

INFLUENCE OF NITROGEN CONTENT OF CARBONS ON THEIR AUTOXIDATION BEHAVIOR

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INTRODUCTION

Carbons, *i.e.* carbon blacks, activated carbons *etc.*, are known to catalyze oxidation reactions, such as the reaction of sulfurous acid or oxalic acid with oxygen [1-3]. It was found that the catalytic activity of activated carbons for the oxidation of sulfurous acid increases with their nitrogen content [4]. It has been shown that active carbons catalyze their own oxidation in alkaline media [5]. The oxidation rate increases with the temperature and with the pH of the solution. The question arose how the nitrogen content influences this autoxidation. Therefore the study was resumed with activated carbons prepared from phenol-formaldehyde resins with different nitrogen contents. The carbonate formed in the reaction with O₂ was determined.

EXPERIMENTAL

The starting polymers were prepared by refluxing phenol with an aqueous formaldehyde solution for 30 minutes together with the polymerisation catalyst (HCl or NH₃) and, for the doped carbons, the nitrogen additives aniline (an) or 3-hydroxypyridine (hp). After carbonisation, the ground and sieved (< 0,1 mm) samples were heat-treated at 1100°C in N₂ and activated with CO₂ at 900°C to 22-26 % 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 mixed with the nitrogen-containing precursor L-arginine (arg).

The designation of the samples is N-PKA for nitrogen-containing activated carbons from phenol-formaldehyde resins followed by a number indicating the added nitrogen in μmol N per gram formaldehyde. Sucrose-derived carbons are designated N-ZKA, followed by a number indicating the mol% of nitrogen atoms added per mol of sugar in the precursor mixture. The

nitrogen content of the samples was determined by the Kjeldahl method, and the apparent surface areas were measured using N₂ adsorption at 77K (single point method).

The oxidation of the samples took place at 80°C in a solution of 200 ml NaOH (0.2 M) bubbled with CO₂-free O₂. A reflux condenser in the exhaust prevented water losses by evaporation. After predetermined reaction periods, samples were taken by a pipet fitted with a glass wool filter. The carbon trapped in the filter was flushed back into the suspension. The samples were acidified, and the liberated CO₂ was carried by a nitrogen stream into 0.004 M Ba(OH)₂; the changes in electrical conductivity due to precipitation of BaCO₃ were measured.

RESULTS AND DISCUSSION

Carbons with higher nitrogen contents exhibit higher oxidation rates. It appears that some highly reactive carbon on the surface is oxidized rapidly in the beginning of the reaction. Thereafter, the reaction rate is reduced. The specific activity for the reaction was defined as the gradient of the oxidation curves at 150 minutes reaction time. The oxidation was followed for 270 minutes. Table 1 shows the characteristics and autoxidation activities of a few carbons. Also the samples which were not doped with N-containing materials, contained some nitrogen due to a contamination of the phenol or sugar. NH₃ as a polymerization catalyst led to an enhanced nitrogen content.

Fig.1 illustrates the relationship between nitrogen content and activity for the autoxidation in alkali for different types of activated carbons. Higher nitrogen contents resulted in higher autoxidation rates. The aniline-doped carbons were the most active samples in the autoxidation. There was a clear correlation between nitrogen content and autoxidation activity. In con-

TABLE 1 - Characteristics and autoxidation activities at 80°C of the activated carbons

Sample	Appar. surface area [m ² /g]	Nitrogen content [μmol/g]	Autoxidation activity [μmol/g·h]
PKA-00 (HCl)	740	60	68
N-PKA(HCl) 100 hp	870	112	86
N-PKA(HCl) 500 hp	795	317	118
N-PKA(HCl) 1000 hp	955	470	172
PKA-00 (NH ₃)	730	165	92
N-PKA(NH ₃) 100 hp	825	205	121
N-PKA(NH ₃) 1000 hp	775	775	204
N-PKA(HCl) 100 an	690	163	140
N-PKA(HCl) 500 an	730	438	196
N-PKA(HCl) 1000 an	835	689	231
ZKA-00	825	98	103
N-ZKA 5 arg	660	418	148
N-ZKA 10 arg	860	509	184
N-ZKA 25 arg	735	793	221

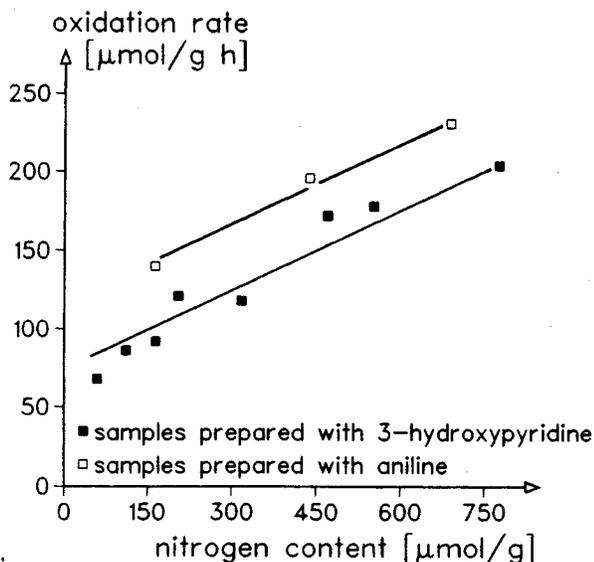


Fig. 1. Correlation of autoxidation activity and nitrogen content.

trast, no such correlation could be observed with the contents of basic surface sites which varied irregularly and on a smaller scale. Carbons prepared with aniline as the additive were more active than those made with 3-hydroxypyridine.

From all samples, CO was formed together with CO₂ during the oxidation, but its amount was too small to be measured quantitatively.

It has been suggested that the catalytic activity of carbons for oxidation reactions is caused by an electron transfer from the carbon to adsorbed oxygen with formation of highly reactive oxygen species such as O₂⁻, O⁻ and OH⁻ [4]. Substitutive incorporation of nitrogen in the graphene layers would raise the Fermi level of the carbon and facilitate this electron transfer. The fact that the autoxidation only takes place in alkaline media can be seen as support for the suggested intermediate oxygen species. At neutral or acidic pH, O₂⁻ would be protonated to HO₂ which disproportionates rapidly to H₂O₂ and O₂.

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REFERENCES

1. M. Zuckmantel, R. Kurth and H.P. Boehm, *Z. Naturforsch.* **34 b**, 188 (1979).
2. R. Kurth, B. Tereczki and H.P. Boehm, *Ext. Abstr., 15th Bienn. Conf. on Carbon*, Philadelphia, PA (1981), p. 244.
3. H.P. Boehm, G. Mair, Th. Stöhr, A.R. de Rincon and B. Tereczki, *Fuel* **63**, 1061 (1984).
4. B. Stöhr, H.P. Boehm, R. Schlögl, *Carbon* **29**, 707 (1991).
5. H.P. Boehm, G. Mair, Th. Stöhr, *Ext. Abstr., 17th Bienn. Conf. on Carbon*, Lexington, KY (1985), p. 381.