CATALYTICAL PROPERTIES OF ACTIVE CARBONS AND THE MAIN FACTORS DETERMINING THEM

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Introduction

The present and previous [1-5] investigations make it possible to determine the mechanism of catalytic processes in the presence of carbons both in the liquid and in the vapor phases. Analysis of the results of these investigations help to determine the main factors on which the catalytic properties of the carbons depend. They mainly consist of the following: 1) the presence of various functional groups on the surface of the active carbon (-0H, -COOH, =NH, -NH₂, -SO₃OH, etc.); 2) the presence of various modifying additives in the carbon material (the heteroatoms N, P, S, Me, the ions, oxides, and salts of various metals); 3) the porous structure of the carbon materials, their structural and sorption characteristics; 4) the electrophysical characteristics of the carbon materials and the structure of the carbon matrix.

In the present communication on the basis mainly of the results of investigations carried out in recent years we examine the principal relationships governing certain catalytic processes taking place on the surface of active carbon, having regard primarily to the chemical nature of their surface, modification of the latter by the cations of metals, the introduction of nitrogen heteroatoms, and electrophysical properties. Methods of controlling the catalytic activity are indicated, and new possibilities for the practical use of carbon materials as catalysts are described.

Experimental

Kinetics of the liquid-phase reactions (synthesis and hydrolysis of esters, carbohydrates, and fats, oxidation of H_2S and SO_2 and dibenzyl ether, decomposition of H_2O_2) were studied as usual for ion-exchange catalysis by a static method; in some cases (the esterification and transesterification of edible fats) a fluidized-bed reactor or a flow-type reactor (the dehydration of alcohols) was used.

The vapor-phase reactions (synthesis and hydrolysis of esters) were conducted in a flow-type circulatory reactor over a wide range of temperatures and concentrations of the initial substances and reaction products.

Carbons with various chemical types of surface were used for the investigation: Activated (anion exchangers) and oxidized (carbon exchangers) carbons from various sources; synthetic materials obtained from polymeric material (FAU, FOU), nitrogen-containing SKN and SKNO, from various types of wood (DOU), birch (BAU), larch waste products (LAU and LOU), from fruit stones (KAU and KAUo), granulated and in cloth from (UT).

Results and Discussion

The investigations showed a clear relation between the catalytic activity of the active carbon and the nature of its surface; the active carbon had practically no effect on the course of reactions of acid type, whereas a significant catalytic effect was observed in the presence of oxidized carbon (OU) containing various protogenic groups on its surface. The catalytic characteristics of oxidized carbons in protolytic reactions (the inversion of sucrose, the hydrolysis of maltose, esters, and fats, the transesterification of edible fats were determined not only by the presence of and the amount of acidic groups (Fig) but also by their qualitative composition.
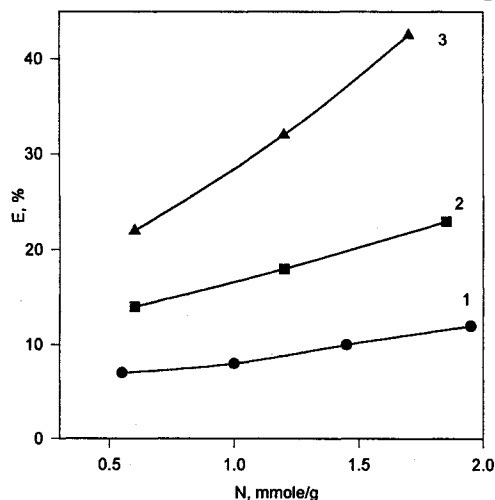

Figure. Dependence of the synthesis rate of butyl acetate (E) at carbons LOU (1), BAUo (2), and FOU (3) on the number of protogenic groups (N).

Since active carbons are well know as highly porous adsorbents, attempts have often been made to relate their catalytic activity to their adsorption capacity, specific surface area, and porosity. Analysis of our own and published data makes it possible to conclude that with active carbons as the catalyst the optimum structure is a structure containing a sufficient

number of connecting pores with radii of 20-50 A or more.

In addition to the presence of a wide range of protonogenic groups and a developed porous structure essential condition for conferring the characteristics of highly effective catalysts onto active carbons is their high conductivity. It was found that carbons with low electric resistance accelerated various types of reactions quite effectively. The observed differences in the catalytic characteristics of oxidized carbons with surface similar in chemical nature and cation-exchange capacity but obtained by different methods can be explained best by their different electrophysical characteristics.

One method of specifically changing the catalytic action of carbon materials and producing carbon catalysts with specific properties is to introduce various heteroatoms (O, N, S, P) into the structure and onto the surface of the carbons and to modify the carbon surface with catalytically active metal cations and their oxides and salts. Our numerous investigations have shown that the substitution of H^+ ions in the surface functional groups of oxidized carbons by metal cations, accompanied by the formation of surface complexes of the Me^{n+} - OC type (OC = oxidized carbon) led to a significant change in the catalytic activity of the obtained cation-substituted forms in such reactions as esterification and the hydrolysis of esters, disaccharides and fats. As found, the increased catalytic activity of the cations sorbed by the carbon is similar to the effect of complexation in solutions. Independs on the polarizing capacity of the metal ions (the atomic electronegativity, the ionic potential and on the stability of the intermediate carbon-substrate and carbon-metal complexes and is determined by the nature of the substituting cation.

We note that the catalytic activity of the cation-substituted forms depends not only on the nature and the amount of the cation but is also determined by the characteristics of the skeleton to which the cations are attached.

Modification of the surface of oxidized carbons by various cations affects the catalytic activity of the carbon material not only in acid-base reactions but also in oxidation-reduction processes (Table).

The results obtained in on examples of reactions of the electronic type (the decomposition of hydrogen peroxide , the oxygen compounds of chlorine, and benzoyl hydroperoxide, the oxidation of cumene, dibenzyl ether, hydrogen sulfide, etc.) made it possible to find ways of controlling (increasing) the catalytic activity of oxidized carbons as a result of the introduction of the modifying cations of various metals (Fe, Co, Cu, Ni, Mn, Cr, etc.) on their surface.

There is every reason to consider that apart from their purely practical value the investigations should also have theoretical significance in the formulation of the scientific principles of predicting and controlling the catalytic properties of carbon catalysts.

References

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Table. Catalytic Characteristics of Carbons from Various Sources and with Various Conductivities in Oxidation-Reduction and Protolytic Reacrions

Carbon sample	Cation-exchange capacity (mmole/g)	Esterification of acetic acid by butanol (%)	Amount of Fe^{3+} sorbed by carbon (mmole/g)	Oxidation rate of cumene $W.10^6$ (mole/sec)	Decomposition rate of H_2O_2 in 15 min (%)	Resistance with direct current at room temperature (Ω)
FOU	2,0	23,2	0,23	157	100,0	30
BAU_o	2,0	21,6	0,29	138	100,0	50
BAU_o	2,0	-	0,7	115	69,5	50
DOU-1	1,8	16,0	0,14	70	37,8	730
DOU-1	1,8	-	0,08	63	30,6	730
DOU-1	1,8	-	0,07	37	16,3	730
DOU-2	1,6	10,0	0,13	2	5,7	126.10^6
DOU-2	1,6	-	0,06	0	4,9	126.10^6