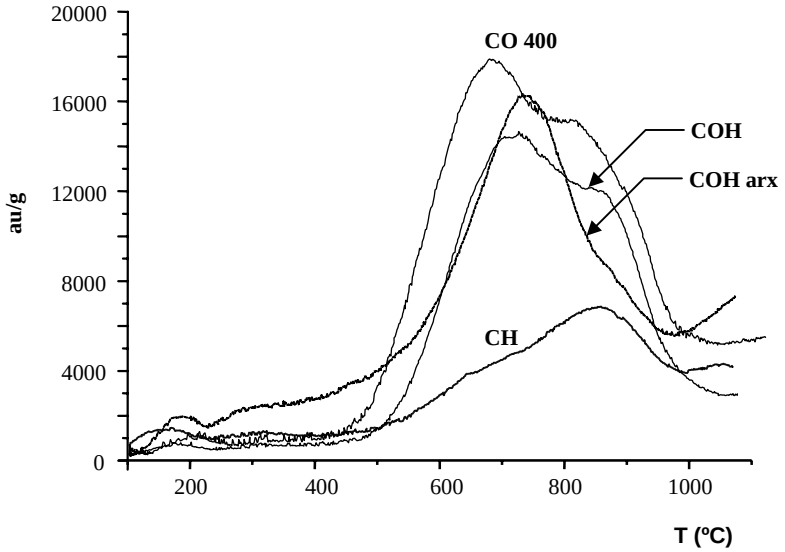

Fig. 4. TPD spectra of activated carbons CH, COH, CO400 and COHarx.

groups like $–CH_2$ and $–CH_3$ [33–36,38–40] and are observed in many activated carbons. The band at 1731 cm^{-1} is associated with lactonic/carbonyl groups [27,38,39]. The band is stronger in case of COX and can be mainly attributed to these groups in agreement with the observed TPD profile. In COH and C activated carbons, the band is small and can be indicative of carbonyl groups according with TPD analysis. The 1569 cm^{-1} band also present in the spectra of carbon C strongly increases in COX while slightly decreases in COH. This band is usually assigned to aromatic ring stretching coupled to highly conjugated carbonyl groups (C=O) [27]. The interpretation is not unequivocally assigned to quinonic groups [38,41–43]. In these carbons, the quinonic group assignment could be corroborated with TPD profiles. The broad and

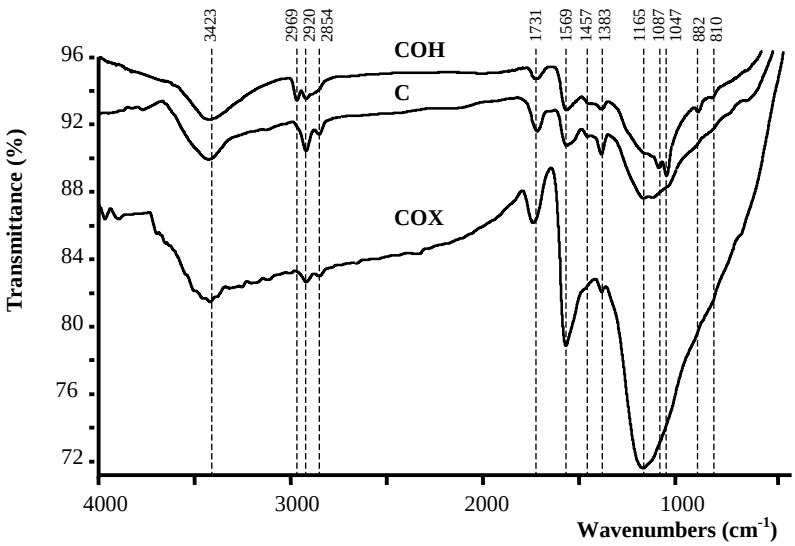

Fig. 5. FTIR spectra of activated carbons C, COX and COH.

Table 3
Characterization of activated carbons by Boehm method, pH_{slurry} and pH_{ZPC}

Activated carbons	Surface functional groups (meq./g)			Acidity (meq./g)	pH_{slurry}	pH_{ZPC}
	Carboxylic	Lactonic	Phenolic			
C	0.13	0.22	0.06	0.35	7.1	2.3
COX	0.43	0.56	0.19	0.98	3.2	2.1
COH	0.23	0.13	0.14	0.36	7.2	3.0

intense band shown at 1165 cm^{-1} by COX spectra is an indication of large concentrations of several functional groups produced after oxidation. This increment of oxygenated surface groups is also corroborated by the TPD profile of COX. Likewise FTIR spectra of C, COX and COH do not show characteristic bands of nitro-groups at 1530–1540 and 1326–1350 cm^{-1} [44–46], nitrate-complexes at 1640 and 1330 cm^{-1} or organic-nitrates at 1640 and 1250 cm^{-1} [44–46]. Thus, there was no indication of nitro-groups formation under the oxidation conditions used.

Table 3 shows Boehm's analysis, the results are for the most part in agreement with those given by TPD and FTIR. The presence of carboxylic, lactonic and probably low-temperature anhydrides is confirmed. The low concentration of phenolic groups onto C proves that high-temperature surface groups observed by TPD can be quinonic. As expected, after oxidation of C the amount of carboxylic, phenolic and lactonic groups largely increase in COX, also its acid character shown by the total acidity, pH_{slurry} and pH_{ZPC}. After COX was hydrogenated (COH) an important decrease in oxygenated surface groups is observed. This is confirmed by a lost of low-temperature groups, such as carboxylic and lactonic, on its TPD profile and an increase of its pH_{slurry}. Phenolic groups onto COH are in similar amount as in COX showing that the reduction conditions used did not affect them.

It must be pointed out that any apparent disagreement between TPD and Boehm analysis shown above is attributed to the different nature of the procedures [39,47]. While one takes place in the gas phase the other is in solution. In such case, hydrolysis of some high-temperature anhydrides may occur increasing the amount of carboxylic like groups detected. Therefore, from TPD, FTIR and Boehm analysis, it is possible to establish the nature and concentration of functional surface groups present in these activated carbons, which are summarized in Table 4.

After these characterizations, it is proposed that the higher concentration of carboxylic and lactonic groups present in COX and CHO activated carbons is responsible for the higher rate and capacity of $NH_{3(aq)}$ adsorption at initial concentrations less than 1000 ppm. The higher acidity of these carbons associated with the surface functional groups allows a strong interaction with aqueous ammonia. The ammonia interaction with surface functional groups of activated carbons has been reported [19,21,48] including an irreversible adsorption [49]. On the other hand, C, CH, and COH activated carbons are less acidic and the surface groups present would require larger initial $NH_{3(aq)}$ concentrations in order to show adsorption.

3.2. Catalytic activity of activated carbons in the CWAO process

In order to avoid diffusion control several experiments were carried out to establish the appropriate reaction conditions. Thus, experimental variables such

Table 4
Summary of surface groups on activated carbons

Activated carbon	Lower-temperature decomposition	Higher-temperature decomposition
C	Carboxylic, anhydride and lactonic	Carbonyl, higher-temperature anhydride, quinonic
COX and CHO	Carboxylic, anhydride and lactonic	Phenolic, carbonyl, higher-temperature anhydride and quinonic
CH, COH and CO400	Very low	Phenolic, carbonyl, quinonic and higher-temperature anhydride

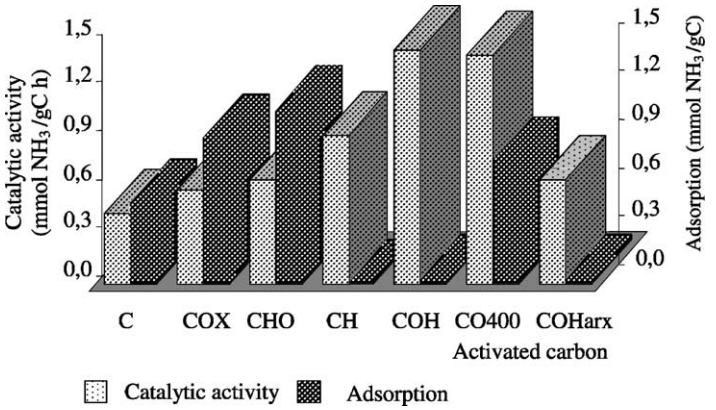

Fig. 6. Catalytic activity and adsorption capacity of activated carbons in CWAO process of aqueous ammonia. Process conditions: 165 °C, 11 atm, 1 h, 1000 ppm. $NH_{3(aq)}$ initial.

as particle size of 0.6–2 mm, agitation of 250–750 rpm, and activated carbon mass to solution volume ratios of 0.75–1.5 ensure that there was not diffusion control. Therefore, CWAO experiments were carried out under the following conditions: particle size of 1–2 mm, 1 g C/150 ml solution, agitation of 500 rpm and $NH_{3(aq)}$ solution of 1000 ppm.

Fig. 6 shows both catalytic activity as well as $NH_{3(aq)}$ adsorption capacity, under N_2 atmosphere, on activated carbons under CWAO conditions. It is observed that all carbons adsorb $NH_{3(aq)}$ but the reduced CH and COH. Aqueous ammonia conversions to N_2 are similar in C, COX and CHO however the highest conversions to N_2 occurs on CH and COH. The most outstanding behavior of these last carbons is that they do not generate total oxidation by-products as was observed for C, COX, and CHO where NO_2^- and NO_3^- were detected. Thus, hydrogenated activated carbons CH and COH present not only the largest conversion to N_2 but also the best selectivity to this product. As shown in Table 4 the major chemical difference of CH and COH from activated carbons C, COX, and CHO is that they did not show lower temperature decomposition groups. To prove the possible unfavorable role of these surface groups a modification on COX was performed. Elimination of undesirable surface groups such as carboxylic, low-temperature anhydride, and lactonic was achieved by heating COX under nitrogen up to 400 °C for 10.5 h. The modified carbon was named CO400. Fig. 6 also shows the behavior of CO400 towards $NH_{3(aq)}$ adsorption and CWAO of $NH_{3(aq)}$. It is observed that after suppression of the low-temperature surface groups the CWAO activity is largely enhanced having a conversion similar to that of COH. However, $NH_{3(aq)}$ retention shows a slight decrease. The increase in retention can be attributed to groups left onto the surface after heat treatment that did not inhibit catalytic $NH_{3(aq)}$ oxidation. Therefore, the groups on activated carbon related to the catalytic activity must be among those who decompose at high-temperatures. A detailed analysis from our results shown below provides a better insight onto which groups can be involved:

- Boehm method does not discriminate quinonic groups and the experiments performed can only detect the so called phenolic groups from those considered high-temperature groups.
- Analysis of TPD profiles provides more information onto the possible groups involved. Fig. 4 shows TPD profiles of CH, COH and CO400. From the areas below the curves it is observed that COH and CO400 have similar quantities of carbonyl–phenolic and quinonic surface groups. Both carbons also have a similar catalytic activity. Smaller quantities of these surface groups on CH parallels its minor catalytic activity.
- Fig. 4 also shows the TPD profile of COH after used in CWAO (COHarx). The shoulder above 800 °C present in CO400, mainly attributed to quinonic surface groups, has diminished but the area related to carbonyl–phenolic groups is similar to that of

Table 5
Results of area deconvolution of TPD profiles using a multiple Gaussian function

Activated carbon	Area (a.u./g)	
	Carbonyl–phenolic	Quinonic
CH	1.48	0.78
COH	1.15	3.12
CO400	4.11	2.11
COHarx	4.18	0.21

COH and CO400. When COHarx was tested in the CWAO process its catalytic activity was smaller to that shown by COH, CO400, and CH. These results would indicate that carbonyl–phenolic surface groups do not have an important catalytic activity on the $NH_{3(aq)}$ partial oxidation.

- By deconvolution of CH, COH, CO400, and COHarx TPD profiles using a Gaussian function and assuming that deconvoluted areas are proportional to group concentrations, their relative amounts can be estimated (Table 5); carbonyl–phenolic are in the order COHarx $\cong$ CO400 $>$ CH $\cong$ COH and quinonic COH $\geq$ CO400 $>$ CH $>$ COHarx. The catalytic activity shown in Fig. 6 is also in the order COH $\geq$ CO400 $>$ CH $>$ COHarx. From these trends, it follows that only the amount of quinonic groups is in the same order as the catalytic activity of the activated carbons.

The above discussion allows to assign an important role to the quinonic surface group on the catalytic oxidation of $NH_{3(aq)}$. These results are in agreement with those presented by Pigamo et al. [17]. They suggested that phenolic or more likely quinonic surface groups are the active centers in the catalytic oxidation of cyclohexanone in liquid phase. Their proposal considers that the activation of molecular oxygen might occur through a redox equilibrium between quinone and hydroquinone at the activated carbon surface. Likewise, Ku et al. [21] studying the reduction of NO with NH_3 in the gas phase over activated carbon proposed the participation of hydroxyl and carbonyl groups in NH_3 adsorption. Teng et al. [19] studying the same reaction proposed that hydroxyl and carbonyl groups are respectively the active sites for NH_3 and NO chemisorption. Therefore it can be suggested that oxidation of $NH_{3(aq)}$ to N_2 may be enhanced by a labile adsorption of NH_3 onto quinonic surface groups.

A temperature dependence study of the rate of CWAO process, in the range of 135–195 °C, on C, COX, and COH gave Arrhenius activation energies of 21.5, 13.8, and 4.5 kJ/mol, respectively. This trend confirms that ammonia conversion to nitrogen is favored by hydrogenated activated carbons in which the most acidic groups had been eliminated.

In summary, the observed decrease in ammonia concentration by CWAO takes place by two different paths depending on the chemical properties of the activated carbon. Thus, a strong adsorption of $NH_{3(aq)}$ occurs onto carboxylic, lactonic and anhydride surface groups. On the other hand, catalytic oxidation of $NH_{3(aq)}$ to N_2 is favored by the presence of quinonic surface groups. Thus, on COX and CHO activated carbons the strong $NH_{3(aq)}$ adsorption inhibits its conversion to N_2. But, on CH and COH activated carbons the $NH_{3(aq)}$ decrease is mainly due to catalytic oxidation.

4. Conclusions

The oxidation of original activated carbon with nitric acid increases all kinds of oxygenated acid surface groups in the modified activated carbon. Hydrogen reduction produced activated carbons, which contain mainly high-temperature anhydride, phenol and quinone surface groups. The surface groups present on any activated carbon greatly affects its activity with respect to $NH_{3(aq)}$ adsorption under environmental conditions as well as in the CWAO process.

Under environmental conditions, carboxylic, lactonic, and anhydride surface groups favor a strong aqueous ammonia adsorption. However, phenol and quinonic surface groups require high $NH_{3(aq)}$ concentrations (>1000 ppm) to obtain a significant ammonia adsorption.

In the CWAO process, the quinonic surface groups are necessary to get high catalytic activity, and selective oxidation towards nitrogen conversion. Carboxylic, lactonic and anhydride groups produce strong ammonia adsorption and low catalytic activity for ammonia conversion.

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