

# CATALYTIC EFFECT OF ALKALINE AND ALKALINE - EARTH METALS IN REACTIONS OF CARBON GASIFICATION AS A RESULT OF FORMATION OF INTERMEDIATE INTERCALATION COMPOUNDS

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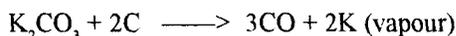
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## Introduction

It is well known that some compounds of alkaline and alkaline-earth metals can exert profound catalytic effects on the gasification reactions of carbonaceous materials with oxygen, carbon dioxide, nitrogen oxides, hydrogen and water vapours. But no theory has been found capable to explain all the experimental results. Thus attempts to explain the catalytic effects by consecutive oxidation and reduction of a metal-catalyst in a carbon - oxidising gas system as well as by formation of intermediate phenolates as an active state have been undertaken [1]. In the present communication we use both the data published and own experiments and quantum chemical calculations to develop the idea about the formation of intermediate intercalation lamellar compounds of the metal catalysts and carbon microcrystallites (graphite clusters) as a deciding factor of their catalytic action.

## Experiments and Calculations

During high temperature treatment (600-800 C) of carbonaceous materials impregnated with alkaline metal carbonates the metal reduction occurs according to Gay-Luissac's reaction, for example:



From our point of view, the free metal formed inserts partially or completely into the interlamellar gaps of a graphite-like microcrystallites of carbonaceous material. The 1s valent electrons of metal transfer on the condensed pi-system, and a macro-anion (anion-radical) is formed in a result of this charge transfer. The electrophysical properties of a carbonaceous material and in particular its paramagnetic parameters have to be altered essentially. That's why we used ESR method to prove the formation of intercalation compounds in a course of high temperature treatment of the carbon - potassium carbonate mixtures. The experiments were performed as follows. The apricot stones impregnated with 3 -10 % (w/w) of potassium carbonate were pyrolysed in an argon-gas atmosphere and in the temperature interval 450 - 900 C in a silica ampoules. The ESR spectra of the

pyrolysed samples were recorded avoiding contact with air. The spectra obtained exhibit asymmetric singlets with a g-factor 2,00318. Raising the temperature of treatment up to 750 C results in more asymmetrical form of a signal. We attribute this to enhancing of the number of agile charge carriers, i.e. to increase of electric conductivity of a material due to increase of amount of potassium intercalated. The ESR signals of the samples treated at the temperatures above 800 C become more and more symmetric. This could be attributed to partial evaporation of a metal, i.e. to decomposition of intercalation compounds. Semiempirical method of self-consistent field has been used for quantum chemical calculations. The models of clusters consisting from two graphite-like planes with 4, 7 and 13 aromatic nuclei each and lithium as an alkaline metal were used for calculations. The initial geometry of a model systems was evaluated using molecular mechanics method. It was shown that effective negative charge on some carbon atoms of two graphite-like planes increases linearly with increasing the number of lithium atoms intercalated. This corresponds to experimental data on increasing conductivity of the samples heated at 700 - 800 C.

## Discussion

Following intercalation, the graphite-like microcrystallites get a high negative charge, hence, their reactivity in the reactions with oxidising agents also increases (as in the gasification reactions). The elementary steps of the gasification of activated carbons with oxygen, nitrogen oxides and carbon dioxide have been discussed. Mechanism of the positive effect of small oxygen amount on the formation of intercalated compounds has been analysed. It has been concluded that as a result of the partial carbon oxidation, edge salt-type compounds CO- K<sup>+</sup> and COO- K<sup>+</sup> are formed. These edge compounds repel adjacent planes and facilitate penetration of potassium into the interlamellar space. Routes for the synthesis of novel carbon adsorbents and catalysts containing intercalated electronegative metals in the microcrystallites have been discussed.

## References

1. Fundamental Issues in Control of Carbon Gasification Reactivity. J.Lahaye and P.Ehrburger (eds.), Kluwer Academic Publishers, 1991.