

# MODIFICATION OF CARBON SURFACE WITH MONOLAYERS s, p, d - ELEMENTS AND THE REACTIVITY IN OXIDATION GASIFICATION

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## Introduction

The urgency of a problem of catalytic oxidation gasification of carbon materials is stimulus for realization of numerous researches in this area. The special importance is acquired by researches on model preparations - diamond and graphite, which allow revealing the contribution of an electronic structure of matrix into processes of reactivity in oxidation gasification. The purpose of the present report is regularities generalization of reactivity in oxidation gasification diamond and graphite by chemical monolayer filling of the surface with compounds of I-VI groups elements.

## Experimental

The researches were conducted on powders of natural diamond and graphite. Synthesis of monolayers was executed by chemical assembly method [1], while interaction of carbon oxyfunctional groups with low-molecular compounds of elements (hydroxydes, halogenides), with formation on the surface of C-O-E chemical monolayer. The parameters of formal kinetics of oxidation by air oxygen (rate and energy of activation) were determined in a temperature range of 750-900K.

## Results and Discussion

In the table are submitted the concentration of elements on the surface of diamond and graphite, which make a chemical monolayer filling. From the XPS data (Table) it follows, that the elements are in the ionic form.

**s-elements.** Ions of alkaline and alkaline-land elements ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) catalize processes of both diamond and graphite oxidation equally well (Table). The initial rate of oxidation increase in comparison with initial samples approximately at 100 times. By the catalytic activity the ions of alkaline metals are drawn up in a row as follows:  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ . The electronic structure of carbon does not have a basic role: the absolute values of oxidation speed of diamond and graphite are close. Most probable explanation of catalysts effect efficiency is their ability to participate in oxidational -reductional process

of oxides and peroxides formation. The least probability of peroxide formation for  $\text{Li}^+$  and  $\text{Ca}^{2+}$  ions explains well the obtained number of catalytic activity of s-elements:  $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Ca}^{2+}$ . Thus, while oxidation gasification of diamond and graphite at the presence of s-elements, the chemical nature of catalyst ions is determining.

**p-elements.** Oxidation gasification of carbon, modified by p-elements, takes place without catalytic effects (for  $\text{Al}^{3+}$  ions); for preparations containing  $\text{P}^{5+}$  ions inhibition of reaction is observed (Table). The role of phosphorus causing decrease of oxidation speed approximately at 10 times, is stipulated by its ability to extinguish oxidizing processes taking place by the radical way. The direct chemical contact of phosphorus compounds and oxyfunctional C-O-P groups causes deactivation of the most active oxidation centers and inhibition of the process.

**d-elements.** For d-elements ions there is another picture of catalytic activity (Table). The biggest catalytic effects that do not yield in the order of value to absolute speeds for s-elements are obtained. The order of position of elements on catalytic activity for graphite  $\text{Ti}^{4+} < \text{Cr}^{3+} < \text{V}^{5+}$  - can be explained by behavior of transitive metals compounds in oxidational -reductional processes, that is stipulated by presence of significant number of conditions with various degrees of oxidation, and is determined by oscillations between them. The transitions into a lower degree of oxidation  $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ ,  $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$ ,  $\text{V}^{5+} \rightarrow \text{V}^{4+}$  are possible, as the catalytic process takes place by rather high temperature and at the presence of carbon atoms of graphite surface, that are its direct participants in composition of C-O-Me complexes. The high concentration of delocalized graphite  $\pi$ -electrons, that can participate in oxidational -reductional cycle, is determining while effecting on the electronic subsystem of catalyst ion. These effects are revealed at significantly bigger extent at vanadium ions, for which the transition  $\text{V}^{5+} \rightarrow \text{V}^{4+}$  happens rather easily, that causes the maximum activity by oxidation of graphite. While oxidation of diamond, modified by  $\text{Ti}^{4+}$  or  $\text{Cr}^{3+}$  ions an opposite picture is observed, and for  $\text{V}^{5+}$  ions even inhibition of process takes place (table). The main reason of such an effect is absence on the diamond of delocalized electrons which are capable to participate in oxidational-reductional process with ions.

**Table 1.** Composition , bonding energy, oxidation rate ( 783K ) and activation energy

Shell		<u>s-elements</u>				<u>p-elements</u>		<u>d-elements</u>		
Element	–	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	P <sup>5+</sup>	Ti <sup>4+</sup>	V <sup>5+</sup>	Cr <sup>3+</sup>
Line	–	–	1s <sub>1/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>3/2</sub>
<u>diamond</u>										
[E], μmol /m <sup>2</sup>	–	3.2	4.4	3.4	2.5	3.5	1.1	3.5	2.7	0.8
E <sub>b</sub> , eV	–	–	1071.4	292.0	–	73.6	132.7	458.2	516.8	576.5
–ln V, [g /m <sup>2</sup> s]	14.5	12.1	11.6	11.4	13.8	14.1	17.5	13.4	15.4	14.3
E <sub>act</sub> , kJ/mol	220	–	168	–	–	256	–	–	258	–
<u>graphite</u>										
[E], μmol /m <sup>2</sup>	–	3.8	4.5	3.7	2.3	5.9	1.1	3.2	5.5	4.9
E <sub>b</sub> , eV	–	–	1072.0	292.8	346.5	74.4	132.8	459.0	517.2	577.5
–ln V, [g /m <sup>2</sup> s]	15.1	12.4	12.3	11.6	14.0	15.3	15.7	14.4	11.4	11.6
E <sub>act</sub> , kJ/mol	210	–	168	–	–	243	–	–	135	–

### Conclusions

The obtained numbers of catalytic activity allow to make a conclusion about determining influence of an electronic structure of a matrix (diamond or graphite) on the electronic subsystem of catalyst while modifying by ions of d-elements, and about absence of such effect for ions of s- and p-elements.

### References

1. Smirnov E.P. Chemical reactions of carbon and synthesis of composites. University Saint Petersburg, Russia, 1-st Inter. Conf. "Chemistry of Highorganised substances", thesis, p.17, 1996.