

# NO REDUCTION BY NITROGEN-DOPED MODEL CARBONS.

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

## Introduction

It has been shown earlier that incorporation of nitrogen affects the gasification behavior of carbons. The reaction rate with  $O_2$  as well as with  $CO_2$  is diminished if the temperature is not too high [1]. A higher apparent heat of activation was found in the reaction with  $O_2$  [2]. The nitrogen-doped carbons had been prepared by carbonization and activation with  $CO_2$  of sucrose with added nitrogen-containing compounds. Nitrogen-containing polymers can also be used as a precursor. Nitric oxide,  $NO$ , is formed in addition to  $N_2$  and  $N_2O$  in the combustion of nitrogen-containing carbons [3]. However, nitrogen is less readily gasified than carbon, and the relative nitrogen content of the residual carbon increases with increasing burn-off [4,5]. In consequence, the  $NO$  concentration in the combustion gases increases with increasing burn-off [5].

The reactivity of such nitrogen-doped carbons in the reduction of  $NO$  between  $300^\circ C$  and  $580^\circ C$  has been studied. Nitrogen-containing carbons exhibit a higher reactivity than control carbons without nitrogen-doping. Nitrogen-containing carbon adsorb more  $NO$  at  $30^\circ C$  than the control carbons.

## Experimental

The carbons were prepared by carbonizing and heat-treating at  $1100^\circ C$  sucrose with additions of glucosamine (gl), arginine (arg) or uracil (ura) [4,5]. The ground and sieved carbons ( $< 0.2$  mm) were activated in  $CO_2$  at  $900^\circ C$  to a burn-off of  $22\% \pm 3$ . The samples are designated N-ZKA followed by a number giving the mol-% of nitrogen atoms added per mol of sugar in the precursor mixture, and the symbol for the additive (control without nitrogen addition: ZKA-00).

The samples were characterized by nitrogen content (Kjeldahl method),  $N1s$  photoelectron spectroscopy (XPS, see [2]), and micropore structure (from  $N_2$  adsorption).

For the reduction of  $NO$ , pulses of  $40 \mu l$   $NO$  were injected into a He stream. The carbon (50 mg) rested on a porous silica frit of 19 mm diameter, as in the combustion experiments [5]. The gas leaving the reactor was analyzed for  $NO$  (and  $CO$  and  $CO_2$ )

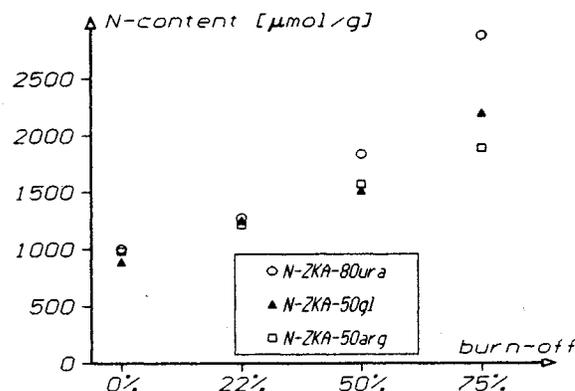


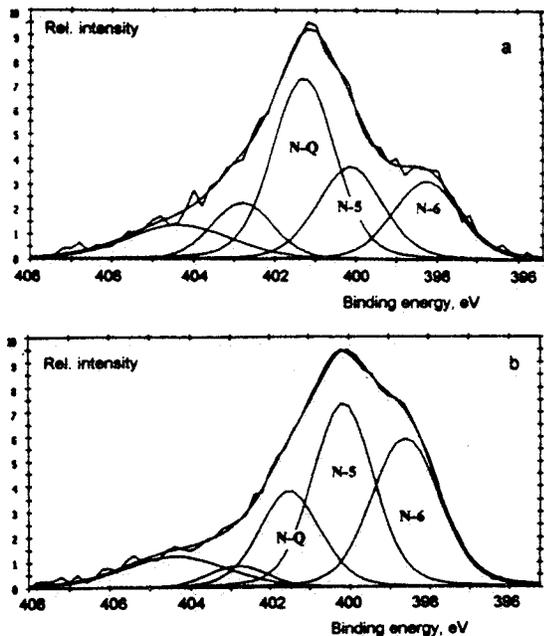
Fig.1. N content of carbons (H.T.  $1100^\circ C$ ) as function of burn-off. 22% b.o. in  $CO_2$  at  $900^\circ C$ , additional b.o., 50 and 75%, with 5%  $O_2$  at  $580^\circ C$ .

by non-dispersive infrared absorption (Hartmann & Braun, URAS 10 E) after converting possible  $NO_2$  to  $NO$  (Horiba, COM-11A).

## Results and Discussion

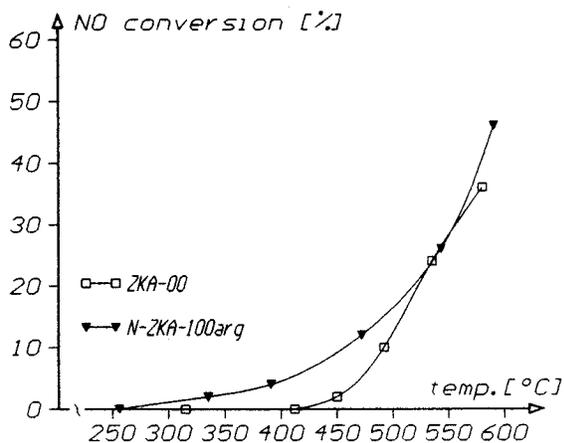
Fig.1 shows the increase of nitrogen content with increasing burn-off in 5%  $O_2$  in He at  $580^\circ C$  for carbons made from sucrose. The results were similar with the carbons prepared by the phenol-resin route. XPS measurements showed significant changes in the binding of the nitrogen after gasification as shown in Fig. 2a and b. The  $N1s$  peaks marked N-6 are attributed to nitrogen in pyridine-like binding at the edges of the graphene layers [5], N-5 corresponds to nitrogen in pyrrole (perhaps also as  $>NH$  in six-membered rings of aromatic systems), and N-Q is ascribed to „quaternary nitrogen“, very likely nitrogen substitutionally bound within the graphene layers with a delocalized electron. The signal at a binding energy near 403 eV might come from structures like pyridine-N-oxide. Fig.2 shows that after 75% burn-off (in  $O_2$ ), N-6 and N-5 have increased at the expense of N-Q; also the signal at 403 eV had decreased significantly.

In our gasification studies, we noticed that the amount of  $NO$  formed depends on the geometry of the reactor [5]. The less  $NO$  was formed, the longer

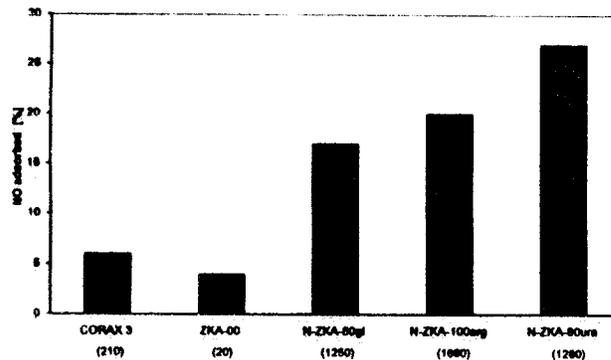


**Fig.2.** N1s photoelectron spectra of (a) N-ZKA-80 ura and (b) N-ZKA-80 ura oxidized with O<sub>2</sub> to 75 % burn-off.

and narrower the bed was for a constant quantity of carbon. Obviously, NO formed in the front of the bed was reduced by the carbon in the rear part. This was confirmed by injecting NO pulses into a He stream before it passed over the carbon. Fig.3. shows the conversion for carbon with and without nitrogen doping. NO reduction was observed above 300°C. The micropore volume and the average micropore width were not significantly different for the doped and the control carbons. Clearly, the reduction activity is higher for the nitrogen-containing carbon, especially at relatively low temperatures. As a consequence, a relatively higher fraction of the



**Fig.3.** NO reduction by ZKA-00 and N-ZKA-100 arg (40 µl pulses in He).



**Fig.4.** Adsorption of NO on various carbons at 30°C (Take-up from 40 µl pulses. in parentheses the N content in µmol/g).

nitrogen in the carbon is released as NO<sub>x</sub> during combustion, the lower the N content is.

NO is adsorbed from a He stream by the carbons at 30°C. However, the full injected quantity of NO was detected after the carbon bed when it was at temperatures between 200° and 300°C. Irreversible adsorption of NO in diamagnetic form at 30°C has been described [7]. As is shown in Fig.4, the NO adsorption is much higher with nitrogen-containing carbons than with the control ZKA-00 or with Corax 3, a furnace black. Possibly this with delocalized electrons introduced by nitrogen substitution.

**Acknowledgement:** We are indebted to Prof. Kapteijn, Delft, for the XPS measurements. Financial support by Fonds der Chemischen Industrie is acknowledged.

## References

1. D.Mang, H.P.Boehm, K.Stanczyk and H.Marsh, *Carbon* 1992, **30**, 391.
2. S.Matzner, H.P.Boehm, Ext.Abstr., *22nd Bienn. Conf. on Carbon*, San Diego.,CA, 1995, p. 600.
3. K.M.Thomas, K.Grant and K.Tate, *Fuel* 1993, **72**, 941.
4. S.Matzner, H.P.Boehm, Ext. Abstr. *21st Bienn. Conf. on Carbon*, Buffalo, NY, 1993, p. 521.
5. S.Matzner, H.P.Boehm, Ext.Abstr., *Carbon'94, Internat. Carbon Conf.*, Granada, 1994, p. 458.
6. J.R.Pels, F.Kapteijn, J.A.Moulijn, Q.Zhu and K.M.Thomas, *Carbon* 1995, **33**, 1641.
7. K.Kaneko, N.Fukuzaki, K.Kakei, T.Suzuki and S.Ozeki, *Langmuir* 1989, **5**, 960.