Oxidative Degradation of Carbons in Alkaline Media

by

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Introduction

Carbons, i.e. activated charcoals, carbon blacks etc., are known to catalyze oxidation reactions, e.g. the reaction of sulfurous acid or oxalic acid with oxygen¹⁻³. Individual carbons show big differences in their catalytic activities, however. It has been found that the catalytic activity can be dramatically increased by treatment with nitrogeneous gases such as NH, or HCN at elevated temperatures 2-4. All carbons showing activity contain some nitrogen. It has been suggested that incorporation of N atoms in the periphery of the carbon layers is the cause of the catalytic activity. The question arose whether catalytically active carbons also catalyze their own oxidation. We have shown in a preliminary report that carbonate is indeed formed from carbons in alkali in the presence of oxygen 4.

Experimental

 CO_2 -free O_2 was bubbled at atmospheric pressure through a stirred suspension of 0.2-0.3 g carbon in 200 ml NaOH (as free from carbonate as possible). The suspension was heated by a constant temperature water bath, usually to 80.0°C. A reflux condenser in the exhaust prevented losses by evaporation. At predetermined intervals samples were taken by sucking a portion of the solution through a porous-glass frit, and pipetting off an aliquot for analysis; the remainder was pushed back through the frit by pure O_2 . The CO_3^{2-} content was determined from the inflections in the potentiometric pH titration curves (with 0.01 M HCl). Alternatively, the CO₂ was carried from the acidified samples by a gas stream, and adsorbed in 0.01 M Ba(OH); the changes in electrical conductivity due to precipitation of BaCO₃ were measured. The increase in the CO_3^2 content of the NaOH solution due to contamination by atmospheric CO2 was negligible with these techniques. Adsorbed CO, on the carbon was less than 10 µmol/g in most cases, only with microporous carbons up to 65 µmol/g were found. For measurements at room temperature, the suspensions were kept in plastic bottles which were stored in a desiccator over KOH pellets.

CO was estimated semiquantitatively with Draeger indicator tubes. In a few experiments it was determined by oxidation to CO_2 with HgO at 100°C. The CO_2 was then determined conductometrically as described.

The carbons employed were two activated peat charcoals, Anthralur Sta and Norit BRX, an activated wood charcoal, Eponit, a furnace black, Corax 3, and a black similar to channel blacks, CK 3. They have been characterized earlier¹. Nitrogen contents were determined by the Kjeldahl method.

Results

The oxidation of carbons to CO_3^2 can easily be followed at 80°C. Fig.1 shows that the reaction is the faster, the more alkaline the solution is. In highly alkaline media on the order of 1000 µmol/g of carbon were oxidized to CO_3^2 within four hours; this corresponds to a weight loss of the carbon of about 1.2 %. The reaction could not be observed at neutral or acidic pH.



Fig.1. Autoxidation of Anthralur at 80.0°C as function of pH.

Sample				
	Surface area m²/g	Autoxidation activity µmol CO₂/g•h	N content before	in mmol/g after
Anthralur	640	26	0.69	-
Norit BRX	(1800)	10	1.20	-
Eponit	760	0	0.21	-
Eponit-NH, -750°C	860	22	2.91	2.49
Eponit-NH, -900°C	1140	44	2.44	1.91
Corax 3	89	10	0.22	-
Corax 3-NH, -600°C	90	13	1.30	1.12
Corax 3-NH ₂ -900°C	500	15.5	2.23	1.88
CV 3	96	8	0.13	-
Natural graphite AF	9	15		-

Table 1. Characteristics and autoxidation activity of the carbons at 80°C and pH 12.

Carbon monoxide was formed together with CO_2 . Its quantitiy corresponded approximately to 5-7 % of the liberated carbonate. In the following, only CO_3^{-1} formation will be considered, therefore.

The oxidation proceeds, albeit much slower, also at room temperature. Fig.2 gives the results for several carbons. The most active carbon - as in all other experiments - was Anthralur, a peat activate. Its activity was an order of magnitude higher than that of typical carbon blacks. Carbon black CK3 showed a lower activity, after treatment with NH, at 600°C, a result which is in contradiction to all other observations made at higher oxidation temperatures. The reason for this is not yet clear.

All further experiments were done at 80°C and at a pH of 12 because CO3 titration is more accurate in dilute alkali. The rate of CO3²⁻ formation decreases considerably after ca. one hour. It appears that some highly reactive carbon on the surface is oxidized rapidly in the beginning of the reaction. The oxidation rates after 60 min. were taken for representation in Table 1. One can see clearly that the reactivity of the carbons is enhanced after treatment with NH3. This effect is not only due to the increase in surface area as follows from the data for the furnace black Corax 3-NH,-600°C. This table shows also that some of the bound nitrogen is lost in the reaction, indicating that it is indeed bound at the surface.

Discussion

It has been suggested that the catalytic activity of carbons is caused by an electron transfer from the carbon to adsorbed species, e.g. 0_2 ³,⁴. Substitutive incorporation of nitrogen would raise the Fermi level of the carbon and facilitate such a charge transfer. The oxygen species which eventually form, 0_2^- , 0^- or OH^{*}, are highly reactive, and one would expect them to attack the carbon it-self. That there is



Fig.2. Autoxidation behavior of several carbons, room temperature, pH 14.1.

no observable reaction at neutral or acidic pH could be caused by protonation of 0_2^- to HO₂ which disproportionates rapidly to H₂O₂ + O₂ (HO₂ is a weak acid with a pK of ca.5). The high activity of the natural graphite AF from Kropfmühl, Bavaria, was surprising, but this catalyst was also quite active in the elimination of HCl from 1-butyl chloride ⁴. We have detected by XPS traces of nitrogen in graphite from Kropfmühl ⁵.

References

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