

S.V.Mikhailovsky, Yu.P.Zaitsev, V.M.Lukianchuk, V.B.Volkov, V.A.Zazhigalov*, A.M.Puziy

Institute for Sorption and Problems of Endoecology, 32-34 Prospect Palladina, Kiev, Ukraine

*Pisarzhevsky Institute of Physical Chemistry, 138 Prospect Nauki, Kiev, Ukraine

INTRODUCTION

The catalytic properties of active carbons (AC) were first studied by O.Warburg [1]. But due to the variety of carbon materials and the involvement of new sources and methods in their synthesis and modification, catalytic processes on AC remain an important area of investigation. The introduction of heteroatoms (N, O, S etc.) into AC significantly alters their catalytic activity. The best known example of this effect is oxygen in oxidized carbons which exhibit catalytic activity in the hydrolytic reaction whereas non-oxidized carbon are more catalytically active in redox reactions [2]. The development of technologies for production of AC by pyrolysis of synthetic polymers allows the introduction of heteroatoms into the bulk lattice [3]. Thus AC with N and O atoms in the lattice have been produced. In this paper data on the catalytic activity of polymer-pyrolyzed AC in liquid- and gas-phase redox reactions is discussed.

EXPERIMENTAL

AC have been synthesized by pyrolysis with further steam activation of granulated vinyl-pyridine copolymer (N-AC) and phenol-formaldehyde resin (O-AC). Other carbon materials were also studied for comparison: acetylene carbon black, apricot stone AC, BAC-MU, and birch AC. Oxidized AC, AC_{ox}, were obtained by the treatment of AC with nitric acid. All chemicals were of analytical grade supplied by "Aldrich". The kinetics of the liquid phase oxidation of organic compounds was measured by oxygen uptake. The concentration of hydroperoxide was determined by volumetric titration. Gas phase oxidation was carried out in a flow reactor, reaction products were analyzed with a thermoconductivity detector in a gas chromatograph. The volume of catalyst in the flow reactor was 2 ml (5-7 mm layer). Quantum chemical calculations were carried out using the semiempirical AM-1 method.

RESULTS AND DISCUSSION

The catalytic activity of N-AC in H₂O₂ decomposition exceeds the activity of all the other carbons tested by

1-2 orders of magnitude [4]. This is definitely due to the presence of nitrogen although its content is only 1-2%. To explain this fact, the electronic structure and charge distribution in the fragments of AC surface have been calculated. A series of polynuclear aromatic compounds with condensed benzene rings have been chosen as the fragments containing one or more N atoms in different positions. The systems containing up to 13 rings have been studied. They are 1.0-1.4 nm in size, which corresponds to the dimensions of crystallites existing in N-AC as determined by X-ray structural analysis. Even in such big fragments, substitution of only one C atom by an N atom, affects the distribution of the electron density all over the fragment leading in general to the increased lability of the conjugated π -electrons. As the rate-determining step in the H₂O₂ decomposition is the transfer of an electron from the catalyst to the antibonding $\pi^*_{2p_{x,y}}$ orbit of H₂O₂, N atoms facilitate the creation of additional catalytic sites. The rate of H₂O₂ decomposition, W_d, depends on the size of the AC particles, indicating that the reaction is internal diffusion-controlled or that it has transition kinetics (between internal diffusion and a true kinetic regime). In general it is impossible to determine the true activation energy for such a process from the temperature dependence of W_d, but since it effectively has first order dependence on [H₂O₂], the reaction should also be first order in the kinetic regime [5]. The apparent activation energy of the internal diffusion-controlled process, E_{dif}, is $\approx 1/2 E_{kin}$. Thus calculated E_{kin} is 44 ± 2 kJ/mol which is in good agreement with E_{kin} obtained for carbon black [6]. This indicates that N atoms in the lattice create additional active sites rather than lower the energetic barrier of the process. Oxidation of many organic substances takes place via a free radical mechanism with degenerated chain propagation. As a rule, this step involves decomposition of an intermediate hydroperoxide, ROOH. The mechanism of ROOH decomposition should be similar to that of H₂O₂ decomposition, hence, N-AC demonstrates high catalytic activity in the oxidation of cumene, styrene, toluene, oleic acid, oleates (Fig.1). It is generally accepted that surface O-containing groups resemble those of organic compounds, such as

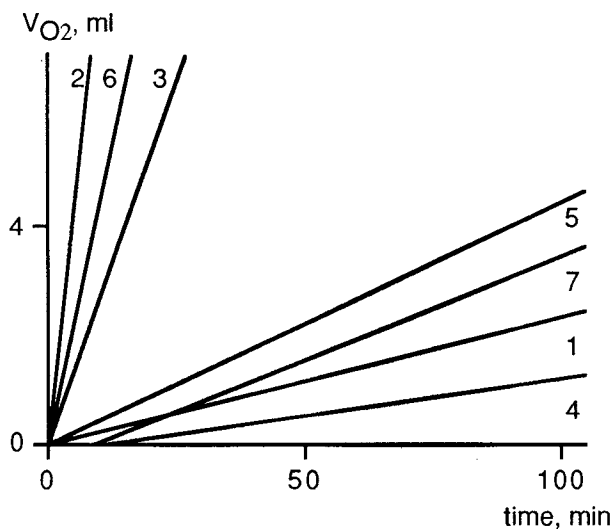


Fig. 1. Kinetics of liquid phase oxidation of hydrocarbons. 1-4 - cumene, 5-7 - styrene. 1, 5 - without catalyst; 2 - N-AC; 3, 6 - N-AC_{ox}; 4, 7 - birch AC_{ox}. T = 343° K, liquid volume - 10 ml, AC - 200 mg. Cation exchange capacity (CEC): N-AC_{ox} - 1.9 meq/g, birch AC_{ox} - 2.5 meq/g.

phenolic, carboxylic, hydroxylic groups. O atoms in these groups decrease electronic density in the AC lattice thus decreasing catalytic activity in ROOH decomposition. In the presence of birch AC_{ox} (Fig. 1, curves 4 and 7) oxidation of hydrocarbons is inhibited. N-AC_{ox} exhibits pronounced catalytic activity in these reactions which suggests that the promoting effect of the lattice N compensates for the inhibiting effect of oxygen. The inhibiting action of AC_{ox} can be attributed to the decay of free radicals reacting with the surface phenolic and hydroxylic groups. As even non-oxidized AC possess some O-containing groups, under certain conditions the inhibiting function of AC can prevail over its catalytic function. In this case the phenomenon of critical catalyst amount is observed (Fig.2).

AC have been used as catalysts in various gas phase oxidation processes at temperatures below 200° C [7]. Polymer-pyrolyzed AC can operate at higher temperatures without decomposition [3]. In addition, the catalytic activity of carbon can be improved by grafting catalytically active species such as transition metal complexes [8]. Among them, V-containing samples give the most interesting results. In n-butane oxidation to maleic anhydride in air, V-O-AC demonstrates higher selectivity compared to the massive V catalyst and V-TiO₂. Carbon catalysts operate at temperatures 100-150° lower than other catalysts. H₂S in air (0.3-12 vol%) is oxidized to S even at room temperature although the

rate of the process is low. At 200°C the most active V-N-AC partially oxidizes S further to sulphur oxides (11 mol% of the total H₂S converted) whereas less active V-AC (apricot stone) produce only trace amount of SO_x (0.8 mol%). In confirmation of these observations three valence states of S have been found after the reaction on the surface of V-N-AC by XPS (E S_{2p} 163.0; 167.2 and 168.5 eV). On V-AC sample only one low valence state of S has been found (E S_{2p} =163.0 eV). The absence of SO_x in the products makes this process suitable for environmental pollution control.

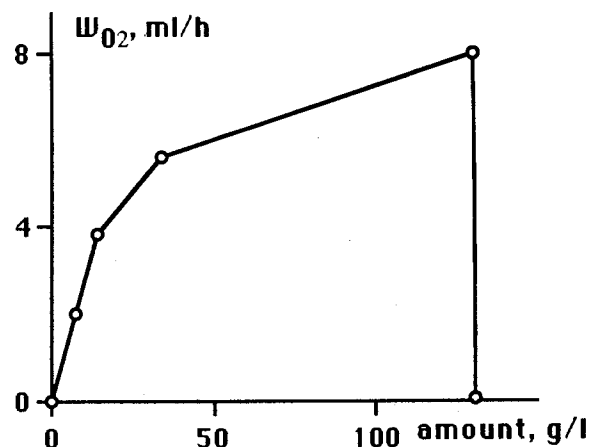


Fig. 2. Liquid phase cumene oxidation in the presence of N-AC.

T = 323° K, [ROOH]₀ = 0.01 mol/l, liquid volume - 3 ml.

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