

# CATALYTIC PROPERTIES OF METAL-CONTAINING OXIDIZED COAL CATALYSTS IN SOME REDOX REACTIONS

*S.S.Stavitskaya, I.A.Tarkovskaya, T.P.Petrenko, N.T.Kartel  
Institute on Sorption and Endoecology NAS of Ukraine  
13 General Naumov Str., Kiev-164, Ukraine 03680*

## Introduction

It has been demonstrated previously<sup>1-4</sup> that the capacity of some metal ions ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , etc.) to accelerate certain redox reactions is not only retained but actually considerably increased on adsorption onto oxidized coal materials (OCM). It has been suggested that the most probable reason for this increase is that the ions are bound by ion-exchange with functional groups of the OCM to form surface complexes which are usually coordinatively unsaturated and consequently capable of adding various particles (molecules, ions and radicals, including reaction components) as ligands. The objectives of the present study were to determine whether the interactions previously described for particular redox reactions<sup>1-4</sup> were applicable for a wide range of OCM and redox reactions, and to establish how the quantity of adsorbed ions and how they were bound affected the catalytic activity.

## Experimental

The study was carried out using the decomposition of  $\text{H}_2\text{O}_2$ , oxidation of various substances (potassium iodide, dyes dissolved in water, mixtures of organic materials) with hydrogen peroxide, and the oxidation of adsorbed acids, hydrocarbons (cumene), and hydrogen sulfide, dissolved in water or in gaseous mixtures, by oxygen.

OCM of various states (coals, fabrics) and origin were used as bases for the catalysts. Samples based on synthetic coal from phenol-aldehyde resins (FOU), nitrogen-containing coal SKN, technical coals BAU, AR-3, and AG-3, woody type DOU, partially oxidized brown coal, activated anthracite and technical carbon cloth were oxidized by a known method. Technically oxidized soot was also used.

To prepare catalysts with the metals bonded in different ways to the OCM they were made either by introducing the components by ion-exchange methods or by soaking the coal or fabric with solution of the corresponding sulfates. In the first case the ions were bound as chelates in the surface complexes<sup>2,4</sup> while in the second case most of the modifying substance was adsorbed either by physical adsorption or as hydrolysis products. For comparison materials were prepared in which the metals were present as oxides (by pyrolyzing salts of organic acids). Samples were made with different (chosen) contents of active components.

## Results and Discussion

Analysis of the materials obtained showed that, as a rule, the metal-containing carbons had higher catalytic activity than the unmodified OCM or the ions in solution.

A regular increase in catalytic activity was observed for ionic forms of OCM as the amount of adsorbed ions increased. A linear dependence of activity was observed as the surface coverage increased to 10-15%. This is demonstrated in Fig. for the decomposition of hydrogen peroxide, the oxidation of dyes by hydrogen peroxide. Similar dependencies were obtained for other processes studied and for other types of OCM.

No regularity of the change in catalytic activity with increasing amount of active ingredient added was observed for catalysts prepared by soaking the OCM with a metal salt. This is apparently connected with the different way in which the surface and pores of the coal are modified and with the relation of the relative amounts to the method of preparing the catalyst. It may be that in this case the mechanism for increasing the catalytic effect of the ions in the surface complexes is hindered. Compositions containing metals as their oxides in general showed a much higher catalytic effect than the initial coal but no marked dependence on the amounts of the components was observed.

These results show that the catalytic activity of metal-containing OCM depends to an important on the amount of modifying component and the way in which it is bonded. A regular increase in catalytic activity depending on the amount of ions adsorbed by the OCM in a variety of reactions – decomposition and oxidation in aqueous solution, liquid and gas phases – is observed only for metallic ions bound by ion-exchange.

It can also be confirmed that this type of relation exists for OCM of different types and origins – synthetic, technical, natural and fibrous. The general character of this relation indicates a coincidence of the mechanisms for accelerating the redox reactions studied by ions adsorbed by the OCM and it corroborates that potential for use in the analysis of traces of elements can be estimated from the quantity of adsorbed metal cations and their catalytic effect in these and other reactions.

In special experiments it was shown that it is possible to combine the adsorption and concentration of micro quantities of cations ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ , etc.) with their subsequent determination from their catalytic affect in a single analytical operation. Determinations of this sort appear to be less effective than traditional methods and in a number of cases they are more sensitive, simpler, and more appropriate.

### References

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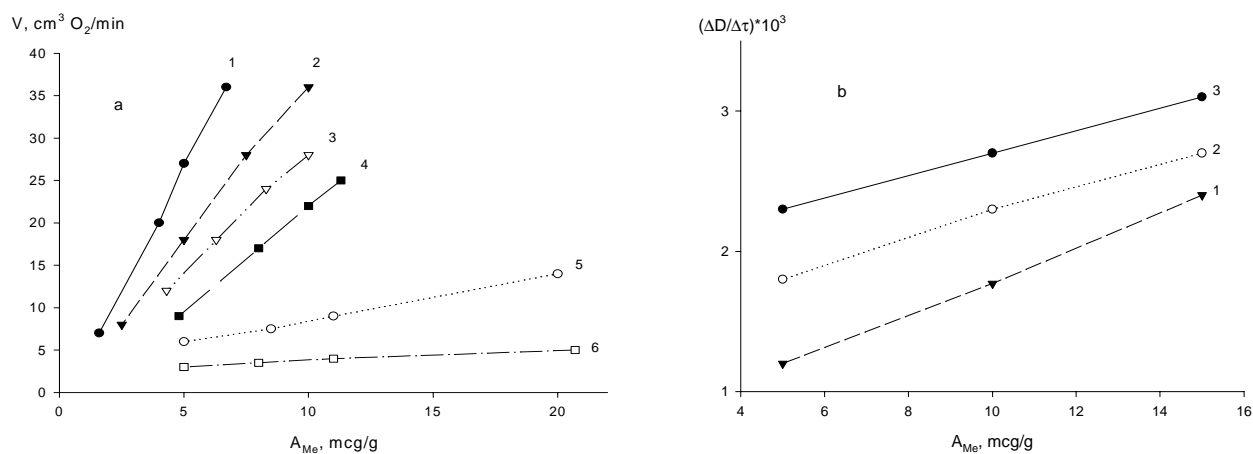


Fig. Dependence of the rate of decomposition of  $\text{H}_2\text{O}_2$  (a) in the presence of cation-containing forms of FOU: Fe(1), Cr(2), Mn(3), Cu(4), Co(5), Ni(6) on the amount of adsorbed ions ( $A_{\text{Me}}$ ). (b) Dependence of the change in optical density ( $\Delta D/\Delta t$ ) of solutions over the Fe form of SCN (1,2) and AR-3 (3) on the concentration of iron ion in the carbon ( $A_{\text{Me}}$ ) for the oxidation of methyl orange (1) and methylene blue (2,3).