

SORPTION-CATALYTIC METHODS OF ANALYSIS WITH CARBON ADSORBENTS

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Introduction

Carbon materials are known as supports for heterogeneous noble metals catalysts [1] and were found to be selective adsorbents of metals of platinum group (MPG) microamounts from acid solutions with complex composition [2,3]. Method of reducing sorption of noble metals from solutions with simultaneous obtaining of supported catalysts was also proposed in our works [4,5]. From the other hand catalytic properties of platinum metals compounds are widely used for their determination with sensitive kinetic catalytic methods of analysis [6]. The possibility of co-operation of two approaches in one process – sorption extraction and catalytic determination of platinum metals on active carbon (AC) surface for MPG determination - was found previously [7]. But proposed method was insufficiently reproduced due to photometric measurement of indicator reaction rate, which is commonly used and which is improper for heterogeneous reactions.

The main aim of the present work is to investigate the possibility of development of catalytic methods of MPG determination on carbon carriers after their sorption with use of redox potential change measurement in reaction media.

Experimental

The main objects of investigation are reactions of manganese (III) reduction by chloride-ions, catalysed by chloride complexes of Pd (II), and manganese (III) reduction by quinone, catalysed by sulphate complexes of Ru (IV). Both of those indicator reactions are selective for determination of microamounts of metal-ions under examination. The catalytic reaction rates were measured as photometrically due to coloured manganese (III) sulphate complex decrease as potentiometrically due to change of redox potential.

In the static adsorption experiments the adsorption values were calculated from the difference of the initial platinum ions concentration in the solution and their concentration after 24 hours contact time (equilibrium concentration was practically reached after 4 - 6 hours contact time).

The set of carbon materials (12 samples), which were considered, includes synthetic carbons, natural and technical coals and products of their proceeding.

Results and Discussion

The direct interaction between all carbon materials to be examined and Mn (III) in sulphuric acid solutions was shown do not proceed as well as in reactions of Mn (III) with Cl^- or Mn (III) with p-quinone without catalysts. More detailed examination of catalytic action of Pd (II) chloride and RU (IV) sulphate complexes in reactions to be mentioned was carried out with activated samples of synthetic carbons SKS (practically without surface functional groups), SKN (with N-containing surface functional groups) and with natural oxydized wood coal DOU, all these AC-s evaluate Pd (II) and RU (IV) mikroamounts completely. It was found also that catalytic effect of Pd (II) chloride and RU (IV) sulphate complexes in reactions of Man (III) reductions do not depends on the presence of these Acs. Dependence of redox-potential in reaction of Mn (III) with Cl^- , catalysed by Pd (II), is not linear, because complex mechanism of this redox reaction with excess of Mn (II) and Cl^- in solutions [8]:



Nevertheless, there is linear dependence between potential at time fixed and concentration of catalyst, this dependence can be used as calibration graph for determination of Pd (II) in solutions, fig.1. Unfortunately, dependence between of potential at time fixed on Pd (II) content on ACs is not definite and reproducible, while catalytic action of Pd on coal surface is demonstrated by change of reaction rate, measured photometrically in the same conditions. This fact may be explained by complex dependence of potential to be

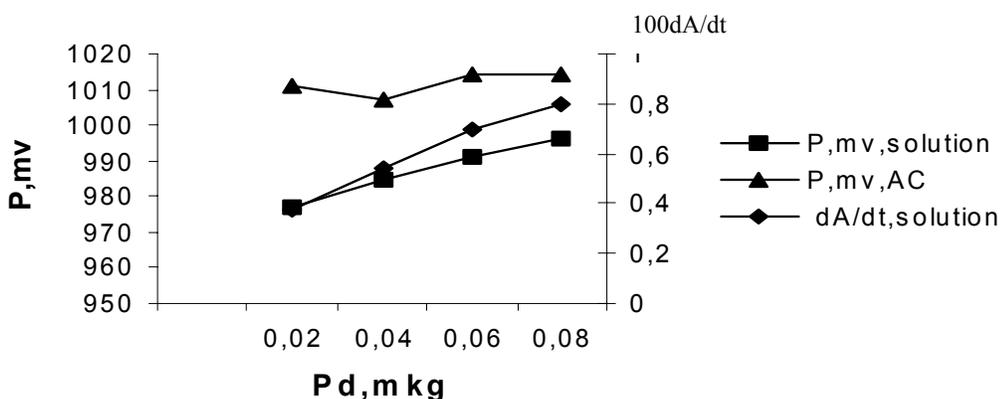


Fig.1. Dependence of potential, measured at 5 min after start of Mn (III) reduction by Cl^- , catalysed with Pd (II) in solutions and the same, catalysed with Pd (II) on AC DOU, and reaction rate, catalysed with Pd (II) on AC DOU, measured spectrophotometrically (0.003 M Mn (III), 0.01 M HCl, 1 M H_2SO_4)

measured on potential of redox-pairs Mn(III)/Mn(II) and Cl₂/Cl⁻ in solution with initial great excess of Mn(II) and Cl⁻ concentrations [8], while optical density of solutions is determined by Mn(II) concentration only. Besides, catalytic action of palladium on AC depends on its state on coal surface, in which palladium may be reduced partly or completely to metallic state.

Determination of ruthenium (IV) mikroamounts by sorption-catalytic method was developed for solutions without chloride-ions, which may be evaluated with Ru (IV) from hydrochloric solutions and which may inhibit reaction between Mn (III) and p-quinone, catalyzed by Ru (IV). Effect of this reaction inhibition may be used for chloride-ions small amounts testing and determination on coals, because s catalytic reaction is very sensitive for chloride-ions.

Kinetic curves of potential changing in reaction of manganese (III) reduction by p-quinone, catalysed by AC with sorbed ruthenium are shown at fig.2. and there is proportional dependence between potential at time fixed and ruthenium content as in solution as on AC carriers.

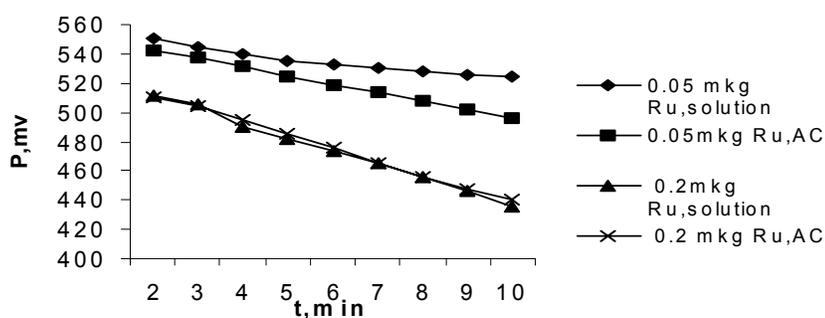


Fig.2. Dependence of potentials in reaction between Mn (III) and p-quinone, catalysed by Ru (IV) in solutions and on coal DOU (0.03 M Mn (III); 0,001 M p-quinone; 3M H₂SO₄)

Catalytic action of Ru complexes in solution and on AC in system Mn(III) + p-quinone do not differ. By comparison photometric and potentiometric data as to catalytic action of ruthenium on AC carriers it was found, that there is reaction between coal DOU and p-quinone, which does not followed by change of Mn(III) concentration. Therefore for determination of ruthenium mikroamounts on AC the dependence of value $P^* = (P_0 - P_{Ru})$ at time fixed on ruthenium content was proposed as calibration graph, where P_0 - potential of reaction media in the presence AC without ruthenium and P_{Ru} that with ruthenium. On fig.3 there are dependence's between P^* for homogeneous and heterogeneous systems and ruthenium content in solution and on AC carrier and dependence of catalytic reaction rate, measured photometrically ($1000dA/dt$) on Ru (IV) content in solution. It was shown that, P^* increases proportionally with ruthenium content increase as in the case of reaction, catalysed with Ru (IV) in solution, as in the case of reaction catalysed by ruthenium on AC carrier. All these curves may be proposed as the calibration graph's for ruthenium mikroamounts determination. So, this way it can determine the quantity ruthenium evaluated by carbon adsorbent immediately after it's sorption.

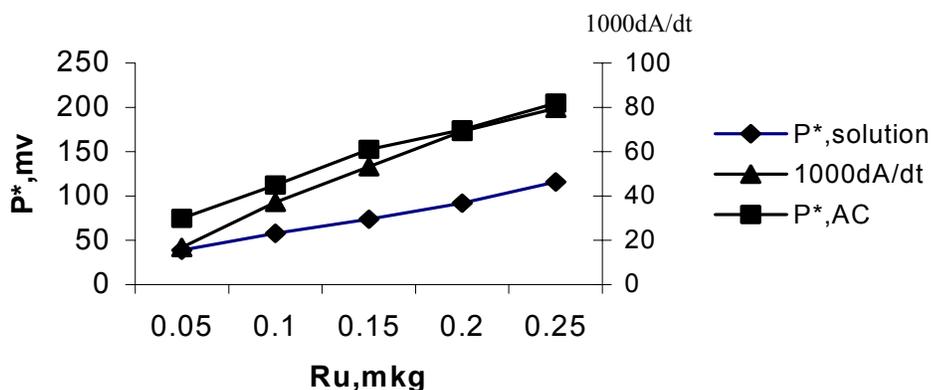


Fig.3. Dependence between values P^* and Ru (IV) content in solution and that on AC DOU, and dependence between catalytic reaction rate, measured photometrically ($1000dA/dt$), and Ru (IV) in solution (reaction Mn (III) + p-quinone; 0.03 M Mn (III); 0,001 M p-quinone; 3M H_2SO_4 .)

Conclusions

Some approaches for developing of sorption-catalytic methods of analysis, combined with metal-ions sorption by carbon material and catalytic action of that carbon in some indicator reaction were shown using potentiometric techniques, especially for determination of palladium and ruthenium mikroamounts. Method of testing of Cl^- presence on carbon materials by their inhibition effect in reaction of p-quinone oxidation by Mn (III), catalysed by ruthenium on these materials carriers, was proposed too.

References

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