

# CHANGES IN THE GASIFICATION BEHAVIOR OF ACTIVATED CARBONS CAUSED BY INCORPORATED NITROGEN

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## INTRODUCTION

It has been previously described that incorporated nitrogen has a retarding effect on the oxidation by O<sub>2</sub> and CO<sub>2</sub> of activated carbons prepared from sugar (sucrose) with nitrogen-containing additives [1-3]. The nitrogen content of the carbons increased during gasification [1]. These first findings are substantiated by measurements with carbons prepared from nitrogen-doped phenol-formaldehyde resins which should have a homogeneous distribution of the nitrogen. Some of the phenol was replaced by aniline in the synthesis of the polymer. For comparison, a carbon prepared from sucrose and uracil was used. The carbons were obtained by carbonisation at 1100°C, followed by activation with CO<sub>2</sub> at 900°C. The nitrogen-containing carbons were characterized by XPS. The oxidation with 5 % O<sub>2</sub> in He was studied thermogravimetrically. As the nitrogen content increased with increasing burn-off, the formation of NO<sub>x</sub> increased as well [2]. Differences in the development of porosity are described.

## EXPERIMENTAL

The starting polymers were prepared by refluxing phenol with an aqueous formaldehyde solution for 30 minutes together with the polymerisation catalyst (HCl) and, for the doped carbon, the nitrogen additive aniline (1000 µmol per g of CH<sub>2</sub>O). After carbonisation, the ground and sieved (<0.1 mm) samples were heat-treated at 1100°C in N<sub>2</sub> and subsequently activated with CO<sub>2</sub> at 900°C to 22 % burn-off. The carbons from sucrose were prepared in an analogous way except for the first preparation step which in this case was a carbonisation of sugar, either pure or mi-

xed with uracil (ura, 0.8 mol N per mol of sugar). The designation of the samples is PKA 00 for the activated carbon from phenol-formaldehyde resin, and N-PKA-1000an for the nitrogen-doped material. Sucrose-derived carbons are designated as ZKA 00 and N-ZKA-80 ura, respectively.

Nitrogen contents of the samples were determined by the Kjeldahl method. The XPS data were obtained with a Perkin-Elmer Phi 5400 ESCA system using Al K<sub>α</sub> radiation. Micropore volumes were determined from Dubinin-Radushkevich plots of the N<sub>2</sub> isotherms (77 K). Calculation of the pore width followed Stoeckli's procedure [4].

The reactivities of the carbons in a mixture of 5 % O<sub>2</sub> in He (60 ml/min) were measured using a thermogravimetric analyzer (Stanton Redcroft, STA 780). 10 mg of the carbon sample were heated at 20 K/min in He (60 ml/min) to the desired temperature, and the system was allowed to stabilize for 30 min. Then the gas was switched to 5 % O<sub>2</sub> in He and the weight loss was recorded as a function of time.

## RESULTS AND DISCUSSION

The carbons are characterized in Table 1. The relatively high nitrogen contents of the carbons prepared from sucrose (based on the nitrogen addition) may be due to the fact that much more carbon is volatilized during carbonization of sugar as compared to the phenol resin. The micropore volumes of the starting materials were comparable, but the volume increased significantly more on further activation of the undoped sugar carbon. The pore width was a little larger with N-PKA-1000an than with the nitrogen-free

TABLE 1 - Characterization of the samples

Sample	initial (at 22 % burn-off)			at 75 % burn-off		
	nitrogen content [µmol/g]	micropore volume [ml/g]	mean micropore width [nm]	nitrogen content [µmol/g]	micropore volume [ml/g]	mean micropore width [nm]
ZKA-00	40	0.38	0.96	80	0.56	2.08
N-ZKA-80 ura	1275	0.47	0.97	2880	0.64	1.86
PKA-00	70	0.43	0.89	170	0.70	1.94
N-PKA-1000 an	805	0.44	1.02	1315	0.60	1.52

TABLE 2 - Reactivities at 580°C in the gasification with 5 % O<sub>2</sub> in He

Sample	initial reactivity (at 22 % b.-o.) [g/g · s]	reactivity (at 60 % b.-o.) [g/g · s]	Ea (at 60 % b.-o.) [kJ/mol]	Pre-exponential factor [g/g · s]
ZKA-00	$2.4 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	144	$1.7 \cdot 10^6$
N-ZKA-80 ura	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	170	$4.6 \cdot 10^7$
PKA-00	$3.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	145	$2.4 \cdot 10^6$
N-PKA-1000 an	$2.6 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	160	$1.5 \cdot 10^7$

material at 22 % b.-o., but on further gasification the width increased much more with the undoped samples. This may be relevant for the gasification behavior.

The gasification behavior in 5 % O<sub>2</sub> in He is shown in Fig. 1. As shown also in Table 2, the carbons prepared from phenol-formaldehyde resin were a little more reactive than samples prepared from sucrose. This may be due to the lower nitrogen content or to a possibly slightly higher active surface area of the carbons from phenol-formaldehyde resin. For this reason, the carbons should be divided into two groups according to their precursor material. The nitrogen-doped samples of both groups exhibit lower reactivities than the corresponding control samples, but this effect is not as pronounced as observed with sucrose carbons without activation [1]. Obviously, the porous structure of the activated samples influences gasification, and the reaction is (partially) diffusion-controlled. With increasing burn-off, the pores of the nitrogen-containing carbons were significantly narrower than those of the undoped samples, and the gasification rate was also smaller. Further experiments under similar conditions showed that the nitrogen content of these samples increases strongly with burn-off; in consequence, the maximum of the NO<sub>x</sub> evolution from the samples under investigation was

always delayed compared to the formation of CO and CO<sub>2</sub> [2].

XPS studies of the nitrogen species in various carbons showed that the nature of nitrogen functionality depends mainly on the temperatures used during the preparation of the samples [5]. The samples under investigation, which all had been heat-treated at 1100°C before activation contained considerable amounts of nitrogen which has been called „quaternary nitrogen“ in the literature (b.e. 401.3 eV) [5,6].

Very likely, this N is bound by substitution in the graphene layers [5]. Pyridinic nitrogen was also detected (b.e. 398.7 eV), small concentrations of pyrrolic nitrogen (b.e. 400.3 eV), which usually is also present, may be hidden under the large peak of „quaternary N“. Obviously, under the conditions of the experiments, these nitrogen functions are very stable against oxidation and in the course of the combustion, inhibit gasification of the carbon itself. Very likely, the inclusion of nitrogen in the aromatic structure of the graphene sheets occurs near the active edge, resulting in a reduction of the active surface area involved in the gasification.

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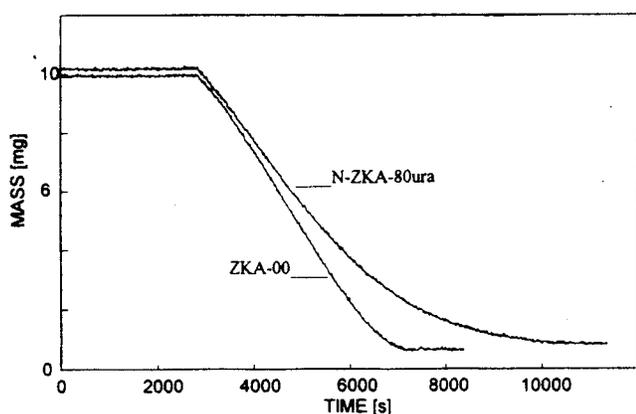


Fig.1. Gasification behavior of the carbons in 5% O<sub>2</sub> in He at 580°C.