

# EFFECTS OF THE REACTION MEDIUM ON THE CHEMICAL NATURE OF THE SURFACE OF CARBON CATALYSTS DURING ESTERIFICATION, ESTER HYDROLYSIS AND HYDROGEN PEROXIDE DECOMPOSITION

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## Introduction

Oxidized carbons and their cation-substituted forms are known to be effective catalysts for many protolytic and redox reactions [1-3]. However, it has been found in independent studies that the initially high catalytic activity of these contacts falls over time in a number of cases but that in their stationary states oxidized carbons can work for a long time without reduction in productivity. To clarify the underlying reasons for these phenomena we have found and developed a method for preparing carbon catalysts with optimum properties, eliminating the negative effects, which complicate the catalytic reactions.

## Experimental

In this study the states of the surfaces of hydrogenated and cation substituted (Na, Ca, Ba, Zn, etc.) oxidized carbons were investigated before and after catalysis (synthesis of butyl acetate, hydrolysis of ethyl acetate and the decomposition of hydrogen peroxide).

Chars from phenolaldehyde resins were to prepare the catalysts: activated FAU and oxidized FOU-H. Cation-substituted forms (M-forms) were prepared by normal ion-exchange adsorption.

## Results and Discussion

Studies showed that in the formation and hydrolysis of esters the initial catalytic activity of protonated oxidized carbons usually decreased considerably. This showed up most clearly when the reactions were carried out in the gas phase. The reactivity of protonated oxidized carbons in ester synthesis decreased 5 to 6-fold during the reaction and by a factor of 2-3 in the hydrolysis reaction after which a stationary state was reached.

The reduction in the initial catalytic activity is probably connected with reaction of the alcohol with some proton-donating group to give esterification of the surface. This would decrease the number of centers capable of activating the acid molecules and catalyzing

The picture with the cation-substituted forms of oxidized carbons was somewhat different. The stationary state was established much more rapidly and the decrease in the initial activity was 10-30%, depending on the nature of the cation and the experimental conditions.

The qualitative state of the surface functional groups of the carbon catalysts before and after catalysis was investigated by IR spectroscopy. The IR spectrum of the H-forms of carbons ( $1750\text{ cm}^{-1}$ ,  $1580\text{ cm}^{-1}$ , and  $1250\text{ cm}^{-1}$ ) after participation in synthesis of butyl acetate shows that the character of the surface has changed: the intensities of all the bands mentioned have decreased and some have disappeared completely. The IR spectra of ion-exchanged oxidized carbons contain the characteristic band for an ionized carboxyl group at  $1590\text{ cm}^{-1}$ . The bands at  $1400$  and  $1030\text{ cm}^{-1}$  are usually assigned to deformation vibrations of the COOH and OH groups respectively. Comparison of the IR spectra of the ionic forms of oxidized carbons before and after catalysis shows that both the position of the bands and their intensities differ very little.

Chemical analyses of the composition of the surface functional groups before and after catalysis of the synthesis and hydrolysis were also carried out in addition to the spectroscopic measurements. The results obtained (Table) confirmed that the overall quantity of proton generating groups as well as the amount of the individual types (strong and weak carboxylic acids, phenol) in the H forms of oxidized carbons decreased considerably after catalysis. According to the chemical analyses, a decrease in the quantity of proton generating groups was also observed in a number of cases, but the decrease was much less noticeable. These changes in the chemical nature of the surface after interaction with components of the reaction media were observed in both gas phase and liquid phase reactions.

the esterification reaction and would partially poison the catalyst. In the hydrolysis similar surface reactions are possible between the surface functional groups and the hydrolysis product, ethanol.

Table. Composition of the Surface Functional Groups in H- and M-forms Before and After Catalysis

Catalyst	Quantity of surface functional groups, mM/g						Reactivity of catalyst, $W \cdot 10^4$ , mole/h.g
	before catalysis			after catalysis			
	1	2	3	1	2	3	
Gas phase synthesis of butyl acetate (623 K)							
FOU-H	0,00	0,45	0,95	0,05	0,11	0,04	6,0
FOU-Na	0,00	0,25	0,49	0,00	0,03	0,22	18,1
FOU-Zn	0,00	0,20	0,43	0,00	0,16	0,36	35,0
Hydrolysis of ethyl acetate (363 K)							
FOU-H	1,10	0,60	0,92	0,35	0,15	0,12	7,0
FOU-Na	0,05	0,22	0,38	0,00	0,09	0,15	11,3
FOU-Zn	0,00	0,24	0,32	0,00	0,18	0,26	15,2
Decomposition of $H_2O_2$ (aqueous solution, 298 K)							
FAU	0,25	9,10	0,10	0,20	0,15	0,15	45
FOU-H	1,20	0,65	0,65	1,25	0,75	0,70	10
FOU-Na	0,06	0,20	0,35	0,07	0,21	0,36	15
FOU-Fe	0,01	0,18	0,21	0,12	0,25	0,31	70

1) Strongly acidic carboxyl groups; 2) weakly acidic carboxyl groups; 3) phenolic groups.

However in all likelihood surface esterification, which poisons the catalyst, is not possible on the metal-substituted oxidized carbons and this facilitates their constant high activity.

The chemical nature of carbon catalysts before and after decomposition of hydrogen peroxide was also studied (Table). Spectroscopy and chemical analysis of the qualitative and quantitative composition of the surface functional groups showed that the chemical nature of the surface of H and Na forms of FOU were practically unchanged during low temperature decomposition of  $H_2O_2$ . However on Fe forms with different degrees of substitution the nature of the surface was observed to change. New bands appeared in the IR spectra and the intensities of bands, attributed to vibrations of -COOH, -C=O- and OH groups increased.

Hence it is possible that side reactions - the formation of surface functional groups - occur during redox reactions of carbon catalysts. However this has a negative effect, i.e., reduction of catalytic activity, only on unmodified carbons. Cation-substituted materials whose catalytic activity does not change after many cycles of use, despite changes in the chemical properties of the surface, are clearly to be preferred.

## References

- (1). Stavitskaya S., Strelko V. Catalytic properties of carbon enterosorbent. *Teor. Eksp. Khim.*, 1995, 2, 76.
- (2) Stavitskaya S. Acid catalysis by oxidized carbons of various origin. *Ukr. Khim. Zh.*, 1997, 7, 27; 8, 96.
- (3) Stavitskaya S., Tarkovskaya I., Petrenko T. Main factors defined catalytic properties of active carbons. *Teor. Eksp. Khim.*, 1996, 6, 336.