

REDUCTIVE SORPTION OF NOBLE METALS BY ACTIVE CARBONS

Yu.Tarasenko, A.Bagreev, V.Strelko

Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Kiev

INTRODUCTION

Active carbons (ACs) have long and successfully been used for the removal of gold and silver from multiple-component solutions [1]. The adsorption of silver diammine complex on graphitized carbon black has been studied in aqueous ammonia solution [2]. But only recently a comprehensive study of the reasons for the selective effect of ACs during sorption of noble metals from solutions of complex salt composition has been started [3,4]. The redox characteristics of different activated carbon fibers were also studied [5].

In this work the theoretical and experimental aspects of interaction of noble (electropositive) metal ions with synthetic ACs were investigated.

ELECTROCHEMICAL MODEL

If ACs are brought in to contact with the solution of noble metals, the spontaneous reduction of metal ions takes place on the sorbent's surface. In many cases reduction proceeds up to the metallic state and islet films appear, developing further over the surface and growing in thickness. Some ideas of reductive sorption (RS) as a spontaneous electrochemical process for reducing ions of electropositive metals by activated ACs in solutions of electrolytes during the sorption were formulated [3]. It was found that the corresponding redox-reactions are conjugated by the electron balance through the carbon matrix and these reactions proceed with carbon matrix's participation [3].

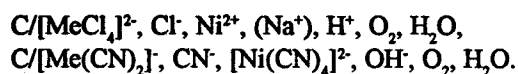
Theoretical description of RS is based on the irreversible thermodynamics extremal principles [6]. Simulating of RS process was carried out by the application of necessary conditions for steady state stability in electrochemical systems. As a result, it was possible to establish:

- criteria for reduction or oxidation reactions proceeding on the AC surface (deposition or dissolution of metal);
- possibility for metal ions' reduction on the carbon granules' external surface or in its volume;
- RS-processes control principles.

EXPERIMENTAL

In experiments synthetic ACs spherical granules were used [7]. They were obtained by the carbonization of styrene-divinylbenzene copolymers (SKS) and vinylpyridine resins (SKN) followed by activation by water vapour. Such ACs are characterized by high mechanical strength, a developed surface, large inherent electric conductivity, increased anion-exchange and reductive properties.

The interaction of noble-metal ions and accompanying impurity ions with synthetic ACs was studied for the following model systems:



These systems were studied by methods of sorption measurements (static, kinetics, dynamic), formation of stationary electrode potential of ACs in solutions (potentiometry), thermal sorption effects (flow microcalorimetry), state of metal in the synthetic ACs surface layers (X-ray photoelectron spectroscopy), morphology of the noble metals on the ACs and metallic phase distribution in carbon granules (electron microscopy) [4].

A comparison of the quantity of adsorbed noble metals (Pd, Pt, and Au) and impurity (Ni) with equilibrium concentrations of the metals in solution shows that from individual solutions, noble metals are adsorbed in amounts 10 - 20 times greater than impurities. In addition, nickel ions present in high concentrations together with noble-metal ions only insignificantly lower sorption of noble metals. Experiments on the adsorption of gold and nickel cyanides from alkaline solutions showed the amount of gold adsorbed to be substantially larger than that of accompanying nickel.

A comparison of the differential thermal effects in the adsorption and desorption of palladium, platinum, and nickel shows that the adsorption of palladium and

platinum anions and nickel cations from acid chloride solutions on ACs is accompanied by exothermic effects, which are 15 - 20 times stronger for Pd and Pt than for nickel cations. Measurements of the thermal effects accompanying the adsorption of gold and nickel cyanide complexes showed that the thermal effect per mole of adsorbed metal was substantially (20 times) larger with gold.

One more characteristic feature is differences in the adsorption reversibility. No thermal effects are observed in desorption of palladium and platinum, whereas with nickel, the exothermic effect of adsorption and the endothermic effect of desorption both have the same magnitude. It follows that the adsorption of nickel is fully reversible, whereas the adsorption of palladium and platinum is practically irreversible under the conditions of our experiments.

The XPES data of the chemical state of noble metals adsorbed on ACs are indicative of the interaction of palladium, 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. The adsorption of gold is accompanied by a surface chemical reaction of the formation of cluster compound with a multicenter metal-metal bond. With palladium and platinum, depending on the composition of the solution, an electrochemical reduction may occur with the formation of either a metallic phase or surface complexes with metal-carbon bonds. The adsorption of nickel only results in donor-acceptor interactions.

MECHANISM AND SELECTIVITY OF REDUCTIVE SORPTION

Importance of potentials of the ACs for RS-processes was determined [8]. Reduction is thermodynamically enabled if the metal-ions' equilibrium potential is more positive than AC surface' potential. So, the value of AC surface' stationary potential and kinetics of its formation are the factors in RS process' control. These factors are dependent on the conditions of RS proceeding: molecular oxygen or another oxidation agent presence in solution AC' potential fixation with electronegative metals [9,10].

An analysis of the reasons for selective sorption of noble-metal ions by ACs carried out with consideration of their ion-exchange and reducing functions, and also the

reactivity of the carbon matrix. Ion-exchange plays an important role in the first stage of adsorption. According to calorimetric and XPES results, sorption of noble metals occurs by way of irreversible exothermal interaction of noble metal ions with the ACs matrix, accompanied by the formation of surface complex. And finally the electrochemical reduction of noble metal ions with carbons is the main factor, causing the selectivity of sorption of noble metals [11].

CONCLUSION

It was found out that reductive processes with ACs are characterized by different types of interactions between carbon matrix and adsorbed ion. Ion-exchange, complex-formation and electrochemical factors play an important role in sorption of noble metals by ACs from solutions and the selectivity is determined by a reductive mechanism of adsorption.

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