

# ACID-BASE INTERACTION OF ACTIVE CARBONS WITH NOBLE METALS

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## Introduction

Active carbons (ACs) have long and successfully been used for the extraction of noble metals from mineralized solutions [1]. However, recently a comprehensive investigation of the characteristics of interaction in systems "ACs – noble metals" has been initiated. So, the theory and electrochemical mechanism of electropositive metal ions sorption on ACs were proposed [2], the role of ion exchange [3] and complex-formation in redox-processes with ACs was determined [4-6] and the reasons of sorption selectivity of noble metals by ACs were proved [7].

In this work the specific features of the acid-base interaction of noble-metal ions and accompanying impurity ions with ACs were studied.

## Systems "ACs – noble metals"

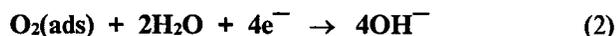
ACs are multifunction materials; they are characterized not only by a pronounced ability for molecular sorption, surface complexation, and ion exchange, but also have strong reducing properties [8].

It is known that noble-metal ions can react readily with various unsaturated organic compounds [9]. These processes are exothermic and result in the formation of stable  $\pi$ -complexes, for example:



Such reactions are typical acid-base interaction [10]. Therefore, ACs, which have a large number of valence-unsaturated, and consequently very reactive, carbon atoms on the surface can also react with noble metal compounds [4,6,7].

In aerated aqueous electrolytic solutions due to the reaction:



ACs behave like an irreversible oxygen gas electrode:



where  $[\text{C}_x^{2+} \dots 2\text{OH}^-]$  is the positively charged carbon

surface with  $\text{OH}^-$ -ions in the outer coating of the double electric layer:



Thus activated ACs are effective electrochemical anion-exchangers; they are polymeric  $\text{OH}^-$ -bases [11].

The electrochemical reduction of metal ions is thermodynamically feasible if the equilibrium potential of the reaction:



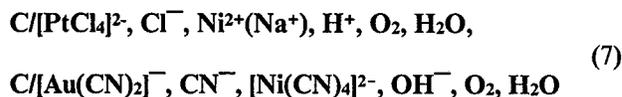
is more positive than the working potential of the AC surface:

$$\Delta\varphi = \varphi(5) - \varphi_{AC} > 0. \quad (6)$$

The adsorption of platinum ions on ACs from hydrochloric acid solutions may be accompanied by their reduction to metal. Ions of  $\text{Ni}^{2+}$ , which is electronegative metal, do not undergo reduction on ACs. ACs in contact with a gold-containing chloride solution is immediately covered with metal, but for cyanide systems metal phase on the ACs surface can not form.

## Experimental

The following model systems:



were studied.

Synthetic ACs were used as sorbents [1]. The adsorption measurements were taken under steady-state conditions at 20°C. Platinum was sorbed from chloride solutions (pH 0 - 2), gold was sorbed from cyanide solutions (pH 10) [7]. Thermal effects, which accompanied the adsorption of noble-metals and nickel on ACs, were measured with flow sorption microcalorimetry. This method allows to determine the

thermal effects of the every stage of interaction of metal ions with the ACs. The chemical state of metals on the surface of ACs was studied by X-ray photoelectron spectroscopy (XPES).

## Results

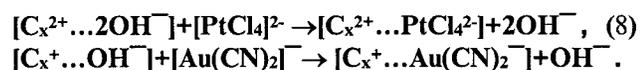
A comparison of the quantity of adsorbed noble (Pt, and Au) and impurity (Ni) metals showed [7] that from individual solutions, noble metals are adsorbed in amounts 10 - 20 times larger than impurity metal.

The differential thermal effects in the adsorption of platinum, gold and nickel showed [7] that the adsorption of platinum and gold from solutions on ACs is accompanied by exothermic effects, which are 15-20 times stronger than for nickel.

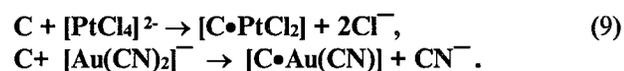
The XPES data showed [7] that the interaction of platinum and gold ions with the carbon matrix resulting in a surface complex that is characterized by a charge transfer from the AC matrix to the noble-metal ion. For platinum, depending on the composition of the solution, an electrochemical reduction may occur with the formation of either a metallic phase or surface  $\pi$ -complexes with metal-carbon bonds. The adsorption of gold is accompanied by a surface chemical reaction of the formation of a cluster compound with a multicenter metal-metal bond. The adsorption of nickel only results in donor-acceptor interactions.

## Discussion

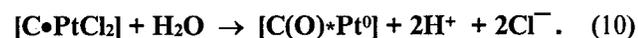
When an activated AC is brought into contact with a solution containing  $[\text{PtCl}_4]^{2-}$  or  $[\text{Au}(\text{CN})_2]^-$ , the first stage is acid-based interaction according to S.Arrenius scheme [11]:



Sorption of platinum and gold occurs by way of irreversible interaction these ions with ACs matrix, accompanied by formation of surface  $\pi$ -complexes according to acid-based W.Lewis - R.Pearson scheme [10]:



And finally, the electrochemical reduction of platinum ions by ACs due to differences in reducing potentials fulfills in connection with M.Usanovich scheme [10]:



## Conclusion

The adsorption of platinum on ACs from chloride solutions and gold from cyanide solutions is determined by processes of the same acid-base nature. The formation of charge-transfer surface  $\pi$ -complexes followed by clustering with gold and reduction to the metals in the case of platinum.

## References

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