

NO REDUCTION BY NITROGEN-DOPED MODEL CARBONS.

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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°C and 580°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°C than the control carbons.

Experimental

The carbons were prepared by carbonizing and heat-treating at 1100°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°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 μ 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)

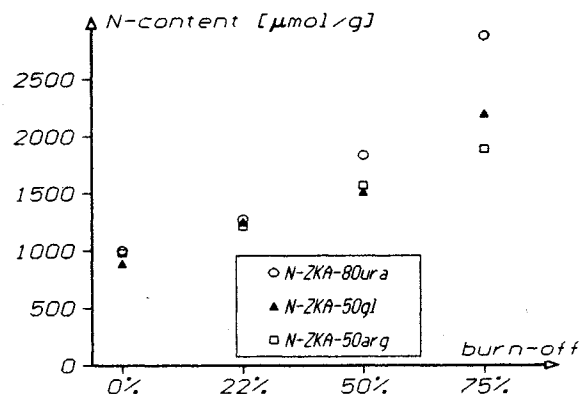


Fig.1. N content of carbons (H.T. 1100°C) as function of burn-off. 22% b.o. in CO_2 at 900°C, additional b.o., 50 and 75%, with 5% O_2 at 580°C.

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°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

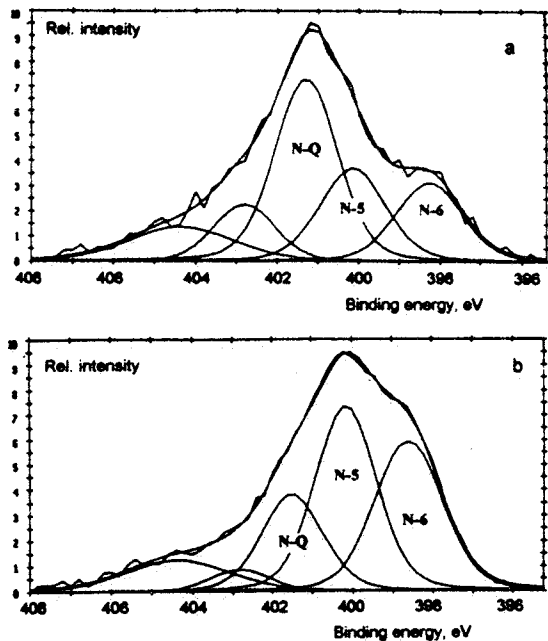


Fig.2. N1s photoelectron spectra of (a) N-ZKA-80 ura and (b) N-ZKA-80 ura oxidized with O₂ to 75 % burn-off.

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

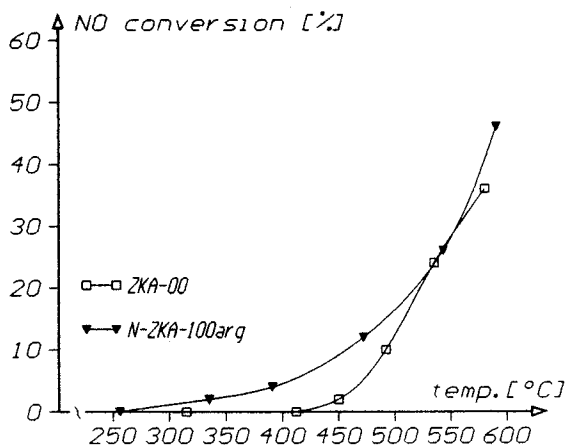


Fig.3. NO reduction by ZKA-00 and N-ZKA-100 arg (40 µl pulses in He).

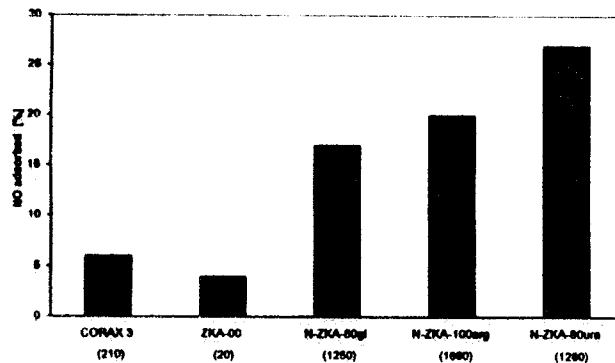


Fig.4. Adsorption of NO on various carbons at 30°C (Take-up from 40 µl pulses. in parentheses the N content in µmol/g).

nitrogen in the carbon is released as NO_x 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.

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