

CATALYTIC PROPERTIES OF PROTON AND CATION-SUBSTITUTED FORMS OF OXIDIZED CARBONS IN REACTIONS OF HYDROLYSIS, ESTERIFICATION, REESTERIFICATION

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Introduction

Activated charcoals, which have been known as effective adsorbents of various compounds from gaseous and liquid media and are commonly used as such in industry and medicine, possess a broad spectrum of catalytic action featuring the acceleration of both oxidation-reduction and acid-base reactions. While speaking about acid-base reactions in details it is worth to be mentioned that these reactions comprise such industrially important processes as esters hydrolysis, esterification of acids and alcohols, inversion of saccharose, isomerizations of olefins, dehydration in gaseous phase and so on. In industry these processes are accelerated by homogeneous (acids) and heterogeneous (solid acids) catalysts such as individual and combined oxides, natural and synthetic aluminosilicates (clays and zeolites), synthetic ion exchange resins.

In this communication we present data describing the catalytic properties of oxidized carbon (OC) in the acid-base reactions.

Experimental

Our numerous studies of carbon catalysts [1-3] were indeed devoted to elaboration of their role, factors accounting for their catalytic properties, search for the possible control of the catalytic activity of carbon materials of various derivation in model and industrial reactions, namely, the hydrolysis of esters, carbohydrates, lipids, esterification, reesterification of edible oils. A relationship was found between the catalytic properties of carbon materials (CM) and the nature of the raw materials, chemical nature of the carbon surface, and electrophysical and other properties of the carbon surface. The catalytic properties of CM may be altered by imparting an ion- or cation-exchange properties, variation of the extent of oxidation, content of surface functional groups (SFG), modification of these groups by catalytically active cations, and change in the content and nature of the inorganic additives.

On the basis of general principles it is clear that catalytic activity (CA) of OC has to be determined by the mobility of proton in the surface groups, such as phenolic and carboxylic ones. Having applied the potentiometric to determine the acidity of surface groups in carboxylic cationites and OC of various types we have shown that the acidity of such groups in carbons far exceeds ($pK \sim 2$) the acidity of carboxylic cationites ($pK = 2,5$). It is likely due to the fact that 2p-electrons of oxygen atoms, forming the surface groups in carbons, are very much delocalized by the π -conjugated system of the graphite-like planes. It reduces the effective negative charge on oxygen and, as a result, the mobility of protons increases and, therefore, -OH and -COOH groups become more acidic.

CA of OC in reactions catalyzed by moving proton have been studied in gaseous phase and in solutions.

The influence of qualitative and quantitative composition of surface protonic groups has been established (Fig.1).

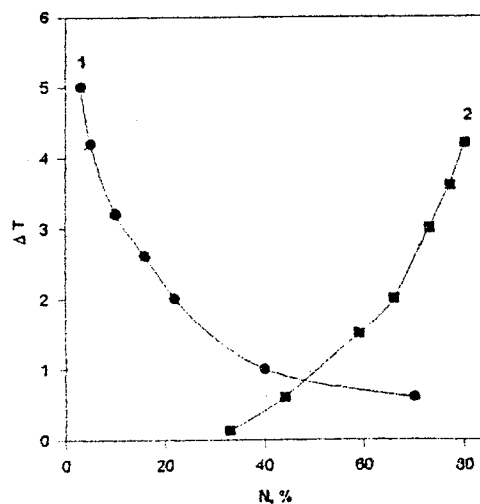


Figure 1. Dependence of the melting temperature of suet (ΔT) from reesterification reaction by OC on the quantity of SFG (N). 1 - phenolic SFG, 2 - strong acidic SFG.

To understand the general principles of catalysis by OC in reactions of esterification we studied in details kinetics and mechanism of synthesis of buthyl acetate in liquid and gaseous phase in the wide range of temperatures (150-450 °C) using the H⁺ modifications of OC. We have found the order of this reaction for each reagent as well as kinetic equation of buthyl acetate synthesis. The apparent value of activation energy (E) in esterification of acetic acid by buthyl alcohol was about 33,6 kJ/mol. The rate constant (C_r) of this reaction increases as the temperature rises.

Apart from esterification processes we studied the catalytic properties of OC of esters, fats hydrolysis, fats reesterification etc. It was found that the hydrolysis degree of ethyl acetate and soybean oil increased as the amount of surface acidic groups rose in linear proportion (Fig.2). In this reactions CA, C_r of carbons increases with temperature, the weighted portion of carbon, contacting time and their oxidation degree.

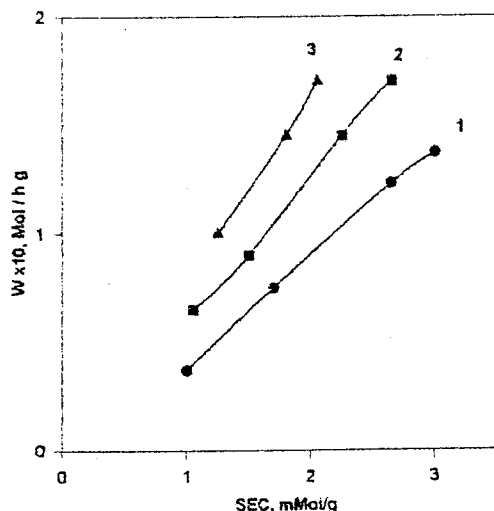
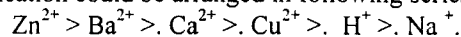


Figure 2. Dependence of hydrolysis rate (W) of suit (1), ethyl acetate (2) and buthyl acetate synthesis (3) by OC on its total static exchange capacity (SEC).

The principle parameters of these catalytic processes (E, C_r) were determined. The effect of porosity of carbons and their oxidation on CA in the reactions of saline modifications was studied in details also.

The CA of OC was found to be exchanged considerably when proton is substituted by some mono-, bi- or trivalent cations. According to their catalytic effect some cations for example in the reaction esterification could be arranged in following series:



In reesterification of fats as catalysts usually use alkaline metals or some alcoholates and hydroperoxides which are not very suitable to work with. Sodium modifications of OC appeared to be much more efficient catalysts in this process.

The mechanism of CA of protonic and cationic forms of OC in the reactions studied have discussed.

It was suggested that the mechanism of acid-base reactions on different H- and cation forms of oxidized carbon materials, soluble acids, synthetic ionites were similar.

Conclusions

In conclusion it has to be mentioned that OC are the efficient catalysts in the acid-base relations both in liquid phase and in gaseous one. We concluded that OC could have more application than ion-exchange resins, natural aluminosilicates or soluble acids due to a number of advantages, such as chemical stability, well developed porous structure and the property not to swell in different solutions, regulated porosity and surface chemistry and, as a result, a continuous controlled change of catalytic activity and selectivity.

References

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