

FACTORS DETERMINING THE SORPTION CAPACITY AND SELECTIVITY OF METAL-SUBSTITUTED CARBON SORBENTS FOR LIGAND SORPTION FROM THE GAS PHASE

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Introduction

In many cases, the selectivity of carbon-based sorbents is connected with formation of surface complexes between active centers of the surface and the substances to be adsorbed. But the feasibility of using such interactions, in particular complexation of metal ions with surface functional groups of the carbon sorbents, has been mainly studied for sorption from aqueous solutions [1,2]. The feasibility of using surface complex formation for selective sorption of substances from the gas (vapor) phase has not been well studied. In [2,3], the hypothesis was discussed that (Meⁿ⁺...OxCarb) surface complexes, formed on substitution of protons of acidic surface functional groups of oxidized carbons (OxCarb), are coordination unsaturated and consequently several molecules (ligands) can be inserted into free sites of the coordination sphere of a single center (surface complex), with formation of structures of the type – C-O-Me...L_n. Such a process (ligand sorption) promotes an increase in the capacity of the cation-substituted sorbents (MeOxCarb) for adsorption of various substances (L), for example water vapor, ammonia, etc. It could be assumed that during ligand sorption, in addition to an increase in the sorption capacity of MeOxCarb, selective absorption of individual components from complex mixtures may also occur, for example, because of the different strengths of the coordination bonds with the metal ions of the surface complexes in the components of these mixtures.

Because of the prospects for increasing the capacity and selectivity by means of modification of carbon sorbents by metal ions, it was of interest to establish if ligand sorption is also possible on different types of carbon sorbents for a large number of examples of sorption from gas/air mixtures of different types of substances (acidic, basic, neutral); to determine the effect on the sorption capacity and selectivity of carbon sorbents from the nature of the modifier (metal ions) and ways they are bound to the surface, the composition of the mixtures, the capacity of the components for complexation, and other factors. Such correlations, in our view, would allow us to determine the principles and routes to create new high-capacity and selective adsorbents for different types of substances from the gas phase, and also to evaluate the feasibility of practical application of such adsorbents.

Experimental

In this work, as the sorbents we used carbon sorbents of different origins with different porous structures and surface types. The starting materials were commercial carbons (AR-3, KAU) of different degrees of activation; heat-treated semicokes (HSC) having fairly small volumes for the sorption pores but a significant number of basic centers [4]; and also activated carbonaceous cloths (ACC) with extended porous structure. With the objective of elucidating the effect of structural characteristics on sorption, we carried out additional activation of the carbons AR-3 and KAU in a CO₂ atmosphere at 850°C for 3, 5, and 8 h (respectively AR-3-1, AR-3-2, AR-3-3 and KAU-1, KAU-2, and KAU-3). The semicokes were treated in a nitrogen atmosphere at temperatures of 300, 500, and 800°C [4] (HSC-1, HSC-2, and HSC-3 respectively). To obtain cation-substituted samples for ligand sorption, the indicated carbon sorbents were first oxidized according to the familiar procedures in [1] by air or nitric acid, and then metal ions were added to their surface by ion-exchange method in [1]: copper, manganese, iron, cobalt, nickel, etc. Furthermore, individual carbon sorbents were also modified by impregnation with nitrates of the corresponding metals, as in [3]. The described methods were used to obtain samples containing differently bound modifying additives in amounts of 0.10-0.12 mg-ion/g (with respect to the metal). In this case, the metal ions were bound on the oxidized samples mainly as a result of substitution of the hydrogen of the protogenic groups with formation of complexes, such as $-(\text{COO})_2\text{-Me}$ or $-(\text{COO})(\text{OH})\text{-Me}$ [1,2]. But in impregnated samples of conventional not oxidized carbons (AC), according to [1,3], for certain synthesis (modification) conditions, the metal compounds are inserted into the pores either in practically unchanged (water-soluble) form or as specifically adsorbed (as whole molecules), or as hydroxides or basic salts (formed as a result of side reactions).

The modified carbon sorbents were designated as follows: additionally activated – AC-1, AC-2, and AC-3; heat-treated semicokes – HSC-1, HSC-2, and HSC-3; Oxidized sorbents – AC-Ox; ionic forms of the oxidized adsorbent – Me-OxCarb; impregnated with metal salts – AC impreg.Me. The basic physicochemical characteristics of the sorbents used are presented in Table 1.

In this work, we used conventional methods [1,5] under static and dynamic conditions to study sorption from gas/air mixtures of water vapor, methanol, carbon disulfide, substances with acidic properties (acetic acid, hydrogen sulfide, sulfur and nitrogen dioxides) and basic properties (ammonia, diethylamine), and also hydrocarbons (methane, benzene, o-xylene). The sorption values under static conditions were usually determined gravimetrically; under dynamic conditions, from the results of analysis of mixtures that had passed through a column, using familiar chemical or gas chromatographic methods.

Comparison of the sorption values for carbon sorbents with different characteristics shows that for practically all the studied substances, in a series of carbons with different degrees of activation, an adsorption increases on the more activated carbons (Table 2). The adsorption capacity series are composed on the basis of experimental data determined for each substance under identical conditions. The series presented are mainly preserved for all activated carbons (AR-3, KAU, ACC, HSC), despite certain

differences in the test conditions for the different substances and sorbents. The values in the last column in Table 2 characterize the differences in the sorption values for the first and last members of the series (the first ratio) and the spread of the differences for different carbon sorbents (the second ratio). The sorption values are also not the same under identical conditions on activated carbons, semicokes, and cloth (Table 2).

Table 1. Physical and Chemical Characteristics of Carbon Sorbents

Sample	W_s , cm ³ /g based on C ₆ H ₆	V_{mi} , cm ³ /g	S_{sp} , m ² /g	A, mM/g		φ , Ω.cm
				Based on HCl	Based on NaOH	
KAU-1	0.60	0.36	650	0.38	0.12	-
KAU-2	0.70	0.42	750	0.58	0.10	-
KAU-3	0.82	0.52	840	0.74	0.02	-
KAU-2 impreg. Cu	0.62	0.34	630	-	-	-
KAU-20Ox	0.68	0.39	720	0.10	2.20	-
Cu-KAU-2-Ox	0.68	0.38	710	-	-	-
Co-KAU-2-Ox	0.67	0.38	720	-	-	-
Fe-KAU-2-Ox	0.67	0.37	710	-	-	-
AP-3-1	0.58	0.33	680	0.54	0.20	97
AR-3-2	0.62	0.32	730	0.68	0.10	56
AR-3-3	0.68	0.38	760	0.76	0.03	35
AR-3-3 impreg. Co	0.60	0.33	690	-	-	-
AR-3-3 impreg. Fe	0.55	0.31	670	-	-	-
AR-3-3-Ox	0.65	0.35	710	0.10	2.25	102
Co-AR-3-Ox	0.64	0.33	690	-	-	-
Fe-AR-3-Ox	0.63	0.31	690	-	-	-
HSC-1	0.08	0.05	-	1.00	0.80	6.1.10 ²
HSC-2	0.10	0.07	-	1.50	0.20	1.3.10 ²
HSC-3	0.12	0.08	-	2.40	-	87
HSC-3 impreg. Fe	0.12	0.08	-	-	-	120
SC-Ox	0.08	0.06	-	0.40	1.60	1.5.10 ²
Co-SC-Ox	0.10	0.08	-	-	-	-
Fe-SC-Ox	0.11	0.08	-	-	-	1.5.10 ²
ACC	0.62	0.51	720	0.62	0.15	72
ACC impreg. Co	0.51	0.39	630	-	-	68
CC-Ox	0.57	0.49	690	0.15	2.35	95
Co-CC-Ox	0.55	0.48	680	-	-	90
Fe-CC-Ox	0.55	0.49	680	-	-	-

Table 2. Sorption of Original and Modified Carbon Sorbents for Absorption of Various Substances

Sample	Substance	Adsorption capacity series for activated, oxidized, and metal-substituted carbon sorbents	Differences between adsorption values in the series
AR-3	SO ₂ , H ₂ S, HAc, CH ₃ OH, CH ₄ , C ₆ H ₆ , o-xylene	AR-3-Ox < AR-3-1 < AR-3-2 < AR-3-3	1:1.2-1:1.9
KAU	SO ₂ , H ₂ S, CS ₂ , HAc, CH ₃ OH, C ₆ H ₆ , o-xylene	KAU-Ox < KAU-1 < KAU-2 < KAU-3	1:1.3-1:1.8
HSC	SO ₂ , H ₂ S, CS ₂ , HAc, CH ₃ OH, C ₆ H ₆ , CH ₄ , o-xylene	HSC-Ox < HSC-1 < HSC-2 < HSC-3	1:1.3-1:2.5
Carbon sorbents	HAc, C ₂ H ₅ NH ₂ , SO ₂	HSC < AR-3 < ACC < KAU HSC < AR-3, ACC < KAU AR-3 < HSC < ACC < KAU	1:3-1:5 1:5-1:6 1:2-1:3
AC, AC-Ox, Me-OxCarb	H ₂ O	AC < AC-Ox < NaOxCarb < Ca-OxCarb < Cu-OxCarb < Cr ^{III} -OxCarb	1:3-1:5
AC, AC-Ox, Me-OxCarb	NH ₃	AC < AC-Ox < CaOxCarb < ACimpreg. Ni < ACimpreg. Co < ACimpreg. Cu < Ni-OxCarb < Co-OxCarb < Cu-OxCarb	1:7-1:15
AC impreg. Me	C ₂ H ₅ NH ₂	AC < AC-Ox < ACimpreg. Ni < AC impreg. Cu < Ni-OxCarb < Cu-OxCarb	1:3-1:5
“-“	NO ₂	AC-Ox < AC < ACimpreg. Ni < Ni-OxCarb < ACimpreg. Cu < Cu-OxCarb	1:3-1:7
“-“	SO ₂	AC-Ox < AC < ACimpreg. Co < ACimpreg. Cu < ACimpreg. Fe < Co-OxCarb < Ni-OxCarb < MnOxCarb < CuOxCarb < Fe-OxCarb	1:3-1:7
“-“	H ₂ S	AC-Ox < AC < ACimpreg. Co < ACimpreg. Fe < Co-OxCarb < Ni-OxCarb < Mn-OxCarb < Cu-OxCarb < Fe-OxCarb	1:3-1:8
”-“	CS ₂	AC-Ox < AC < ACimpreg. Co < ACimpreg. Fe < ACimpreg. Ag < Co-OxCarb < Cu-OxCarb < Fe-OxCarb	1:3-1:7
“-“	CH ₃ OH	AC < AC-Ox < Na-OxCarb < Ca-OxCarb < Cu-OxCarb < Cr ^{III} -OxCarb	1:3-1:5
“-“	HAc	AC-Ox < NaOxCarb < AC < CaOxCarb < ACimpreg. Cu < MnOxCarb < CoOxCarb < Ni-OxCarb < Cu-OxCarb < Fe-OxCarb	1:2-1:4
“-“	CH ₄ , C ₆ H ₆	AC-Ox < CuOxCarb < Acimpreg. Cu < AC	1:1.1-1:1.2
“-“	o-xylene	AC < ACimpreg. Cu < AC-Ox < Cu-OxCarb	1:1.3-1:1.4

However, this is not connected only with the structural characteristics. While for hydrocarbons and some other neutral substances the increase of adsorption in the series AR-3-1 – AR-3-3, KAU-1 – KAU-3 approximately corresponds to the degree of increase in the pore volumes and specific surface area (by a factor of 1.2 to 1.5), for sulfur dioxide, for example, sorption may increase more significantly (by a factor of ≈ 1.5 to 2.5).

Evidence that in this case the pore dimensions and volumes are not the determining factors comes in particular from the fact that significant amount of SO_2 (45 to 120 mg/g) are absorbed also by low-porosity semicokes (on AR-3 under the same conditions, 90-135 mg/g) with fairly small volumes for the sorption pores, but a significant number of basic surface functional groups (Table 1). The approximate correspondence between the increase of adsorption and the increase in the content of basic groups on the surface in HSC samples was also observed for other acidic substances: for CH_3COOH , from 4.1 to 8.9 mM/g, the value of τ (the duration of the “protective effect”) for H_2S increased by a factor of 1.8; for NO_2 , by a factor of 2.5.

For basic substances (ammonia, diethylamine), for all the studied carbon sorbents we observed an inverse correlation: higher sorption on the oxidized forms (also see [1]). The sorption values were also not identical on conventional and oxidized carbons for water vapor, methanol, and carbon disulfide and even for hydrocarbons, in particular o-xylene. The chemical nature of the surface had practically no effect only on sorption of such hydrocarbons as methane and benzene. However, the differences in the sorption values on carbon sorbents due the different nature of the surfaces, also known previously for some of the indicated adsorbates [1,2,5], turned out to be not so significant as when using carbon sorbents modified by metal ions.

The studies showed that under identical conditions, the greatest increase of adsorption for a series of substances capable of forming coordination bonds with the investigated cations may be achieved when using cation-substituted forms of the oxidized carbons. Significantly lower sorption values were observed under analogous conditions on carbon sorbents in which the dopant metal cations were introduced by impregnation, even for close and in some cases even for higher modifier contents. This is evident if we examine the adsorbability series, presented in Table 2, for the original, additionally activated, metal-compound impregnated, oxidized, and cation-exchanged carbon sorbents, and also for the example of sorption of sulfur compounds (SO_2 , CS_2) and nitrogen compounds (NH_3 , NO_2) by different carbon sorbents (Figs.1 and 2). Here, in most cases the values of τ for SO_2 and other substances significantly exceeded the corresponding values not only for the hydrogen forms of the oxidized carbons, but also for the original not oxidized carbon sorbents.

The established correlation suggest that on the cation-substituted forms of oxidized carbons, for substances capable of coordination binding with modifying metal ions, probably ligand sorption occurs with absorption of several molecules of the substances on the same active center ($-\text{C}-\text{O}-\text{Me}\dots\text{L}_n$). Such interactions probably are not typical for hydrocarbons, where modification of the carbon sorbents has practically no effect on sorption. As follows from the data obtained, ligand sorption depended markedly on the nature of the modifying cations, which is probably connected with the relative strength of

the coordination bonds Me...L in the surface complex formed. In fact, the sorbability series for water vapor, ammonia, amines, acetic acid for sorption by cationic forms of carbon sorbents are similar to the corresponding stability series for aqua complexes, ammoniates, amine and acetate complexes [6]. We see an approximate correlation also between the sorbability series of sulfur dioxides and the strength series of sulfate complexes, although the latter may be considered only as very approximate analogs surface complexes MeOxCarb-SO₂. The advantages of the cation-substituted forms compared with the "impregnated" samples most likely are connected with the fact that, on the complicated active center OxCarb-Meⁿ⁺, where the carbon matrix may also participate in complexation [1,2], more favorable conditions are created for sorption than during interaction of substances (ligands) with metal salts within the pore space.

As the system for determining the possibility for selective absorption of individual substances, we chose mixtures containing sulfur compounds (sulfur dioxide, hydrogen sulfide) and a large excess of methane: SO₂ (H₂S) : CH₄ = 1 : 20 (by weight), based on the fact that hydrocarbons have much less tendency toward formation of coordination bonds with the modifying metal ions [6,7]. Study of the system SO₂ (H₂S) – CH₄ is also of practical importance, since sulfur compounds are catalytic "poisons" for the sensitive elements of sensors for methane content in gas/air mixtures in the corresponding gas analyzers. The experiments showed (Fig. 1a) that in the presence of a large excess of methane, sorption of SO₂ by unmodified carbon sorbents significantly decreases; a substantial decrease is also observed when using impregnated carbons and cloth. The same effect is also observed in sorption of H₂S. However, when using cation-substituted (Fe, Cu, and Co) forms of oxidized carbons and cloths, the duration of the "protective effect" with respect to SO₂ (H₂S) remains practically unchanged, which suggests selective sorption of sulfur compounds.

For sorption from mixtures, where formation of coordination bonds between the substituting metal ions and various components of the mixture are about equally likely, we observe a complicated correlation between the sorbability of the individual components and their relative content. In particular, in the presence of water vapor, in a number of cases (such as in systems containing carbon disulfide, ammonia, etc.), we observe a significant decrease in the sorption values for the target components. It is quite likely that, specifically due to significant competition from the water molecules for the site in the coordination sphere, "ligand sorption" occurs on MeOxCarb (as our experiments showed for the case of ammonia sorption) more efficiently for absorption from gas/air mixtures than for absorption from aqueous solutions.

Based on these studies, we can say that modification with metal ions may be an effective means of increasing the sorption capacity and selectivity of carbon sorbents for sorption from the gas (vapor) phase. This approach is advisable for designing absorbers for such substances as sulfur and nitrogen compounds, water, carboxylic acids, etc. which can form sufficiently stable complexes with typical complexing ions (nickel, cobalt, copper, iron, manganese, etc.). The selectivity of such sorbents may be apparent in mixtures with substances that do not tend to form coordination bonds with Me-OxCarb surface complexes (hydrocarbons, neutral organic compounds, etc.).

The sorption capacity and selectivity of MeOxCarb can be controlled to some degree by the nature of the substituting cations, since the sorption values clearly correlate with the strength of the OxCarb-Me...L bond.

The indicated properties are typical for various types of carbon sorbents: granulated, fiber, pre-activated, and also heat-treated semicokes. The structural characteristics of the original carbon sorbents probably do not have a direct effect on the potential for ligand sorption or the course of that process. But the origin and pretreatment (activation, heat treatment) of the carbon sorbents is important to the extent that they determine the degree of order in the carbon matrix, which is a π -conjugated condensed system of graphite-like planes, and also the mobility of the electrons in the chain of conjugated bonds, that can be characterized by the electrical conductivity, since the carbon matrix can have an effect on surface complexation [1,2]. This is supported in particular by the favorable effect on sorption processes from increasing the conductivity φ of carbons (see the data in Tables 1 and 2).

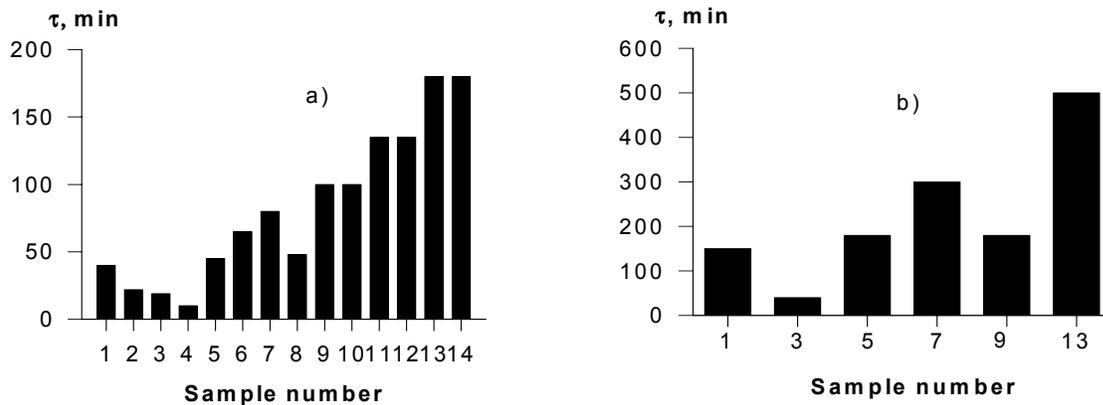


Figure 1. Duration of the "protective effect" for samples of OxCarb (1), AC (3), AC impreg Cu (6), AC impreg Fe (7), Co-OxCarb (9), Cu-OxCarb (11), Fe-OxCarb (13) for sorption of sulfur dioxide (a) and hydrogen sulfide (b) from one-component (relative to SO_2 and CS_2) gas/air mixtures and in the presence of an excess of methane by OxCarb (2), AC (4), AC impreg Fe (8), Co-OxCarb (10), Cu-OxCarb (12), Fe-OxCarb (14). Test conditions: a) AR-3 carbon, amount of adsorbent equal to 2g, SO_2 concentration of 0.2 vol.%, flow rate 250 mL/min; b) KAU carbon, amount of adsorbent equal to 5 cm³, CS_2 concentration of 100 mg/m³, flow rate 200 mL/min.

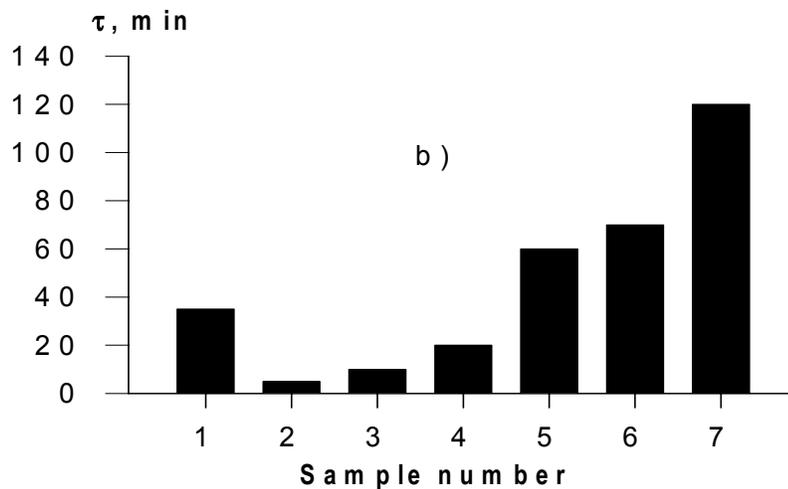
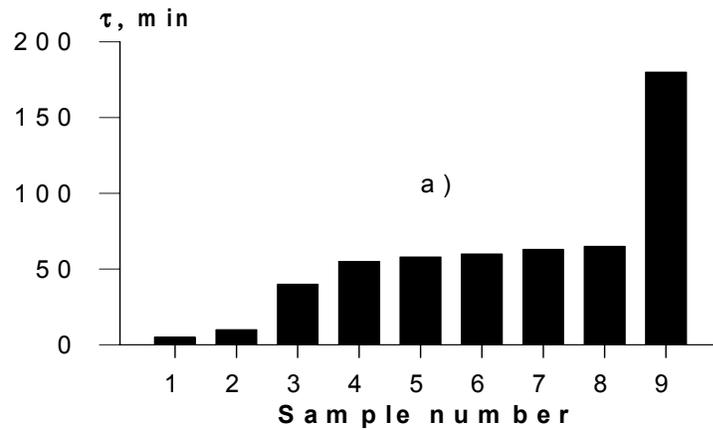


Figure 2. Duration of the “protective effect” for semicokes (a) [1) HSC-Ox; 2) HSC-1; 3) HSC-2; 4) HSC-3; 5) HSC impreg. Fe; 6) HSC impreg. Cu; 7) Co-HSC-Ox; 8) Fe-HSC-Ox; 9) Cu-HSC-Ox] and carbonaceous cloth (b) [1) CC-Ox; 2) ACC; 3) ACC impreg. Ni; 4) ACC impreg. Cu; 5) Ni-CC-Ox; 6) Co-CC-Ox; 7) Cu-CC-Ox] for sorption of nitrogen dioxide (a) and ammonia (b) from one-component gas/air mixtures. Test conditions: a) adsorbent volume of 5 cm³, NO₂ concentration of 65 mg/m³, flow rate 150 mL/min; b) amount of adsorbent equal to 2 g, NH₃ concentration of 150 mg/m³, flow rate 250 mL/min.

Conclusions

We synthesized high-capacity and selective MeOxCarb for absorption of sulfur and nitrogen compounds from gas/air mixtures and mixtures with hydrocarbons, for sorption of nitrogen dioxide, ammonia, amines, hydrogen sulfide, etc.

We have established that it is feasible to significantly increase the capacity and selectivity of carbon sorbents by modifying them with metal ions during sorption from gas/air mixtures of sulfur dioxides and nitrogen, hydrogen sulfide, carbon disulfide, diethylamine, acetic acid, etc.

We have determined the role of surface complexation and other factors affecting sorption.

We have determined the routes and principles for creating and using new high-capacity and selective sorbents for these materials based on various carbonaceous materials (activated carbons, carbonaceous cloths, semicokes).

We also have developed methods to use them effectively in systems for fine purification of air in various instruments and closed rooms, and for protection of sensitive elements of sensors for the content of methane and other compounds from catalytic "poisons" (SO₂, H₂S).

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