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CARBON
IN CATALYSIS

Factors Determining the Catalytic Properties of Active Carbons in Some Acid–Base and Redox Reactions[1]

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Abstract—The results of the authors' investigation of the catalytic properties of active carbons in acid–base and redox reactions are summarized. The general principles of controlling the activity of carbon catalysts are described, the main factors in the catalytic processes occurring on these catalysts are revealed, and new ways of using the catalytic properties of carbon sorbents from various sources are considered.

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The first papers concerned with the ability of carbons to accelerate the oxidation of alcohols, olefins, sulfur dioxide, and other substances appeared more than 100 years ago. Since then, numerous investigations into the catalytic properties of carbons have been undertaken (see, e.g., [1–3]) and a wide variety of catalytic properties has been discovered in carbon materials (CMs). It has been established that CMs can catalyze various processes, including redox and acid–base reactions.

In recent years, a series of papers have appeared that provide a significantly deeper insight into CMs as catalysts and clarify the causes of their catalytic activity [3–5]. Numerous investigations in this field have been carried out by the present authors [3–12].

Knowledge of the causes of the catalytic action of CMs would help deliberately select carbons with desired properties and control their sorption and catalytic properties.

The present and previous [3–22] investigations elucidated the mechanisms of catalytic processes in the presence of carbons both in the liquid and in the vapor phases. Analysis of the results of these investigations helps determine the main factors in the catalytic properties of carbons. These factors are the following: (1) the presence of various functional groups (–OH, –COOH, =NH, $-NH_2$, $-SO_3OH$, etc.) on the surface of the active carbon; (2) the presence of modifiers in the CM (N, P, S, and Me heteroatoms; ions; oxides salts of various metals); (3) the porous structure and the structural and sorption properties of the CM; (4) the electrical properties of the CM and the structure of the carbon matrix.

In the present communication, which is based mainly on recent results, we consider the principal relationships governing some catalytic processes (Table 1) on the surface of active carbons, taking into consideration the chemical nature of the surface, the modification of the surface by metal cations, the presence of nitrogen heteroatoms, and electrical properties. Ways and means of controlling catalytic activity are suggested, and new prospects of CMs as catalysts are considered.

EXPERIMENTAL

Carbons with chemically different surfaces were used in this investigation, namely, synthetic active carbon derived from polymers and activated by anion exchange (FAU), synthetic oxidized carbon obtained from polymers and modified by cation exchange (FOU), synthetic nitrogen-containing carbon obtained from polymers (SKN), oxidized wood charcoal (DOU), activated carbon from birch wood (BAU), activated carbon from larch wood waste (LAU), oxidized carbon from larch wood waste (LOU), activated carbon from fruit pits (KAU), natural coal (semicoke) from the Kansko-Achinskoe deposit (KPK), carbon cloth (UT), and the commercial carbon AR-3. The letter O added to a carbon designation will indicate that the carbon is oxidized. The oxidized carbons were modified by exchanging H^+ ions in surface functional groups for metal cations [3].

The investigations showed a clear relation between the catalytic activity of an active carbon and the nature of its surface; the active carbon has practically no effect on the course of reactions of the acid type, whereas a significant catalytic effect was observed in the presence of oxidized carbon (OC) containing various protogenic groups on its surface [3, 4, 12–22]. The catalytic characteristics of OCs in protolytic reactions (the inversion of sucrose; the hydrolysis of maltose, esters, and fats; the transesterification of edible fats [3, 8–11]) are determined not only by the presence and amount of acidic

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[1] The article was translated by the authors.

Table 1. Reactions accelerated by carbon sorbents

Reaction	Experimental conditions	Catalysts
	Acid–base reactions	
Esterification of acetic acid with butyl alcohol	Liquid- or vapor-phase synthesis in a batch or circulation flow reactor, $T = 393–723$ K, reactant ratio of 1 : 20 to 20 : 1	FOU, DOU, LOU, BAUO, UTO, KPKO
Esterification of aliphatic acids with glycerol	Stirred batch reactor (1.3×10^{-3} Pa, 2 h) or fluidized-bed reactor, $T = 373–473$ K	DOU, SKNO, BAUO, and their Na forms
Transesterification of edible fats and their mixtures	The same conditions; bovine and pig fat; soybean, palm, and sunflower oil	DOU, SKNO, BAUO, and their Na forms
Hydrolysis of ethyl acetate	Vapor- and liquid-phase hydrolysis at $T = 423–673$ K in a circulation flow or batch reactor (stirred thermostat, 24 h)	FOU–H, FOU–Me (Me = Na, Ca, Cu, Zn, Fe, Ni, Co, K, Mg)
Dehydration of methanol and isobutanol	Flow reactor, 3 h, $T = 493–623$ K	FOU, DOU
Hydrolysis of vegetable oil	Static conditions, stirred thermostat, $T = 309–323$ K, 24 h	SKNO, KAUO, and their Zn, F, Co, Mn, and Cu forms
Hydrolysis of sucrose and maltose	The same	The same plus FOU and DOU
Hydrogenation of vegetable oil	Static conditions, agitation with a hydrogen stream, 1–13 h, $T = 433–503$ K	Ni-containing FOU and DOU carbons
	Redox reactions	
H_2O_2 decomposition	Static conditions, thermostat, $T = 293$ and 309 K	FAU, BAU, CKT, AR-3, KAU, SKN, KPK, LOU; their Fe, Co, Ni, Mn, Cu, and Cr forms; C + Me_xO_y (Me = Mn, Cr, Ni, Fe, Cu)
Decomposition of oxygen compounds of chlorine	Static conditions, agitation in lightproof vessels, $T = 295$ K	DOU–Co, DOU–Ni
Decomposition of dibenzyl ether hydroperoxide	Thermostated bubbling reactor with a reflux condenser, 1–6 h, $T = 293–323$ K	Cation-substituted forms (Co, Ni, Mn, Fe, Cu) of DOU, LOU, SKNO
Dibutyl ether oxidation of	The same	The same
Cumene oxidation	Gas metering apparatus, agitation, $T = 343$ K	SKN, FAU, DOU, UTO, and their Cr, Fe, Co, Mn, Cu, and Ni forms
Oxidation of H_2S and SO_2	Stirred batch reactor, $T = 294–309$	SKN, UTO, DOU, and their Cr, Fe, Co, Mn, Cu, and Ni forms

groups (Fig. 1) but also by their composition [4]. For example, in the transesterification of edible fats, the transesterifying ability of the carbon–sodium catalyst increases sharply with an increase in the number of strongly acidic carboxyl groups and decreases with an increase in the number of phenolic groups. The positions in which these groups are bound to the carbon framework are also important for catalysis [3]: the same reaction is accelerated differently by carbons from different sources (Fig. 1) [3, 8].

Table 2. Rate constants of the formation of butyl acetate from acetic acid and butanol on oxidized carbon per protogenic site

Acid : alcohol ratio	$k \times 10^{23}$, l^2 mol^{-1} s^{-1}			
	523 K	573 K	623 K	673 K
1 : 20	1.3	2.4	4.2	8.0
1 : 10	1.4	2.4	4.3	–
1 : 5	1.5	2.2	4.0	–
1 : 1	–	2.6	4.0	–
5 : 1	–	–	4.7	–
10 : 1	–	2.5	4.7	8.8
20 : 1	2.6	–	–	8.9

The kinetics and mechanism of the vapor-phase and liquid-phase synthesis of butyl acetate on OC were studied in great detail, a kinetic equation was derived for these processes, the reaction orders with respect to each reactant were determined, rate constants at various temperatures were calculated (Table 2), and the activation energy of the process (E_a) was found [3, 4].

The agreement between the reaction orders and E_a values for analogous reactions in soluble acids, ion-exchanger catalysts, and carbon catalysts is strong evidence that the mechanism of the protolytic reactions on OC in the liquid and vapor phases is the same as the familiar mechanism described for both homogeneous and heterogeneous processes.

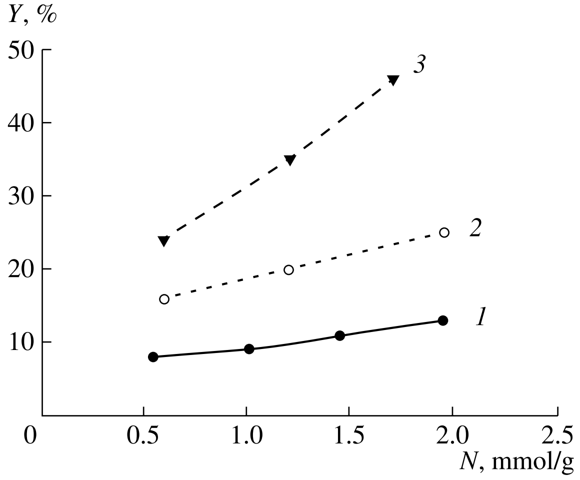

Fig. 1. Butyl acetate yield on the (*1*) LOU, (*2*) BAUO, and (*3*) FOU carbons as a function of their protogenic group content.

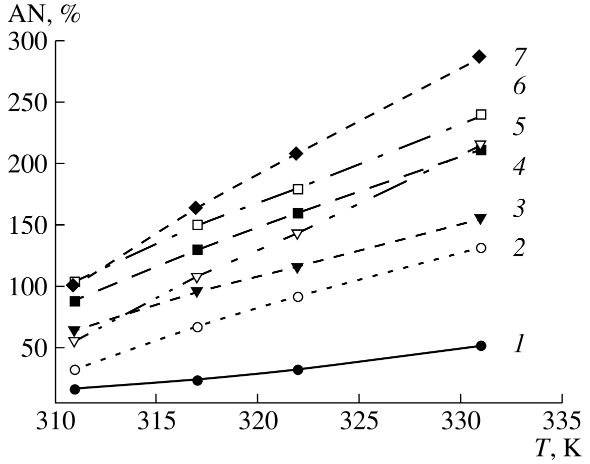

Fig. 2. Temperature dependence of the acid number (AN, as percent of the initial value) for fat hydrolyzed on (*1*) SKN, (*2*) SKNO, (*3*) SKNO-Zn, (*4*) SKNO–Cr, (*5*) SKNO-Fe, (*6*) SKNO–Ni, and (*7*) SKNO–Cu.

Since active carbons are high-porosity adsorbents, there have been numerous attempts to relate their catalytic properties to their adsorption capacity, specific surface area, and pore structure. Analysis of our data and the literature suggests that the optimum structure of active carbons as catalysts is a structure containing a sufficient number of connecting pores with a radius of 20–50 Å or larger. The presence of pores of a certain size favors the mass transfer of the reactants and reaction products, thereby affecting the direction and productivity of the process and ensuring efficient catalysis.

Another essential condition for an active carbon to be an efficient catalyst is high conductivity [3]. The best catalysts for various reactions are carbons with a comparatively low electric resistance (Table 3). The differences between the catalytic characteristics of oxidized carbons with similar chemical natures and cation-exchange capacities (CEC), but obtained by different methods (e.g., DOU-62 and DOU-44, Table 2), are best explained by their different electrical properties (see also [2, 3]).

Our investigations [3, 4, 6–19, 21, 22] have shown that the replacement of H^+ ions in the surface functional groups of C by metal cations, accompanied by the formation of Me^{z+}–oxidized carbon surface complexes, yields cation-substituted carbons with a substantially different catalytic activity in esterification and the hydrolysis of esters, disaccharides (Tables 4, 5), and fats (Fig. 2). The effect caused by cation exchange is similar to the effect of complexation in solutions. The catalytic activity of the cation sorbed by the carbon depends on the polarizing power of the metal ion (atomic electronegativity, ionic potential (Table 6)) and on the stability of the intermediate carbon–substrate

Table 3. Catalytic properties of carbons from various sources and with various conductivities in redox and protolytic reactions

Carbon	CEC, mmol/g	Amount of sorbed Fe^{3+}, mmol/g	*Y*, %	Cumene oxidation rate, $w \times 10^6$, mol/s	Percentage of H_2O_2 decomposed in 15 min	*R*, Ω
FOU	2.0	0.23	23.2	157	100.0	30
BAU	2.0	0.29	21.6	138	100.0	50
		0.18		133	100.0	50
		0.14		131	96.0	50
		0.07		115	69.5	50
DOU-62	1.8	0.14	16.0	70	37.8	730
		0.08		63	30.6	730
		0.07		37	16.3	730
DOU-44	1.6	0.13	10.0	2	5.7	1.26×10^8
		0.06		0	4.9	1.26×10^8

Note: DOU-44 and DOU-62 are air-oxidized charcoals from birch wood calcined at 200 and 400°C, respectively [23]. *Y* is the butyl acetate yield in the esterification of acetic acid with butanol. *R* is dc resistance at room temperature.

Table 4. Hydrolysis of ethyl acetate, sucrose, and maltose on initial and modified carbon enterosorbents

Carbon	[M], mg-equiv/g	Hydrolysis rate constant, $K \times 10^7$, s^{-1}								
		ethyl acetate			sucrose			maltose		
		310 K	323 K	333 K	303 K	313 K	323 K	303 K	313 K	323 K
KAU	0.45	0.2	0.2	6.2	0.1	0.6	0.93	0.1	1.2	2.0
KAUO-H	1.40	0.6	5.9	7.6	1.8	3.9	9.0	5.1	8.7	12.0
SKN	0.50	4.5	7.2	10.0	0.2	0.9	1.4	0.1	1.4	2.3
$SKNO_1$-H	1.40	1.3	2.3	3.4	4.3	14.2	22.0	2.8	8.1	11.9
$SKNO_2$-H	2.60	0.8	6.0	8.8	7.1	17.4	28.0	8.6	13.4	25.6
SKNO-Fe	0.54	2.1	2.6	3.3	2.8	5.4	9.7	–	–	–
SKNO-Cu	0.63	–	–	–	–	4.4	8.7	–	–	–
SKNO-Ni	0.47	1.7	3.6	4.1	2.1	4.7	8.5	–	–	–
SKNO-Cr	0.56	–	–	–	0.9	3.3	6.1	–	–	–
SKNO-Mn	0.28	–	–	–	0.7	1.6	2.8	–	–	–
SKNO-Zn	0.40	5.5	7.0	–	–	–	–	–	–	–
SKNO-Co	0.46	2.1	4.5	5.7	–	–	–	–	–	–

Note: [M] is the modifying ion content. $SKNO_1$-H and $SKNO_2$-H are the H forms of SKN carbon oxidized to different extents.

and carbon–metal complexes (K_{st}) and is determined by the nature of the substituting cation (Table 6, Fig. 2), its amount, and other factors [3].

Note that the catalytic activity of cation-exchanged carbons depends not only on the cation nature and content, but also on the properties of the carbon framework. It is clear from Table 5 that the liquid-phase synthesis of butyl acetate proceeds several times more rapidly on conducting cation-exchanged carbon than on nonconducting cation-exchanged resin KU-2.

Table 5. Atomic catalytic activity (ACA) of metals sorbed on carbon and resin in the synthesis of butyl acetate

Substituting cation	Number of active sites per gram of catalyst, $N \times 10^{-22}$, g^{-1}	ACA* $\times 10^{22}$, mol h^{-1}l^{-1}	
		oxidized carbon	resin
H	12.60	1.4	1.5
Cu	1.74	8.1	2.5
Cu	1.35	8.2	–
Zn	0.81	11.5	2.1
Zn	0.57	11.7	–
Ni	1.02	6.7	0.6
Ca	0.57	11.5	0.4
Ba	1.89	3.7	–
Ba	1.29	5.0	0.4
Ba	0.66	8.2	–
Na	10.38	0.5	0.2
Na	7.5	0.6	0.9
Na	2.7	0.5	9.8

* Per active metal site.

The cation-exchanged forms of oxidized carbon exhibit catalytic activity in protolytic reactions not only at fairly high temperatures, but also under conditions of the human organism [7–12, 15] ($T = 309$ K, specific pH values and catalytic media, etc.). For example, carbon enterosorbents of the SKN and KAU type in the H form, particularly those modified with various microelements (Zn, Cu, Co, Fe, Mn, Ni), promote the hydrolysis of sucrose, maltose (Table 4), triglycerides (Fig. 2), and their analogues (esters) (Table 4) not only in model experiments, but also in real media (in the stomach and gastrointestinal tract) [12, 15].

Modification of the surface of oxidized carbon with various cations affects the catalytic activity of the carbon material not only in acid–base reactions, but also in redox processes. The results obtained in [3, 6, 7] concerning reactions of the electronic type, namely the decomposition of H_2O_2 (Table 1), oxygen compounds of chlorine, and benzoyl hydroperoxide and the oxidation cumene, dibenzyl ether, H_2S, and other compounds, provided ways of enhancing the catalytic activity of oxidized carbons by the introduction of modifying metal cations metals (Fe, Co, Cu, Ni, Mn, Cr, etc.) onto their surface. The authors of these investigations attribute the increased catalytic activity of the resulting salt forms of oxidized carbon to the formation of chelates favoring the event of catalysis on the carbon surface. As in the case of protolytic reactions, the catalytic action of the ionic forms of oxidized carbon is determined by the nature of the substituting cation, the capacity of this cation for forming surface complexes with acid groups of carbon [3], the stability of these

Table 6. Liquid-phase synthesis of butyl acetate in the presence of oxidized carbon and its cation-substituted forms

Substituting cation	Atomic electronegativity	Ionic potential	K_{st}		Ester yield, 10 mol/g
			$MeAc^+$ complex ions	Me^{z+}–carbon surface complexes	
H	2.15	0.6	1.8×10^{-5}	–	0.26
Cu	2.10	2.8	5.7×10^{-3}	6.0×10^{-6}	0.21
Zn	2.03	2.4	2.2×10^{-2}	5.0×10^{-4}	0.14
Ni	–	–	–	–	0.10
Ca	0.98	1.9	0.29	6.7×10^{-4}	0.09
Bs	0.95	1.3	0.40	–	0.08
Na	0.82	1.0	–	4.0	0.05

complexes, and other factors. The strongest oxidase and catalase properties are exhibited by SKN-type synthetic nitrogen-containing carbons, whose graphite-like lattice is perfect and extensive [3, 12]. These factors narrow the band gap, reduce the electron work function, and increase the electron-donating capacity of the carbon, thus favoring electronic-type catalytic reactions.

It is likely that the carbon enterosorbents used in medicine favor the rapid decomposition of H_2O_2 and presumably other peroxide compounds and thereby execute a protective function, preventing the substances appearing in biological liquids at various stages of metabolic processes from participating in radical-chain oxidation processes. In other words, the modified carbon enterosorbents that we investigated for the first time speed up many vitally important processes and favor the catalytic transformation of a considerable part of the metabolites in the organism; that is, they exert a detoxifying effect. We believe that this fact should be taken into account and deliberately used in medical practice.

The established general principles of controlling the catalytic activity of synthetic and technical carbons are also valid for carbons obtained from nontraditional raw materials [23] (wastes from the wood chemical, fish, and food industries; cellulose; synthetic fiber) and for natural coals. By special treatment of these materials, one can readily modify the properties of their surface and obtain cheap and efficient carbon catalysts for dechlorination of mercury brine, liquid-phase etherification, peroxide decomposition, etc. This makes it possible to use carbon catalysts in commercial syntheses and in solving environmental problems.

Activated carbon, which is a comparatively cheap material, shows high chemical, thermal, and radiation stability. It can tolerate numerous operation cycles (including at a high temperature) without losing its activity and is readily regenerable.

The studies reported here suggest the following conclusions. Oxidized carbons, which contain various protogenic groups on their surface, are the most efficient catalysts for many industrially important acid–base reactions, such as esterification, transesterification, hydrolysis, and dehydration. Both model redox processes (H_2O_2 decomposition) and commercial ones (the oxidation of cumene, dibenzyl ether, and hydrogen sulfide; the decomposition of chlorine–oxygen anions; etc.) are effectively catalyzed by active carbons.

By introducing appropriate amounts of various modifiers (metal ions; metal oxides; N, O, P, and S heteroatoms; etc.) and by using carbon from various sources and with various chemical surface types, it is possible to vary and control the catalytic properties of the active carbon and to produce carbon catalysts with desired characteristics.

The studies presented here are also of theoretical significance since they contribute to the scientific principles of predicting and controlling the catalytic properties of carbon catalysts.

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