

# NITROGEN ENRICHED ACTIVATED CARBONS AS ADSORBENTS AND CATALYSTS IN DESULFURIZATION TECHNOLOGIES

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## Introduction

Activated carbons (ACs) are widely used as adsorbents and catalysts in desulfurization technologies. Among AC applications in desulfurization are air purification from hydrogen sulfide and methyl mercaptan from waste water treatment plants [1-2], sulfur dioxide removal from flue gases [3-6], and deep desulfurization of gaseous fuel in fuel cell power plants [7]. Desulfurization efficiency is significantly improved when AC works not only as adsorbent of sulfur containing species, but also as a catalyst for selective oxidation of these compounds to less volatile ones which are then strongly adsorbed on a carbon surface. The catalytic properties can be improved by incorporation of nitrogen into the carbon matrix. This process results in an increase in the carbon basicity and polarity. Moreover, dramatic changes in catalytic properties of AC in electron transfer reactions take place.

The objective of this paper is to investigate the ability of nitrogen-containing AC for working as an oxidation catalyst and adsorbent for deep air purification from H<sub>2</sub>S, CH<sub>3</sub>SH and SO<sub>2</sub>.

## Experimental

**Materials.** Nitrogen enriched activated carbons were prepared by impregnation of carbons of different origins with melamine or urea followed by high-temperature treatment (HTT) in inert atmosphere at 850-950°C. Among the precursors for nitrogen immobilization the following carbons were used: bituminous coal based carbons SBC (INCAR, Spain) and BPL (Calgon), wood based commercial carbon BAX-1500 (Westvaco) and experimental EBC (INCAR), as well as experimental fruit stone based carbon KAU (ISPE, Ukraine). Other series of ACs were prepared by pyrolysis of ion-exchange resin containing methylpyridinium and pyridinic nitrogen groups (SCN) and a porous styrene-divinylbenzene copolymer containing no hetero-elements (SCS). The nitrogen

modification procedures were described in details elsewhere [8-11]. For comparison the results obtained on commercial catalytic carbon containing nitrogen, Centaur (Calgon), are also discussed. After nitrogen modification the additional letter U (urea) or M (melamine) are added to the names of the carbons. The exhausted carbons after the breakthrough tests are referred to with an additional letter, E.

**Methods.** The dynamic tests were carried out at room temperature to evaluate the capacity of the ACs for H<sub>2</sub>S, CH<sub>3</sub>SH and SO<sub>2</sub> removal [8-11]. Moist air (relative humidity 80% at 25°C) containing 3000 ppm of H<sub>2</sub>S, CH<sub>3</sub>SH or SO<sub>2</sub> was passed through a column with 6 ml of adsorbent at 500 ml/min. The outlet concentrations of gases were monitored with electrochemical sensors. The tests were stopped at the breakthrough concentrations of 500 ppm for H<sub>2</sub>S, 50 ppm for CH<sub>3</sub>SH and 350 ppm for SO<sub>2</sub>. The adsorption capacities of each carbon were calculated by integration of the area above the breakthrough curve (from the inlet concentration of gas, flow rate, breakthrough time), and carbon weight.

Sorption of nitrogen was used to characterize the porosity of adsorbents. Nitrogen isotherms were measured using an ASAP 2010 (Micromeritics) at -196 °C. Before experiments the samples were outgassed overnight at 120°C under the vacuum of 10<sup>-5</sup> Torr to a constant pressure. The isotherms were used to calculate the total specific surface areas (S<sub>t</sub>), micropore volumes (V<sub>mic</sub>), total pore volumes (V<sub>t</sub>), average micropore sizes (L<sub>mic</sub>) and pore size distributions using Density Functional Theory (DFT).

pH of carbon surface for initial and exhausted samples was estimated by placing 0.4g of carbon powder in 20 ml of water. The suspension was equilibrated during night and then its pH was measured. The amount of acidic and basic surface groups was determined by titration, with either 0.05N NaOH or 0.05N HCL.

In order to evaluate either the species present on the initial carbon surface or surface reaction products, thermal analysis was carried out using TA Instruments Thermal Analyzer. The instrument settings were: a heating rate of 10°C/min in a nitrogen atmosphere, 100 ml/min flow rate. The products of CH<sub>3</sub>SH oxidation were studied by GC/MS on Shimadzu GAS Chromatograph/Mass Spectrometer model QP5050 with XTI-5 column. The samples for GC/MS analysis were extracted from exhausted carbon samples using methanol.

The content of carbon, hydrogen, nitrogen, sulfur and oxygen was analyzed by LECO CNHS-932 and VTF900 instruments. In some cases XRF and EDX methods were used to determine the amount of sulfur adsorbed and the presence of metal impurities. The surface chemistry of nitrogen containing carbons was studied by XPS method (LEYBOLD LHS 11). The values of binding energy were calibrated with respect to C1s peak at 285.0 eV. The N1s envelopes were used to characterize different forms of nitrogen [12].

## Results and Discussion

Modification of ACs with melamine and urea resulted in a significant increase in the nitrogen content (Table 1). Introduction of nitrogen also leads to changes in the surface chemistry of carbons. Indeed, after nitrogen doping all carbons became more basic than the initial counterparts, which is reflected as a rise of surface pH, absolute amount of basic functional groups and a relative carbon basicity expressed as a ratio of the number of basic groups to the total number of groups present on the surface.

Table 1  
Nitrogen content, pH of carbon and amount of basic and acidic groups

Sample	N content %wt.	pH	Amount of groups, mmol/g		
			basic	acidic	basic/total
SBC	1.0	9.1	0.05	0.5	0.09
SBC-M	5.4	9.2	0.72	0.11	0.87
BPL	0.4	7.4	0.40	0.50	0.44
BPL-U	1.1	8.5	0.60	0.35	0.63
BPL-M	6.8	8.0	0.68	0.24	0.74
BAX	0.2	7.2	0.35	0.90	0.28
BAX-U	3.1	7.4	0.65	0.70	0.48
SCS	0	8.1	0.62	0.12	0.84
SCN	2.4	9.1	0.56	0.25	0.69

The development of nitrogen functionality for different types of nitrogen enriched carbon was extensively studied by X-ray photoelectron spectroscopy (XPS) [12-15]. It was found that the type of a carbon precursor and nitrogen modification agent result in the same surface functionalities when the treatment is done at temperatures higher than 850°C [4,6,12-15]. During HTT of nitrogen-containing precursors, nitrogen atoms are incorporated into carbon rings and located at the edges of graphene layers as pyridinic (BE = 398.7 eV), pyrrolic (BE = 400.3 eV) and pyridone (BE = 400.5 eV), or in the interior as “quaternary” nitrogen (BE = 401.3 eV). When carbons are exposed to oxygen containing atmosphere the pyridine-N-oxides (BE = 403-405 eV) are formed. It is interesting to note that the energy state of “quaternary” nitrogen observed in N-carbons is very close to the state of real quaternary nitrogen in methylpyridinium group ( $>N^+-CH_3$ ) of vinylpyridine resin - precursor used for preparation of polymeric carbon SCN type [12]. The pyridinic nitrogen contributes to one  $p_{\pi}$ -electron to the graphitic  $\pi$ -system, while pyrrolic and “quaternary” nitrogen contributes to two  $p_{\pi}$ -electrons to the graphitic  $\pi$ -system. These extra electrons delocalized over graphene layers can dramatically change catalytic properties of a carbon matrix in reactions involving electron transfer.

Modifications with nitrogen-containing species may also result in changes in the porous structure. For all initial and N-modified carbon samples the nitrogen

adsorption isotherms were measured and then structural parameters were calculated [8-11]. All adsorbents have highly developed micro- and mesopore structure. The examples of the results are presented in Table 2. For majority of the samples after N-modification and HTT a 10 to 25% decrease in textural parameters is observed (Table 2). An exemption is the BAX-U sample whose precursor carbon (BAX) was prepared by chemical activation at 550 °C.

Table 2  
Structural parameters of carbons calculated from nitrogen adsorption isotherms

Sample	$S_t$ m <sup>2</sup> /g	$V_t$ cm <sup>3</sup> /g	$V_{mic}$ cm <sup>3</sup> /g	$L_{mic}$ nm
BPL	1000	0.71	0.40	1.16
BPL-U	883	0.67	0.34	1.17
BPL-M	811	0.70	0.31	1.19
BAX	1350	1.29	0.50	1.32
BAX-U	1087	0.80	0.40	1.15
SCN	973	0.83	0.43	1.07

The ability of N-containing ACs to work as oxidation catalyst and adsorbents for deep air purification from H<sub>2</sub>S, CH<sub>3</sub>SH and SO<sub>2</sub> was investigated in dynamic conditions. From the breakthrough curves the capacities for removal of sulfur-containing gases were calculated [8-11]. Examples of data for selected samples are collected in Table 3. In all cases a significant increase in the capacity is found for N-containing carbons compared to the initial ones, which suggests the feasibility of application of N-enriched ACs in desulfurization technologies [8-11].

Table 3  
Amount of gases adsorbed and the pH of the exhausted carbons

Sample	H <sub>2</sub> S ads mmol/g	pH(E)	CH <sub>3</sub> SH ads mmol/g	pH(E)	SO <sub>2</sub> ads mmol/g	pH(E)
SBC	0.74	4.4	6.17	4.7	-	-
SBC-M	7.44	2.0	7.92	3.5	-	-
BPL	0.12	7.9	2.50	6.9	-	-
BPL-M	10.1	1.8	9.19	3.7	-	-
BAX	0.26	4.2	0.58	6.8	0.53	2.2
BAX-U	7.94	2.0	6.25	4.9	1.09	1.9
SCS	0.76	3.9	-	-	0.84	2.3
SCN	5.88	1.4	9.38	2.9	4.95	1.3
Centaur	3.06	1.5	4.79	2.2	2.56	1.5

The process of SO<sub>2</sub> adsorption/oxidation has been studied extensively and such parameters as the porosity, surface chemistry, ash content and gas phase composition were taken into consideration [2-5,10,14-15]. It was found that in oxygen atmosphere and in the presence of water, SO<sub>2</sub> is adsorbed on the

surface of AC, then oxidized to  $\text{SO}_3$  by oxygen radicals and after hydration with adsorbed water it is condensed in pores as  $\text{H}_2\text{SO}_4$  [2-5,10]. The presence of nitrogen-containing functional groups significantly enhances the adsorption capacity due to activation of molecular oxygen and creation additional basic sites for adsorption of oxidation products in molecular or ionic form. Figure 1 demonstrates the dependence of  $\text{SO}_2$  adsorption measured in wet, dry and dry anaerobic conditions on the incremental basicity of surface in pores with sizes between 6.8 and 8.6 Å. The graph indicates that both the pore structure and surface chemistry are very important factors which should be taken into account in designing highly effective  $\text{SO}_2$  adsorbents.

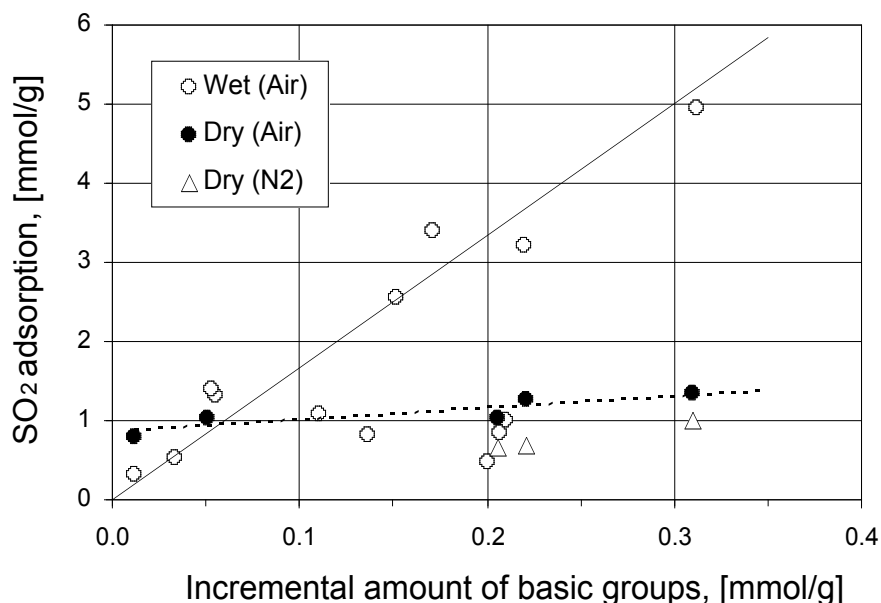


Figure 1. Dependence of  $\text{SO}_2$  adsorption on the incremental basicity of surface in pores with sizes 6.8 and 8.6 Å. Lines show the trend in the data.

Caustic impregnated and virgin activated carbons are among most effective adsorbents for  $\text{H}_2\text{S}$  removal from different gas media at low temperatures [1-2]. It was found that presence of water and basic environment on ACs contributes to the dissociation of  $\text{H}_2\text{S}$  and facilitates its oxidation to sulfur and sulfur dioxide [1-2,8]. The proposed mechanism involves  $\text{H}_2\text{S}$  adsorption on the carbon surface, its dissolution in a water film, dissociation of adsorbed  $\text{H}_2\text{S}$  in the water film, surface reaction with adsorbed oxygen with formation of elemental sulfur or  $\text{SO}_2$ , and further oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  [1-2]. It was proposed that two types of active sites are probably responsible for catalytic action: one is the carbon active sites where molecular oxygen is adsorbed and activated, and the second ones are the small sulfur clusters or polysulfides where oxygen can also be chemisorbed. The oxidation products are adsorbed in carbon micropores. The reaction proceeds until all micropores or carbon active sites are filled with adsorbed sulfur or until low pH of oxidation products suppresses dissociation of  $\text{H}_2\text{S}$ .

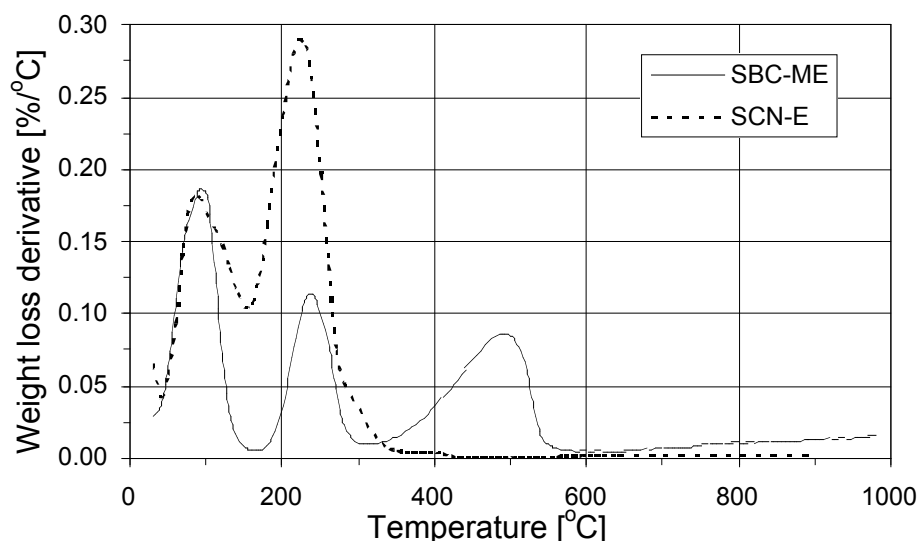


Figure 2. DTG curves in nitrogen for the samples after H<sub>2</sub>S adsorption

The main feature of H<sub>2</sub>S adsorption on N-containing ACs is its deeper oxidation (low pH of exhausted carbon) and higher removal capacity than on carbons without nitrogen (Table 3) [8,9]. To identify the products of H<sub>2</sub>S adsorption/oxidation, thermal analysis in nitrogen was performed on the exhausted carbons. The results are presented as DTG curves with three main peaks (Fig. 2). First peak at 100°C represents desorption of water, second peak at 250°C is assigned to desorption of SO<sub>2</sub> and decomposition of H<sub>2</sub>SO<sub>4</sub>, and the third one at 400-450°C is related to the removal of elemental sulfur. From these data the selectivity for SO<sub>2</sub> oxidation was calculated as the molar ratio of SO<sub>2</sub> formed to total amount of sulfur adsorbed.

To see the effect of nitrogen incorporation, the normalized capacity (with respect to the surface area of adsorbents) and selectivity for SO<sub>2</sub> oxidation was plotted versus the ratio of atomic content of nitrogen to carbon determined from elemental analysis (Fig. 3). Four series of N-modified carbons were chosen for this analysis. The results follow, in general, the same trend. While the specific capacity increases until the plateau is formed (saturation), the selectivity changes in the opposite direction. This is likely due to a limited accessibility of oxygen to sulfur active sites in the bulky crystals.

Adsorption/catalytic removal of methyl mercaptan on N-enriched activated carbons follows in general the same trend as the adsorption of hydrogen sulfide. The process is pH dependent and enhanced in the presence of water and oxidation proceeds due to the surface reaction between adsorbed CH<sub>3</sub>SH and active oxygen radicals. N-doping improves the catalytic activity. The oxidation products are adsorbed in carbon micropores [11,16]. In spite of these similarities CH<sub>3</sub>SH adsorption has specific peculiarities: due to less water solubility and smaller dissociation constant the oxidation requires more basic conditions. Owing

to higher bond energy in S-C than in S-H the reaction proceeds to dimethyl disulfide and methyl methanethiosulfonate formation at room temperature. Water and dimethyl disulfide compete for adsorption sites on the carbon surface. The dependence of the normalized  $\text{CH}_3\text{SH}$  breakthrough capacity on the N/C atomic ratio has the maximum in the capacity at N/C content of about 2% [11,16].

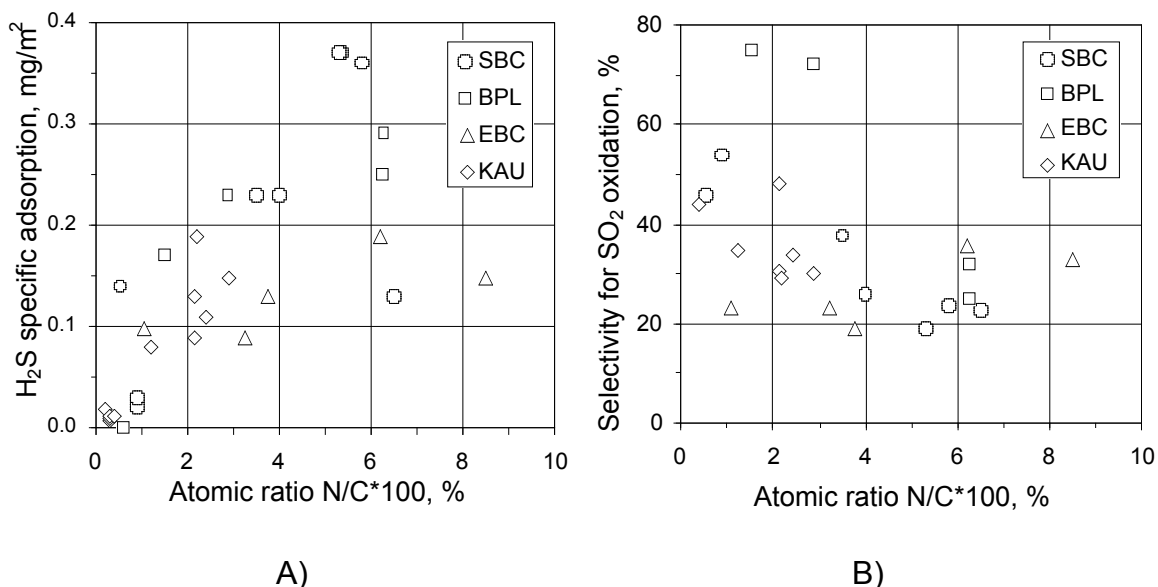


Figure 3. Dependence of the normalized  $\text{H}_2\text{S}$  breakthrough capacity (A) and the selectivity for  $\text{SO}_2$  oxidation (B) on the N/C atomic ratio in the carbon matrices.

The observed improvement of adsorption-catalytic properties of nitrogen containing carbons in desulfurization reactions can be explained from the point of view of the electronic theory of catalysis. The extra  $\pi$ -electrons of pyrrolic and quaternary nitrogen occupy the high-energy states in the conduction band. It is likely that from there they can be transferred to the adsorbed oxygen and superoxide ions  $\text{O}_2^-$  can be formed. Those superoxide ions can easily trigger the formation of  $\text{OH}^*$  and  $\text{HO}_2^*$  radicals in reaction with water. All of these species are much more reactive than molecular oxygen and may oxidize described above sulfur compounds, when they are adsorbed on carbon surface.

## Conclusions

Nitrogen enriched activated carbons can be successfully used in desulfurization technologies to remove hydrogen sulfide, sulfur dioxide and methyl mercaptan from wet air at ambient temperatures. Nitrogen incorporation has a positive effect on adsorption capacities for all gases studied. Unique surface chemistry of these materials can dramatically change catalytic properties of a carbon matrix in reactions involving electron transfer.

**Acknowledgement** This research is supported by NATO Collaborative Linkage grant NATO EST CLG 978688.

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