

Adsorption and Gas-Chromatographic Properties of Silver-Modified Silicas

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Abstract—Ag⁰ and Ag(I) nanoparticles are immobilized on the surface of a macroporous silica and amino silica. The adsorption kinetics of a basic dye, methylene blue (MB), from aqueous solutions and the adsorption isotherms of alkyne phenylacetylene from an octane solution are measured. The dependence of the rate constants of MB adsorption on the conditions of immobilization and silver reduction is considered. Silica containing immobilized Ag(I) is shown to have a high adsorption activity with respect to phenyl acetylene. By gas chromatography, it is shown that silver-modified silica has a higher selectivity with respect to alkenes. The reduction of silver on the silica surface and the complexation of silver ions with aminopropyl groups of amino silica lead to a significant decrease in the selectivity of composites.

Keywords: silver nanoparticles, silica, adsorption, gas chromatography.

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INTRODUCTION

Silver nanoparticles and silver-modified supports are widely used in electronics, spectroscopy, catalysis, water purification, medicine, and gas chromatography [1–4]. In this work, we investigated the adsorption and gas-chromatographic properties of composites that are based on silver nanoparticles immobilized on the surface of silica and silica modified with γ -aminopropyltriethoxysilane. The composites with immobilized Ag(I) and Ag⁰ were studied.

EXPERIMENTAL

Silica (silochrome 1) and amino silica containing particles 0.16–0.3 mm in size were used for immobilizing silver. Amino silica was obtained by modifying silica with γ -aminopropyltriethoxysilane from a toluene solution [5]. The specific surface of the silica determined by thermal desorption of nitrogen was 24 m²/g. The immobilization of the ammoniac silver complex on the silica was performed by three methods: without silver reduction, by partial silver reduction with formaldehyde (the molar ratio of formaldehyde and silver nitrate was 0.6 : 1), and by reduction in a tenfold excess of formaldehyde with respect to the quantity of silver nitrate. The samples were rinsed with water and dried at 120°C. The contents of silver in samples were 93 and 185 $\mu\text{eq/g}$ or 3.9 and 7.8 $\mu\text{eq/m}^2$, respectively.

Sorption of silver nitrate on silica modified with aminopropyl groups is the fourth method of silver immobilization. Silica modified with γ -aminopropyl-

triethoxysilane that contains 60 $\mu\text{eq/g}$ (2.5 $\mu\text{eq/m}^2$) amino groups was used for this purpose. The content of amino groups on the amino silica surface was determined by back titration with a 0.01 N solution of hydrochloric acid. The content of silver immobilized by sorption on the amino silica was determined by the dithizone method [6] in terms of the change in the concentration of silver ions in the solution, and the value was 30 $\mu\text{eq/g}$ (1.25 $\mu\text{eq/m}^2$). Relying on the ratio between the contents of aminopropyl groups and silver ions immobilized on the sorbent, we can conclude that, upon sorption, a complex of one silver ion with two aminopropyl groups of the modifier occurs on the surface. The reduced form of this sample obtained after its treatment with formaldehyde and removal of organic compounds from its surface by calcination at 600°C was studied.

Measurements of the adsorption kinetics of diphenyl thiazine dye, methylene blue, from water were carried out. Adsorbent batches of 10 mg each were shaken in 5 ml aqueous dye solutions. The concentration of the dye in the solution after adsorption was determined using a spectrophotometer at a wavelength of 600 nm.

The isotherms of phenylacetylene adsorption from an octane solution were measured. The concentration of phenylacetylene was determined in terms of the optical density of the solutions at 245 nm.

Gas-chromatographic measurements were carried out using a Tsvet 100 chromatograph equipped with a flame ionization detector (glass columns with dimen-

Table 1. Composite samples, methods for their preparation, and content of silver

Sample no.	Sample	Sample composition		Preparation method
		mg/g	$\mu\text{eq}/\text{m}^2$	
1	initial silica	0	0	impregnation of silica with AgNO_3 ammoniac solution from no. 2 by reduction in excess of formaldehyde
2	Ag(I)silica(10)	10	93	
3	$\text{Ag}^0/\text{silica(10)}$	10	93	
4	Ag(I)/silica(20)	20	185	impregnation of silica with AgNO_3 ammoniac solution from no. 4 by reduction in deficiency of formaldehyde
5	$\text{Ag(I)+Ag}^0/\text{silica(2G)}$	20	185	
6	$\text{Ag}^0/\text{silica(20)}$	20	185	from no. 4 by reduction in excess of formaldehyde sorption of AgNO_3 on amino silica
7	$\text{Ag(I)/silica amino(5)}$	5	46	
8	$\text{Ag}^0/\text{silica(5)}$	5	46	from no. 7 by calcination at 600°C
9	calcined silica	0	0	from amino silica by calcination at 600°C

sions of 70×0.2 cm). Nitrogen was used as a carrier gas. The rate of carrier gas flow was kept constant around 30 ml/min, while the parameters of chromatographic retention were varied. Prior to the experiment, the sample was conditioned in a chromatographic column under a nitrogen flow at 150°C for 20 h. As adsorbates, the following hydrocarbons were used: *n*-alkenes ($\text{C}_6\text{--C}_8$), *n*-alkanes ($\text{C}_6\text{--C}_8$), cyclohexane, and cyclohexene.

In order to determine the adsorption properties of the sorbents, the specific retention volumes, V_g , were measured for all adsorbates in the range of a low filling. The differential molar change in the internal energy of adsorption ($-\Delta U$) equal to the differential heat of adsorption (Q_v) was determined over the dependence of the specific retention volumes on the temperature

($\ln V_g = f(1/T)$). The selectivity (α) of the composite surface to the retention of olefins was estimated in terms of the $V_g(n\text{-alkene})/V_g(n\text{-alkane})$ and $V_g(\text{cyclohexene})/V_g(\text{cyclohexane})$ ratio values [7].

RESULTS AND DISCUSSION

The characteristics of composites and methods for their preparation are listed in Table 1.

In order to determine the effect of modifying the silica surface with silver nanoparticles, we measured the kinetics of adsorbing methylene blue from the aqueous solutions on the initial silica (see Table 1, no. 1) and on two samples modified with silver from the ammoniac complexes (see Table 1, nos. 5 and 6). The content of silver in these samples was the same; its value was $187 \mu\text{eq}/\text{g}$. The surface concentration in this case was rather high; its value was $7.8 \mu\text{eq}/\text{m}^2$. In maximally hydroxylated silica, the concentration of hydroxyl groups is similar to this value [8]. One sample did not contain silver. In the second sample, silver was reduced partially in a deficiency of formaldehyde. The molar ratio between formaldehyde and silver was 0.6 : 1. In the third sample, silver was completely reduced in a tenfold excess of formaldehyde. Both silver-containing samples became yellow after reduction, which indicates the presence of Ag^0 nanoparticles on the silica surface.

The kinetics of methylene blue adsorption on these three samples is shown in Fig. 1. It is clear that the least adsorption is observed for nonmodified silica, while the most adsorption is seen for the silica sample that contains silver partially reduced by formaldehyde. The adsorption of the dye on the silica modified with silver that was reduced in a tenfold excess of formalde-

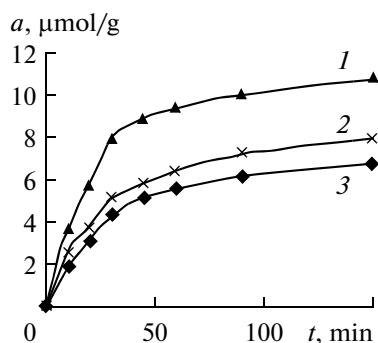


Fig. 1. Kinetics of adsorption of methylene blue from water measured on the following samples: (1) $\text{Ag(I)+Ag}^0/\text{silica(20)}$; (2) $\text{Ag}^0/\text{silica(20)}$; (3) initial silica. The initial concentration of methylene blue is $30 \mu\text{mol}/\text{l}$, the volume of the solution is 5 ml, and the weight of the sorbent is 10 mg.

Table 2. Limiting adsorption a_∞ ($\mu\text{mol/g}$) and adsorption rate ω ($\mu\text{mol}/(\text{g min})$) of methylene blue on the initial (1) silica and silica modified with partially reduced silver (5) and with completely reduced silver (6). The content of silver is 187 $\mu\text{eq/g}$. The specific surfaces of the sorbents are denoted by S (m^2/g). The initial concentration of the dye is 30 $\mu\text{mol/l}$, the volume of the solution is 5 ml, and the weight of the sorbent is 10 mg

Parameter	Sample		
	1 Initial silica	5 (Ag(I)+Ag ⁰ /silica(20))	6 (Ag ⁰ /silica(20))
S , m^2/g	24	27	27
a_∞ , $\mu\text{mol/g}$	8.5	11	9.7
ω , $\mu\text{mol}/(\text{g min})$	0.14	0.31	0.15

hyde is significantly lower than on the sample containing partially reduced silver.

The kinetic data were treated in accordance with the Langmuir adsorption theory using the following relation [9]:

$$da/dt = k_f(a_\infty - a) = k_r a - k_f a,$$

from where $\ln(a_\infty - a) = \ln a_\infty - k_f t$,

where a ($\mu\text{mol/g}$) is the adsorption, a_∞ ($\mu\text{mol/g}$) is the adsorption after equilibrium is reached, t (min) is the time, and k_f (min^{-1}) is a rate constant. When $t \rightarrow 0$ and $a \rightarrow 0$, the adsorption rate is $\omega = k_f \cdot a_\infty$, $\mu\text{mol}/(\text{g min})$.

The values of the equilibrium adsorption and the rate of adsorbing the dye on the initial silica and two silver-modified samples are shown in Table 2. According to these data, the maximum adsorption rate, $\omega = 0.31 \mu\text{mol}/(\text{g min})$, is observed for the silica that contains partially reduced silver. For the initial silica and silica modified with silver in a tenfold excess of formaldehyde, the adsorption rate is significantly lower; their values of 0.14 and 0.15 $\mu\text{mol}/(\text{g min})$, respectively, are almost the same.

A significantly lower adsorption activity of the silica that contains immobilized silver reduced in excess of formaldehyde in comparison to the activity of the silica containing silver reduced in deficiency of formaldehyde might be related to the presence of univalent silver particles that have an affinity for the thiazine group of the dye in the second case. The specific surface measured by thermal adsorption of nitrogen is similar for both modified samples; its value is 27 m^2/g , which, within the error, is close to the specific surface of the initial silica, whose value is 24 m^2/g .

The adsorption of methylene blue on the silica with immobilized Ag⁰ was measured; this type of silica was obtained by sorption of silver nitrate on amino silica followed by reduction and calcination at 600°C (see Table 1, no. 8). This sample became yellow after its calcination. The content of silver was 0.03 meq/g. The adsorption of the dye was similar to the adsorption of sample no. 9, which was prepared from the initial silica sample by its treatment with formaldehyde and was

calculated in the same manner as the silver-modified sample. Thus, this silver-containing composite has no affinity for the dye.

Relying on the data on the adsorption of methylene blue, we can conclude that the conditions of silver reduction play a significant role in obtaining adsorptionally active forms of silver immobilized on the silica surface. Reduction of silver in a large excess of a reducer followed by the calcinations of amino silica with adsorbed silver leads to a loss in adsorption activity.

The isotherms of adsorption of phenylacetylene from its octane solution on the initial silica (Table 1, no. 1) and on the silica containing unreduced silver in the amount of 7.8 $\mu\text{mol}/\text{m}^2$ (Table 1, no. 4), partially reduced silver (Table 1, no. 5), and completely reduced silver (Table 1, no. 6) are shown in Fig. 2. According to these data, the adsorption on the unmodified silica is insignificant. The limiting adsorption a_m is less than 0.1 $\mu\text{mol}/\text{m}^2$. Adsorption dramatically increases by approximately a factor of 30 ($a_m = 2.7 \mu\text{mol}/\text{m}^2$) on the silica modified with unreduced silver. The high adsorption activity of this kind of composite occurs owing to the ability of phenylacetylene to form complexes with univalent silver by interacting with π -elec-

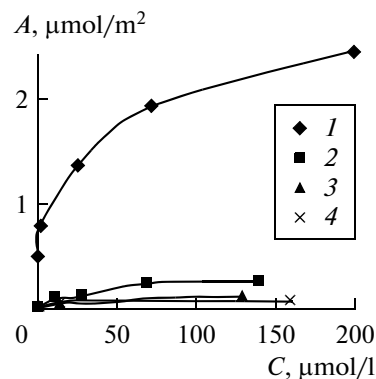


Fig. 2. Isotherms of adsorption of phenylacetylene from *n*-octane solutions on the following samples: (1) Ag(I)/silica(20), (2) Ag(I)+Ag⁰/silica(20), (3) Ag⁰/silica(20); (4) initial silica.

Table 3. Heats of adsorption, Q (kJ/mol), of the normal alkanes and alkenes, $Q = Q_{\text{alkene}} - Q_{\text{alkane}}$, and retention volumes, V_g (cm³/g), at 100°C on the silica and silver-containing Ag/silica composites

Adsorbent	Number of atoms in molecule	<i>n</i> -alkanes		<i>n</i> -alkenes		$\Delta Q = Q_2 - Q_1$
		Q_1	V_g	Q_2	V_g	
Initial silica	6	33.1	1.3	42.2	2.2	9.1
	7	38.7	2.3	47.3	4.2	8.6
	8	44.4	3.9	52.3	7.6	7.9
Ag ⁰ /silica(10)	6	49.8	2.7	52.7	4.0	2.9
	7	55.9	3.8	58.5	11.3	2.6
	8	60.0	5.7	65.3	55.9	5.3
Ag(I)/silica amino(5)	6	30.8	3.2	38.8	2.7	8.0
	7	36.7	7.1	46.0	6.0	9.3
	8	42.0	16.5	50.9	15.6	8.9
Ag(I)/silica(10)	6	37.8	2.4	81.5	—	—
	7	47.3	5.0	508.6	—	—
	8	56.9	10.5	—	—	—

trons of the acetylene group and phenyl ring. Three molecules of silver immobilized in the limiting monolayer correspond to one phenylacetylene molecule. This ratio indicates a significant availability of immobilized silver for adsorption, since it is distributed over the silica surface rather uniformly. Complete silver reduction causes a loss in the adsorption activity of its nanoparticles. Adsorption on the corresponding composite (Table 1, no. 6) becomes the same as on the unmodified silica. Adsorption is a somewhat higher on the composite containing partially reduced silver than on the initial silica ($a_m = 0.25 \mu\text{mol}/\text{m}^2$).

The inverse gas chromatography method [10, 11] is successfully used for investigating the surface chemistry and the adsorption properties of different materials. By means of this method, we studied changes in the properties of the silica surface occurring upon its modification with silver.

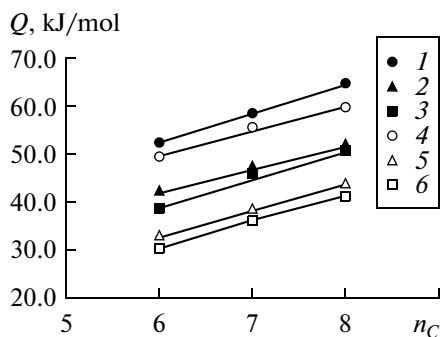


Fig. 3. Q (kJ/mol) vs. the number of carbon atoms n_C in a molecule of *n*-alkenes (1–3) and of *n*-alkanes (4–6) found on the Ag⁰/silica, initial silica, and Ag(I)/silica amino composites, respectively.

The heats of adsorption calculated in accordance with the $\ln V_g = f(1/T)$ relation and the retention volumes of *n*-alkanes and alkenes on the surfaces of the following four sorbents at 100°C are shown in Table 3: on the initial silica; silica modified with unreduced (Table 1, no. 2) and reduced silver; and on the sample that contains the silver nitrate complex immobilized on amino silica (Table 1, no. 7).

The linear dependence of the values of the heat of adsorption on the listed samples on the number of carbon atoms in *n*-alkane and *n*-alkene molecules is shown in Fig. 3. According to the data presented in Table 3 and Fig. 3, the values of the heat of adsorption of *n*-alkenes are higher than the values of *n*-alkanes containing the same number of atoms in a molecule for all investigated surfaces. This is due to an extra specific interaction of π -bonds in *n*-alkenes with active sites on the surface.

The immobilization of silver nanoparticles on the silica surface leads to an increase in the values of the heat of adsorption of *n*-alkanes on the initial silica and silica modified with unreduced silver, Ag(I)/silica(10) (Table 1, no. 2), and reduced silver, Ag⁰/silica(10) (Table 1, no. 3). The growth in the heat of adsorption of *n*-alkanes, which indicates an increase in the adsorption capacity of the surface, most likely is due to an increase in the specific surface occurring upon deposition of silver particles on it [12].

Another situation is observed in the case of depositing silver on amino silica. The values of the heat of adsorption of *n*-alkanes decrease slightly (on average by 2 kJ/mol) upon moving from the initial silica to the amino silica containing sorbed silver nitrate (Table 1, no. 7). Most likely, this is due to a decrease in the num-

Table 4. Selectivity values α (V_g *n*-alkene/ V_g *n*-alkane) for the Ag/silica composite at 40°C

α	Initial silica	Ag(I)/silica(10)	Ag ⁰ /silica(10)	Ag(I)/silica amino(5)
<i>n</i> -hexene/ <i>n</i> -hexane	2.2	150	4.7	0.7
<i>n</i> -heptene/ <i>n</i> -heptane	3.0	118	2.0	0.8
cyclohexene/cyclohexane	4.1	250	—	—

ber of adsorption sites (because of the screening of hydroxyl groups on the silica surface during surface amination) [8].

In order to determine how the properties of the silver-containing composite surfaces depend on the methods of their preparation, the selectivity values of the retention of olefins were used. The selectivity values, αV_g (*n*-alkene)/ V_g (*n*-alkane), on the silver-containing composites prepared by different techniques at 40°C are listed in Table 4. According to the data from Table 4, on the Ag(I)silica (Table 1, no. 2) containing silver in the amount of 93 $\mu\text{mol/g}$, the retention volumes of *n*-hexene and cyclohexene have very high values, meanwhile the retention volume values of *n*-hexane and cyclohexane are small. A strong retention of olefins indicates a high selectivity of this composite to unsaturated hydrocarbons that occurs owing to the specific interaction of π -electrons of alkene molecules with Ag(I). In this case, a partial chemisorption of olefins is observed: the first probes do not come out of the column, which makes it impossible to measure their heat of adsorption. On the Ag/silica (Table 1, no. 3) containing the same amount of reduced silver, 93 $\mu\text{eq/g}$, *n*-alkenes are retained more strongly than *n*-alkanes containing the same amount of carbon atoms in a molecule. However, the difference in retention is slight for this case. There is no selectivity of retaining *n*-alkenes in comparison to *n*-alkanes on the amino silica containing immobilized silver nitrate (Table 1, no. 7). According to the difference in the retention and the data from Table 4, the selectivity of olefin sorption on the Ag(I)/silica composite (Table 1, no. 2) is many times higher than the selectivity on the initial silica and also on the Ag⁰/silica (Table 1, no. 3) and Ag(I)/amino silica (Table 1, no. 7).

Thus, a significant specific sorption of *n*-alkenes and *n*-alkanes is observed on the composite containing immobilized silver(I). The reduction of silver on the silica surfaces, as well as the complexation of silver ions with surface amino groups, leads to a significant decrease in the specificity of the corresponding com-

posite sorbents. The gas-chromatographic data are in agreement with the data on the adsorption from the solutions.

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