

CHEMICAL SURFACE PROPERTIES, ELECTROCHEMICAL AND CATALYTIC ACTIVITY OF N-, O- AND H-CONTAINING ACTIVE CARBONS

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Introduction

The influence of heteroatoms (N, O and others) on catalytic properties of active carbons (ACs) in electrons transfer reactions, as it has been shown earlier [1], arises due to their semiconducting properties. In the case of nitrogen heteroatoms, this effect essentially depends on its position in the graphitic matrix [1,2].

ACs are known to be able to reduce oxygen dissolved in water, as well as electropositive metal ions; this depends on the degree of carbon oxidation [3].

It is of great interest to research the similar effects for carbons treated with hydrogen because these carbons are characterized by higher hydrophoby and lower affinity to oxygen [4].

The influence of electronic structure of modified by N-, O- and H-containing ACs on their electrochemical and catalytic properties is discussed in this communication.

Experimental

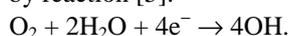
To estimate of semiconductor properties of ACs containing N, O, H heteroatoms, the quantum-chemical calculations of respective graphitic clusters were carried out. Energies of boundary molecular orbitals and widths of forbidden zones, which characterize electron-donor and electron-acceptor properties of carbonic materials, were calculated using the semi-empirical molecular orbital AM-1 method.

High-purity synthetic ACs based of porous divinylbenzene or vinylpyridine copolymers were used for experimental investigations. Original ACs were eliminated by heating its in an argon atmosphere at 850⁰ C for 1 hour, followed by cooling it in an inert atmosphere to room temperature. To obtain oxidized modifications, the samples of ACs were contacted with air or nitric acid. To obtain hydrogen modifications, the samples of ACs were heated in hydrogen atmosphere at 900⁰ C for different time (15, 30, 60 and 120 minutes).

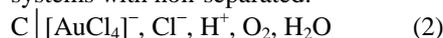
Electrochemical properties of synthesized ACs were estimated by means of kinetics of oxygen electrode potential formation in water electrolyte solutions in system:



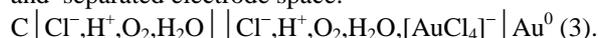
by reaction [5]:



Reductive ability of ACs towards electropositive metals in case of direct contact of carbon with electrolyte solutions containing noble metal ions was studied in systems with non-separated:



and separated electrode space:



The catalytic activity of carbons was estimated in model reactions of decomposition of hydrogen peroxide and accumulation of aldehydes in alcohol-water solutions.

Results and Discussion

The analysis of calculated data shown that the introduction of various quantities of N, O and H heteroatoms influences the values of boundary orbitals' energies and the width of forbidden zone, as it is represented in Fig.1.

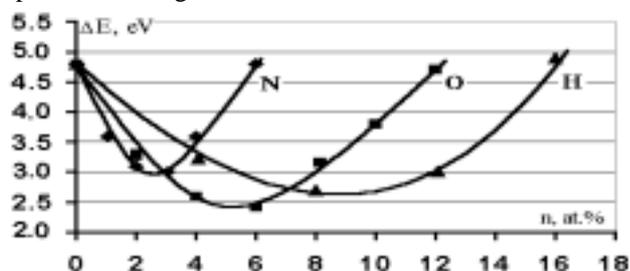


Figure 1. Influence of heteroatoms (N, O, H) concentration on width of forbidden zone of ACs.

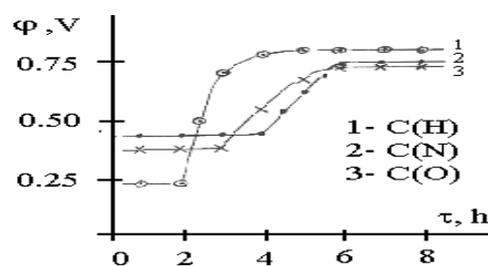


Figure 2. Kinetics of oxygen electrode potential formation of ACs.

In all cases this dependence has a minimum at 3-9 atomic % the element added. It is worth noticing that the clusters containing 3-7% of oxygen in groups of

furan and carbonyl types have the minimal width of forbidden zone, contrary to peripheral oxygen-containing groups, i.e. are of the best donor ability in the row of oxidized carbons.

It has been shown by us earlier that the difference of potentials $\Delta\varphi$ (stationary and initial) of carbons characterizes their semiconductor properties and determines their reductive and catalytic activity [3].

The kinetic curves of oxygen electrode potential formation on ACs are shown in Fig. 2 as an example. The most high reductive ability is manifested by the carbons containing oxygen atoms which are included in π -conjugated graphitic clusters, the reductive ability of carbons with peripheral functional groups being suppressed (table 1).

Table 1. Connection of width of forbidden zone and reductive ability of oxidized ACs.

Experiments carried out in systems (2,3) at their reductive sorption showed the principal difference in their behavior. If oxygen is in the carbon matrix, the reduction of noble metals, in particular, gold, occurs according to the electrochemical mechanism. If oxygen is in containment of peripheral groups, it occurs according to the chemical mechanism.

Analyzing the catalytic activity of ACs in the process of decomposition of H_2O_2 and comparing it with literature data, a conclusion can be made that synthesized hydrogen forms of ACs manifest high catalytic activity in Red/Ox- reactions. Decomposition of H_2O_2 on hydrogen ACs occurs as quickly as on SCN carbons [6].

Active carbons					
$\Delta E, eV$	2.6	2.6	2.5	3.0	4.8
$\Delta\varphi, mV$	580	500	380	400	120

Rate constants of H_2O_2 decomposition calculated for various times of ACs treatment with hydrogen (1-15, 2-30, 3-60 and 4-120 minutes) are practically invariant (table 2).

This may testify that the catalytically active surface of ACs is formed at the first minutes of treatment with hydrogen and don't vary in time. In the case of alcohol oxidation (table 2), the variation of catalytic activity of hydrogen forms of carbons depends on the time of their pretreatment and the demonstrated that, under the influence of alcohol-water media, the increase of the

part of active surface occurs due to wetting; this leads to more fast accumulation of aldehydes.

Table 2. Characteristic of catalytic activity of hydrogen-containing carbons.

Samples	k, min^{-1}	$C_e, \text{mg/l}$
1	0.28	2.1
2	0.31	2.6
3	0.25	2.6
4	0.27	3.0

Conclusions

The obtained results show that the modification of ACs with N-, O-, H- heteroatoms leads to regulation of π -conjugated system in carbon clusters and, therefore, to control their reductive ability and electrochemical and catalytic properties.

References

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