

# INFLUENCE OF NITROGEN CONTENT OF ACTIVATED CARBONS ON THEIR AGING BEHAVIOR.

St. Matzner, T. Kuretzky and H.P. Boehm  
Institut für Anorganische Chemie der Universität München  
Meiserstrasse 1, D-80333 München, Germany.

## Introduction

Carbons, in particular activated carbons, find widespread application as adsorbents, catalysts, and supports for catalytically active materials. However, their performance is often impaired by prolonged storage under ambient conditions. This „aging“ is due to a gradual oxidation of the carbon surface [1-3]. The reaction with activated carbons proceeds faster at 60°C at a relative humidity (r.h.) of 80 % than at 110°C under ambient air [4,5]. Deposition of Pt or Pd on the carbon enhanced the aging reaction. This was attributed to oxygen spillover from the metal to the carbon surface [4].

Carbons catalyse many reactions, especially oxidation reactions with O<sub>2</sub>. Incorporation of nitrogen in the carbons enhances strongly their catalytic activity [6]. Evidence has been presented that by substitutional binding of nitrogen atoms electrons are injected into the conduction band, facilitating formation of reactive O<sub>2</sub><sup>-</sup> from adsorbed O<sub>2</sub> [7].

## Experimental

The commercial activated carbons used have been described [4,6], Anthralur (Ant) was produced from peat, and Eponit (Ep) from wood. After extraction with hydrochloric acid and washing with water, they were outgassed at 300°C (suffix -u for untreated) or treated with ammonia at 900°C (suffix -NH<sub>3</sub>-900°). The N contents were 670 and 1230 μmol/g for NH<sub>3</sub>-treated Anthralur and Eponit, respectively. 200 μmol/g of Pt were deposited on the carbons by incipient-wetness impregnation with H<sub>2</sub>PtCl<sub>6</sub> solution followed by reduction with H<sub>2</sub> at 250°C.

Other activated carbons were prepared by carbonization (up to 1100°C) of sucrose with addition of glucosamine (gl), arginine (arg), arginine hydrochloride (arghcl) or uracil (ura). The resulting carbons were activated with CO<sub>2</sub> at 900°C to a burn-off of 22 ± 3%. Such carbons are designated by N-ZKA-, followed by a number (mol% of nitrogen atoms added per mol of sucrose in the precursor mixture) and the symbol for the additive. The undoped control carbon is called ZKA-00.

The carbons were characterized by nitrogen content (Kjeldahl method), apparent (BET) surface area, and acidic and basic surface sites (neutralization adsorption of 0.05 N NaOH or HCl, respectively [5]). The procedures for the aging experiments at 60°C (80% r.h.) and at 110°C have been described [4].

Catalytic activities were determined from the increase in electrical conductivity of a 1.65 · 10<sup>-3</sup> M SO<sub>2</sub> solution in pure O<sub>2</sub>-bubbled water after addition of the catalyst [6,7]. The catalysts were usually stored under air in glass vessels with screw-on plastic lids. Some samples were filled under nitrogen cover into glass ampoules which were evacuated to ca. 1 Pa and sealed. The sample sizes of the materials stored under air were corrected for their water content (2-3 wt.%).

## Results and Discussion

The aging experiments at elevated temperatures were performed with activated carbons that had been loaded with 200 μmol/g platinum in order to have larger effects. As is shown in Fig.1, there was a considerable increase in the concentration of acidic sites (carboxyl groups, lactones, phenols) with time when the samples were aged at 60°C in a moist atmosphere. After treatment with NH<sub>3</sub> at 900°C, there were fewer acidic surface groups on the carbons. The differences in the rate of increase

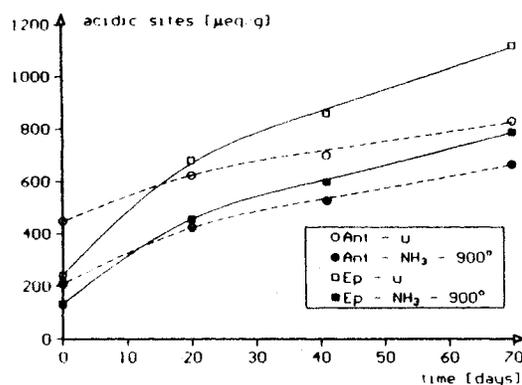


Fig.1. Formation of acidic surface groups on activated carbons (supporting 200 μmol/g of Pt) during storage at 60°C and 80 % relative humidity.

Table 1. Acidic and basic surface sites and catalytic activity of the activated carbons from sucrose after one year storage *in vacuo* or under air.

Sample	N content μmol/g	Acidic surface sites μmol/g		Basic surface sites μmol/g		Catalytic activity μmol H <sub>2</sub> SO <sub>3</sub> / g . s	
		vacuum	air	vacuum	air	vacuum	air
ZKA-00	20	90	80	470	440	~0	~0
N-ZKA-75 gl	1170	95	95	760	710	4.14	3.37
N-ZKA-5 arg	450	55	90	560	460	2.02	0.76
N-ZKA-100 arg	1250	40	75	630	570	4.30	3.54
N-ZKA-25 ura	960	50	160	720	530	3.58	1.64

of acidic sites was higher for the Eponit carbons than for Anthralur. However, in one case, Anthralur, the NH<sub>3</sub>-treated carbon was slightly more active than the control, in contrast to the Eponit carbon. The effect of the NH<sub>3</sub> treatment was small in both cases. On aging in a drying oven at 110°C, there was no significant difference in the behavior of all four samples.

Therefore, the aging behavior of carbons prepared by pyrolysis of sucrose with addition of N-containing compounds was studied. In this case the nitrogen is more homogeneously distributed. A decrease of the catalytic activity in H<sub>2</sub>SO<sub>3</sub> oxidation was observed when the carbon samples had been stored under air for some time before the catalytic tests were performed. Table 1 shows a significant drop in catalytic activity (expressed as μmol of H<sub>2</sub>SO<sub>3</sub> converted to H<sub>2</sub>SO<sub>4</sub> per second and gram of catalyst) after one year compared to samples that had been stored in evacuated ampoules with as little exposure to air after preparation as possible. Activities measured a short time after preparation (storage under air) were a little smaller in most cases than with the vacuum-stored samples.

There were no significant changes in the nitrogen content after storage in air and only slightly lower apparent surface areas (or, rather, micropore volumes). However, there was a significant increase in the quantity of acidic surface groups and a concur-

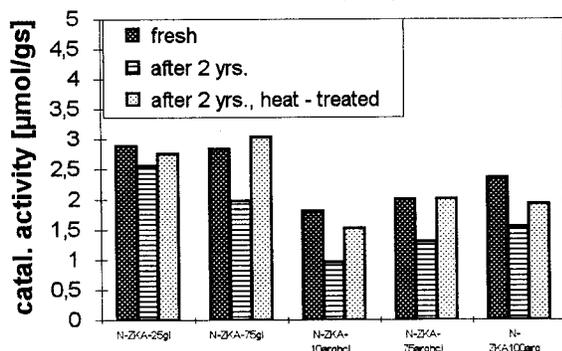


Fig.2. Change of catalytic activity in the oxidation of H<sub>2</sub>SO<sub>3</sub> after 2 years storage and its restoration by heat treatment at 900°C (under N<sub>2</sub>).

rent decrease in the concentration of basic surface sites (Table 1). The changes were small with the undoped control carbon ZKA-00.

The decrease of catalytic activity was relatively larger than the decrease in apparent surface area. Therefore, blocking of micropores by chemisorbed oxygen does not seem to be the cause of the changes. Possibly, the binding of electronegative oxygen atoms at the periphery of the layers leads to a localization of conduction electrons.

In consequence, the catalytic activity should be restored when the surface oxides are removed by thermal treatment. As Fig. 2 shows, the activity is indeed significantly increased, and largely restored or even surpassed in several cases. Simple outgassing at 300°C had little effect.

Our results indicate that nitrogen doping of the carbons enhances the aging process, i.e. surface oxidation, at room temperature.

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