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The Role of Ion Exchange and Sorptive-Reduction for Interaction of Active Carbons with Noble Metals

Svitlana KOPYL, Vladimir LAPKO, Anatoliy LYSENKO, Yuriy TARASENKO and Isao TOMIZUKA*

Institute for Sorption and Problems of Endoecology

National Academy of Science of Ukraine, 13 Gen. Naumov Str., Kiev 03164, Ukraine

**Guest researcher from Japan Science and Technology Corporation*

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Abstract

The sorption behavior of ions on active carbons (ACs) was compared for three elements of the copper group, Cu, Ag and Au, between a basic AC and an acidic AC, and between a deaerated and aerated conditions. The difference among the sorption conditions was explained by assuming that the sorption proceeds partly by an ion exchange and partly by the reductive sorption. It was also discussed in terms of electrochemical impedance spectroscopy and quantum chemical analysis.

1 Introduction

Active carbons (ACs) are widely used as poly-functional materials. In addition to adsorbing properties, they have properties of ion solution environments on to or into a solid material. ACs are known to a sorpting exchange, surface complex-creator and reductor.[1]

As carbon has a high affinity to oxygen, ACs contain a certain amount of oxygen in the matrix or on the surface, irrespective of their manufacturing procedure. Some types of carbon always contain 4-6 % of oxygen in the matrix, when its thermally degassed in an inert atmosphere, cooled to room temperature and then contacted with air.[2] This oxygen is included of furan, pyron and carbonyl groups with the ACs. These carbons have the basic character, and they are electrochemical anion-exchangers with good reductive properties in electron transfer reactions.[3] Some types of carbon, oxidized by various oxidizers (HNO_3 , H_2O_2 etc.) or by a humid air at 400-450 °C, contain definite surface functional groups. They have the acidic character and cation-exchanger properties.[4]

The purpose of our work was to study characteristics of the sorption reaction of a basic and a acid AC from an identical parent AC when they come to contact with aqueous solutions of ions of three elements of the copper subgroup, Cu, Ag and Au in a deaerated and aerated conditions .

2 Experimental

A synthetic AC in a form of spherical grain was employed for this experiment. It was obtained by carbonization of a copolymer of vinylpyridine, followed by activation by water vapor. The AC contains 2-3 at. % of N and 4-8 at. % of O. Samples of basic and acidic carbons were prepared from AC by known techniques.[5,6]

Sorption experiments were performed in solutions of 0.01 M of HAuCl_4 (at pH=1) in 0.1 M HCl, 0.01 M CuCl_2 (at pH=1) in 0.1 M HCl, and 0.01 M of $\text{Ag}(\text{NH}_3)_2\text{Cl}$ (at pH=10) in 0.1 M NH_4OH . A solution of 0.1 M HCl ($M = \text{mol dm}^{-3}$) was used for electrochemical impedance spectrometry. Stationary electrode potential

of the ACs was observed in a solution of 0.1 M Na_2SO_4 as well as in the same solution pH-controlled with NaOH up to pH=10.[6,7] These solutions are denoted here as the solution A and the solution B, respectively.

Quantum chemical calculations were performed with the semi-empirical PM3 method by taking the d-orbitals of metal ions into account. Carbon matrix was simulated as graphite-like C_{54} cluster, containing 19 condensed aromatic rings. N-, and/or O-containing carbons were simulated by the heteroatoms into the π -conjugated system of carbon matrix ($\text{C}_{54-m-n}\text{N}_m\text{O}_n$). Calculation was performed for the energies of the highest occupied molecular orbitals (E_{HOMO}) and the chargers on metal atoms at their interactions with carbon clusters.

3 Results and Discussion

3.1 Ion exchange and reductive properties

In the deaerated solution, there was no significant difference among the amounts of sorbed elements on the basic AC and that on the acidic AC. They were 3.8 mmol/g, ~ 0.9 mmol/g and ~ 0.5 mmol/g for Au, Ag and Cu, respectively.

Table 1 The relationship between the number of proton-containing groups and the adsorption capacity in the aerated solution.

Sample	Number of O-containing groups in meq/g			Amount of sorbed elements (mmol/g)	
	weak-acidic -COOH	strong-acidic -COOH	phenol -OH	Cu	Ag
No.1 Basic	0.0	0.0	0.0	0.07	0.9
No.2 Acidic (1.0)*	0.2	0.2	0.6	0.17	0.35
No.3 Acidic (1.32)	0.2	0.8	0.32	0.23	0.48
No.4 Acidic (1.63)	0.4	0.8	0.43	0.28	0.65
No.5 Acidic (1.92)	0.4	0.8	0.72	0.31	0.74
No.6 Acidic (2.24)	0.4	0.9	0.94	0.36	0.82
No.7 Acidic (2.5)	0.4	1.0	1.1	0.39	0.88

* Samples 2-7 are acidic carbons with a different degree of proton-containing groups (according to Boehm titration).

In the aerated solution, the amount of sorption on the acidic AC was larger than on the basic AC for Cu, but the reverse was the case for Au and Ag. This fact was explained by assuming contribution of an ion exchange mechanism for Cu and partially for Ag. The acidic AC is a cation-exchanger. Au is present in a form of anion, $[\text{AuCl}_4]^-$, in the solution, while Ag and Cu are present in forms of cation, $[\text{Ag}(\text{NH}_3)_2]^+$ and Cu^{2+} . Data of the Table 1 show that the increasing of the content of carboxyl and phenol groups on AC leads to the increasing of the adsorption of Cu and Ag cations. The presence of these groups is not important for gold adsorption. Ion exchange for $[\text{AuCl}_4]^-$ on AC surface does not occur. Therefore, Au adsorption is less for strong acid carbons (1.3 mmol/g) than for basic carbon (3.8 mmol/g). Cations of $[\text{Ag}(\text{NH}_3)_2]^+$ is reduced up to metal on the basic carbon.

As compared with the deaerated solution, the sorbed amounts changed insignificantly for Au and Ag, but it decreased for Cu in the aerated solution. The reason for the decrease in the sorbed amount for Cu is accounted for by observing chronological variation of the electrode potentials of the ACs in the solutions A and B (Fig. 1). In Fig.1 the basic AC and the acidic AC were kept in the oxygen-free solutions at the start of the experiment. At the moment of the arrow, designated with " O_2 ", oxygen was introduced into the solutions. Then, the potential increased immediately for every case. The increase was particularly large for basic AC in the solution A (curve1). According to the conception of the reductive sorption (RS),[8] when a complex ion of a metal

in electropositive state is sorbed on the surface of an AC, its spontaneous electrochemical reduction is thermodynamically possible, if equilibrium potential of metal ions ($\varphi Me^{n+}/Me^0$) is more positive, than that of AC surface potential (φAC):

$$\Delta \varphi = \varphi Me^{n+}/Me^0 - (\varphi AC) > 0, Me - Au, Ag, Cu \quad (1).$$

Figure 1 shows, the oxidation/reduction potentials of all the elements are higher than the electrode potential of the basic AC in the deaerated solutions. RS by the basic AC is possible for all elements in the deaerated conditions. In the aerated conditions, while the potential $\varphi Me^{n+}/Me^0$ for Au in the solution A and for Ag in the solution B is higher than the electrode potential of the basic AC, the potential $\varphi Cu^{2+}/Cu^0$ in the solution A is lower than the electrode potential of the basic AC. Therefore, RS is possible for Au and Ag, but not for Cu.

The obtained results show that the molecular oxygen dissolved in electrolytes has essential influence on sorption-electrochemical processes of the ACs.[7,9] This conclusion is also confirmed by impedance measurements of an AC (Fig. 2).

Fig. 1 Variation of AC potentials in the solutions A (1– basic AC, 2 – acidic AC) and in the solution B (3–basic AC), together with the levels of the oxidation/reduction potentials of the relevant elements.

R_e – resistance of electrolyte; R_{tc} – resistance of charge transfer; C_{dl} – double layer capacity; C_a – capacity of adsorption; W – Warburg resistance.

Fig. 2 Impedance in 0.1M HCl under various environments (a) and its equivalent circuit (b)

It is seen from Figure 2 that, with increasing in oxygen concentration in the solution, the radius of the arc in the region near the origin decreases. It means that, with increase in the concentration of the dissolved oxygen, the resistance of charge transfer (R_{tc}) decreases, i.e. current characteristics of system increase.[10] The capacity C_a , calculated from equivalent circuit (Fig. 2b), characterizes the process of oxygen adsorption on carbon surface and it is proportional to the oxygen concentration in the solution.

3.2 Quantum chemical analysis

The obtained results for the process of metals reduction on AC are correlated by quantum chemical calculations of N-, O-containing graphite-like cluster electronic structure, simulating real carbon. Figure 3, as example, shows the structure of complexes of carbon cluster with Cu^{2+} and their E_{HOMO} . It is established that: 1) copper cations are coordinated with graphite-like cluster at aromatic cycle; the total negative charge is maximal on the distance of 15 - 18 nm from the surface cluster; 2) with the increase of electron-donor cluster properties (the shift of the value of E_{HOMO} to more positive energy) the positive charge on copper atom $\rho(Cu)$ decreases:

$$\rho(\text{Cu}) = -0.039 E_{\text{HOMO}} - 0.192; \quad r=0.966; \quad n=7 \quad (2)$$

Taking into account, that E_{HOMO} orbitals of investigated clusters are π (Pz) - orbitals, the obtained results testify, transfer of electronic density is carried out from the conjugated π -system clusters to $4s, p$ and $3d$ -orbitals of Cu^{2+} . This process of reduction is less effective for the acid carbons than for basic carbons; E_{HOMO} shifts to region of the more negative energy. Apparently, in this case the main role is played by local interactions of groups COO^- with cations of metal.

Fig. 3 The structure of graphite-like carbon clusters (without of hydrogen atoms) with Cu^{2+}

So, all there results permit to present the general scheme of the interaction of ions of copper subgroup metals with active carbons. Obviously, the adsorption of ions of gold on active carbons in deaerated and aerated conditions is accompanied by reduction of ions $[\text{AuCl}_4]^-$ to a metal state on carbon surface:

Ions of $[\text{Ag}(\text{NH}_3)_2]^+$ are less strong oxidizers, so, at the interaction of these ions with carbon it is possible as their reduction as the ion exchange:

The interaction of the acid carbon with copper ions occurs by ion exchange mechanism only:

and only the basic carbons in deaerated conditions can reduce Cu^{2+} up to metallic state.

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