

GEOMETRICAL AND CHEMICAL MODIFICATION OF SILICA MATRICES AT HIGH PRESSURES OF REAGENTS

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Abstract

The effect of temperature and composition of modifying mixture, as well as mode of carrying out the process of hydrothermal (with water and with the mixture of water and some organic substances) modification of silica gels and silica in the form of hydrogel-xerogel, on the parameters of the pristine adsorbents have been studied. The peculiarities of interaction between some organic substances and dispersed silica at high pressures and high temperatures were considered. These investigations were performed by IR spectroscopy, differential thermal analysis, and the porous structure characterization of the modified silicas. It was shown that depending on the nature of the compound used for modification such organic substances can promote the process of silica mass transfer. During this process, the possibility occurs of the occlusion of the modifying reagent inside silica globules, changes in the parameters of the porous structure, physical or chemical bonding of the modifier molecules with the silica surface. Possible mechanism of geometrical and chemical modification of silica adsorbents is discussed.

Introduction

Over a period of several years the Polish team from the Chemical Department of Maria-Curie Skłodowska University in Lublin in co-operation with the Ukrainian team from the Institute of Surface Chemistry of National Academy of Sciences of Ukraine have made studies into the elaboration of methods of geometrical and chemical modification of silica matrices, including silica modification under high reagent pressure [1-14]. Obtained data can be subdivided into some groups:

- regularities of chemical and geometrical modification of silicas by water-alcohol mixtures;
- peculiarities of interaction of organic substances with silica at high pressure of reagents;
- synthesis and characterization of new type carbon-silica adsorbents - carbo-aerosils.

In this paper we will summarize briefly main results concerning modification of silicas by water, water-alcohol mixtures and organic compounds under high reagent pressure.

Geometrical and chemical modification of silicas by water and water-alcohol mixtures

The formation processes of silica texture depend on many factors and therefore they are difficult to be controlled. Consequently, xerogels are often modified either thermally or hydrothermally in order to obtain silica gels of the required properties.

Peculiarities of hydrothermal treatment of silica in the form of hydrogel-xerogel were

studied in the paper [2]. From an analysis of the obtained data there emerges a new hydrothermal silica treatment based on hydrogel-xerogel. This includes, first, processes specific for hydrothermal treatment of both hydrogels and xerogels, as well as drying gel in an autoclave and second, it combines the advantages of both treatment forms. That is, the new procedure allows one to regulate specific surface area (S), pore volume (V_p) and also to synthesize very high-porosity samples characterized by high V_p , and low S values, with sufficiently large mechanical strength. One of the technological drawbacks of this kind of hydrothermal treatment is its low efficiency (at least $<300^\circ\text{C}$) because the level of autoclave loading with silica does not exceed 25 %. Thus, the treatment can be effective in the temperature range $350\text{--}400^\circ\text{C}$. It is also necessary to point out that hydrogel-xerogel hydrothermal treatment is more effective for preparation of spherical and microspherical silica gels characterized by smaller porosity and higher mechanical strength.

The paper [11] was devoted to investigations on the mechanism of high pressure hydrothermal treatment of pyrogenic silicas (aerosils) as well as titania- and alumina-containing fumed silicas. The aerosils were modified by using different sizes of primary particles as well as by containing 8 and 9 % w/w of Al_2O_3 and TiO_2 respectively. Hydrothermal treatment process was performed in the gas phase (overheated steam with and without addition of ammonia) in the temperature range $100\text{--}350^\circ\text{C}$. The changes of surface properties of the adsorbents tested caused by hydrothermal modification were determined on the basis of adsorption isotherms of water, methanol, carbon tetrachloride, *n*-hexane and benzene, and using the data relating to chemisorption of hexamethyldisilazane as well as on the basis of specific surface area determined by the method of thermal desorption of argon. It was stated that the hydrothermal treatment of fumed silica leads to the increase of hydroxylation degree of their surface. In the hydrothermal treatment mechanism the processes of mass transfer of silica in the gas (steam) phase play a very important role. The intensity of these processes depends on the size of primary particles (globules) of modified adsorbent, on its chemical composition, and on the presence of ammonia in steam. The possibilities of utilizing the processes occurring in the vapour (steam) phase to prepare porous coverages (layers) were demonstrated.

The effect of fumed silicas on hydrothermal treatment of narrow and mesoporous silica gels possessing various sizes of primary globules was studied [12]. The hydrothermal treatment was carried out in the autoclave at 200°C (6 h) in the liquid and gaseous phases. In the systems studied, aerosil was in the form of mechanical mixture with silica gel or constituted a separate phase in the aqueous suspension form. It was stated that the presence of pyrogenic silica during the hydrothermal modification of silica gels affects the size of their specific surface area, average pores size and curves of pores volume distribution based on their radii. The extent of observed changes depends on the porous structure of initial adsorbents. The investigations show that it is possible to transfer the silica mass through the gaseous phase during the hydrothermal treatment. It was also pointed out that intensity of silica mass transfer observed during the hydrothermal modification in the gaseous phase does not differ from the mass transfer in the liquid phase systems. It was observed that for both silica gels studied relative efficiencies of the hydrothermal treatment are similar. This makes it possible to predict the extent of structural changes in the silica matrix, for silica gels of different porous structure, under the similar hydrothermal treatment conditions.

Possibility of simultaneous geometrical and chemical modification was shown on the example of treatment of silicas by water-butanol mixtures at 250°C for 5 hrs [1]. Two laboratory samples of silica gels were modified, namely pure aerosilogel ($V_p = 1.37\text{ cm}^3/\text{g}$) which was produced from suspension of fumed silica (aerosil, $S=343\text{ m}^2/\text{g}$) in water by an

extrusion route, and narrow-pore silica gel ($S=244 \text{ m}^2/\text{g}$ and $V_p = 0.28 \text{ cm}^3/\text{g}$) characterized by the ability to form closed pores during the hydrothermal treatment with pure water. Water-butanol mixtures were used as modifiers and these mixtures contained the following amounts of water (% w/w): 20.5 (saturated solution of water in alcohol), 32, 38.5, 42.5 (heterogeneous azeotrope) and 91.0 (saturated solution of *n*-butanol in water). The modifying reagent was introduced into an autoclave either in a form of the mixture or in a form of individual (separate) compounds. In both cases into the autoclave there were introduced such amounts of water and *n*-butanol which are necessary to obtain equilibrium vapour pressure for a given temperature. The temperature of treatment was 150-350°C and time of treatment 1-6 hrs. Some from obtained results are presented in Tables 1-3 and Fig. 1,2.

The experimental observations were as follows: possibility of simultaneous geometrical and chemical modification of wide-porous aerosilgel is realized if water content in the reaction mixture was less 32 % w/w; besides surface butoxy groups there is a fraction of butanol molecules which are occluded in an interior of the aerosilgel globules; as usually at hydrothermal treatment silica mass transfer takes place and the smallest silica particles which possess maximum surface energy are the first to be dissolved, therefore as a result of this process, the dissolved silica is transferred and deposited onto bigger particles whose surface energy is smaller; we observed the decrease in *S* of modified silica, and increase of pore diameter from 16 up to about 70 nm and dissolution and mass-transfer processes are intensified and accelerated when high pressures and temperatures are used; in the majority of cases alcohol molecules provide the inhibiting effect on the globule growth process.

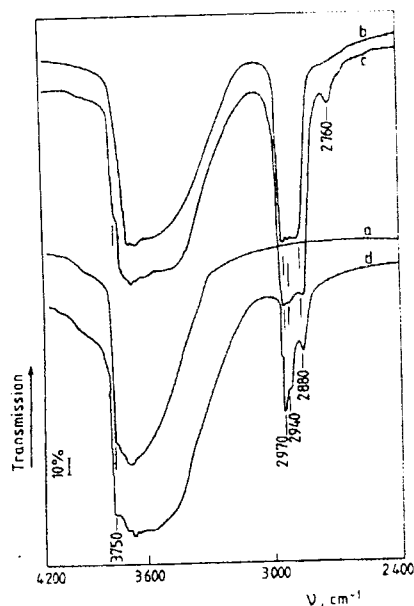


Fig. 1. IR spectra of aerosilgel (a) after modification at 250°C by *n*-butanol (b) and its mixtures with 20.5 (c) and 38.5% w/w water (d)

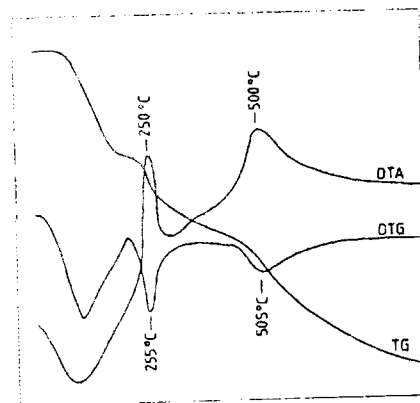
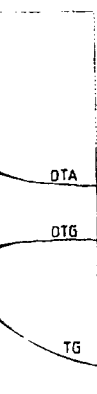


Fig.2. Derivatograms of the silica gel modified by the mixture contained 57.5% (w/w) of *n*-butanol and 42.5% of water

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Studies of modification process of two silica gels which are characterized by different porous structure with water/butanol mixture in hydrothermal conditions have shown that there exists a possibility of simultaneous physical and chemical modification of wide-pore aerosilogel ($V_p=1.37 \text{ cm}^3/\text{g}$, water content in modifying mixture $< 32 \text{ \% w/w}$) and in a larger degree of narrow-pore silica gel ($V_p=0.28 \text{ cm}^3/\text{g}$, water content in modifying mixture is 43.54 \% w/w). It is shown that a fraction of butanol molecules is occluded in the interior of the globules of aerosilogel, whereas in the case of silica gel the closed porous structures containing the butoxy groups are formed. These butoxy-groups can be removed only at high temperatures, i.e. $485\text{--}525 \text{ }^\circ\text{C}$.

Table 1

The effect of water/*n*-butanol mixture composition on the parameters of the aerosilogel porous structure after treatment in an autoclave 5 hrs at $250 \text{ }^\circ\text{C}$

Modifying reagent	Form of the Modifier	Specific surface area, S , m^2/g	Total pore volume, V_p , cm^3/g	Pore diameter, d_p , nm
Initial silica		343	1.37	16.0
<i>n</i> -C ₄ H ₉ OH		214	1.21	22.5
20.5% H ₂ O+79.5% <i>n</i> -C ₄ H ₉ OH	mixture separately	188	1.20	28.0
		186	1.25	30.0
32.0% H ₂ O+68.0% <i>n</i> -C ₄ H ₉ OH	mixture separately	159	1.30	38.5
		166	1.35	32.0
38.5% H ₂ O+61.5% <i>n</i> -C ₄ H ₉ OH	mixture separately	144	1.37	45.0
		139	1.38	50.0
42.5% H ₂ O+57.5% <i>n</i> -C ₄ H ₉ OH	mixture separately	127	1.37	52.0
		132	1.37	51.0
91.0% H ₂ O + 9.0% <i>n</i> -C ₄ H ₉ OH	mixture separately	127	1.39	53.5
		112	1.37	60.0
H ₂ O		103	1.38	68.5

As known, under hydrothermal modification the globular structure of silica gels may change into a spongy structure, crystalline or glassy state depending on the conditions. These

processes occur in the whole mass of modified silica and therefore its surface becomes heterogeneous. This heterogeneity depends on the amount of water used for the modification. A large amount of water in relation to silica gel permits one to prepare more homogeneous grains, but it also makes the nature of decondensation and recondensation processes more violent which, in turn, leads to a considerable reduction of the specific surface of the modified silica. Due to the inhibiting effect of alcohol molecules the processes of the globule growth are less evident and thus easier to control, even at large water amounts, homogeneous grains of modified silica are obtained in this route.

Table 2

The effect of water / *n*-butanol mixture composition on the parameters of the aerosiligel porous structure after treatment in an autoclave 5 hrs at different temperatures

Modifying reagent	Temperature, °C	Specific surface area, S, m ² /g	Total pore volume, V _p , cm ³ /g	Pore diameter, d _p , nm
Initial silica		343	1.37	16.0
<i>n</i> -C ₄ H ₉ OH	200	270	1.25	18.5
	250	214	1.21	22.5
	300	231	1.27	22.0
20.5% H ₂ O+79.5% <i>n</i> -C ₄ H ₉ OH (mixture)	200	215	1.28	24.0
	250	188	1.20	28.0
	300	151	1.30	34.5
20.5% H ₂ O+79.5% <i>n</i> -C ₄ H ₉ OH (separately)	200	220	1.31	24.0
	250	186	1.25	30.0
	300	166	1.30	35.5
38.5% H ₂ O+61.5% <i>n</i> -C ₄ H ₉ OH (mixture)	200	156	1.38	38.0
	250	144	1.37	45.0
	300	68	1.37	80.5
38.5% H ₂ O+61.5% <i>n</i> -C ₄ H ₉ OH (separately)	200	155	1.37	36.0
	250	139	1.38	45.0
	300	56	1.37	98.0
H ₂ O	200	177	1.37	31.0
	250	103	1.38	68.5
	300	60	1.37	91.5

Table 3

The effect of water/*n*-butanol mixture composition on the parameters of the finely porous silica gel structure after treatment in an autoclave for 6 hrs at different temperatures

Modifying reagent	Temperature, °C	Specific surface area, S, m ² /g	Total pore volume, V _p , cm ³ /g
Initial silica		244	0.28
20.5% H ₂ O+79.5% <i>n</i> -C ₄ H ₉ OH	150	206	0.20
	200	129	0.16
	250	107	0.08
	300	13	0.04
	350	10	0.02
38.5% H ₂ O+61.5% <i>n</i> -C ₄ H ₉ OH	150	215	0.27
	200	150	0.25
	250	106	0.23
	300	58	0.22
	350	37	0.17
42.5% H ₂ O+57.5% <i>n</i> -C ₄ H ₉ OH	150	165	0.19
	200	102	0.15
	250	9	0.03
	300	6	0.03
	350	4	0.04
91.0% H ₂ O+9.0% <i>n</i> -C ₄ H ₉ OH	150	38	0.21
	200	25	0.18
	250	10	0.04
	300	7	0.02
	350	5	0.02

Peculiarities of silica modification at high pressures of some organic and organosilicon compounds

In the paper [5] an effect of the following factors on the chemical and geometrical modification of aerosilogel (prepared from fumed silica) was studied: the physicochemical characteristics of the modifying reagent pressures, the preparation conditions for the silica surface, the reaction temperature, the reagent pressures, the duration of treatment and the method employed for the modification process. The course of the surface reaction was followed by IR spectroscopy, differential thermal analysis and adsorption. It was demonstrated that the geometrical parameters of the porous silica structure may be changed during high-pressure modification. From an analysis of the experimental data obtained [5], the

following conclusions were drawn. The effect of the substance used for modifying the surface properties of the silica depends above all on the method whereby the process is conducted (liquid, vapour or solution, temperature, pressure) and on the mechanism of its interaction with the surface. An analysis of the kinetic data indicates that 4-5 h are sufficient for completion of the surface modification process. Because the pressure of the modifying substance considerably exceeds that of the water vapour desorbed from the silica surface, an initial thermal treatment of the adsorbent in a vacuum (practically always indispensable in normal processes involving the gaseous and liquid phases) is often not necessary. Virtually the whole extent of the modification process (80-90%) can be achieved at pressures which are only 0.2-0.3 times the equilibrium value. All increase in temperature favors a greater extent of modification, temperatures of the order of 200-300 °C are usually sufficient to attain a maximum degree of surface coverage with bound organic radicals. For modifications proceeding under high reagent pressures, chemical modification is most likely as well as immobilization of the organic phase on the surface by adsorption forces. In order to determine the type of interactions involved in such cases, accurate washing of the silica with an appropriate solvent is indispensable for removing the adsorbed organic phase, followed by checking the sample using various techniques. However, when physical or chemical immobilization occurs, geometrical modification of the adsorbent, i.e. a change in the parameters of its porous structure, takes place.

The modes of interaction between organic substances and aerosilgel at high pressures and high temperatures were considered in the paper [6]. The following types of substances were used as modifiers of the silica surface: (a) substances which did not interact chemically with the silica surface; (b) substances capable of polymerization or polycondensation; and (c) substances capable of chemical reaction with the surface. From an analysis of data obtained for 26 modified adsorbents, it results that depending on the nature of the substance used for modification such substances can promote the process of silica mass transfer. During this process, the possibility occurs of the occlusion of the substances inside silica globules, changes in the parameters of the porous structure, physical or chemical bonding of the modifier molecules with the aerosilgel surface, destruction of the reaction products, etc.

From an analysis of the experimental results obtained [6], the following observations were made. Compounds which do not react chemically with a silica surface may favor silica mass transfer processes at higher pressures, although this effect is markedly less than that brought about by hydrothermal treatment. In a number of cases, it is possible to observe the occlusion of the organic molecules inside silica globules. Intensive attachment of polymers or oligomeric compounds onto the silica surface is observed for compounds capable of polymerization (1-olefins) or polycondensation (diphenylsilanediol) under high pressure conditions and elevated temperatures. A significant decrease in the surface area and total pore volume values from those for the initial silica matrices is noted under these conditions. With compounds capable of chemical reaction with surface silanol groups, milder conditions for their chemisorption are observed at high pressures. In a number of cases (*t*-butanol, monochloroacetic acid), it is possible to carry out reactions that are not observed in conventional gas- and liquid-phase processes. It is quite likely that the chemisorption mechanism is changed in such circumstances. In addition to reactions with the silanol groups of the silica, direct addition reaction involving surface siloxane bonds occur quite widely with many nucleophilic and electrophilic reagents at increased pressures. The influence of evolved gaseous reaction products should be taken into account in many substitution processes conducted in closed vessels at increased pressures. It is also necessary to take into account the

possible destruction of the initial reagents.

Synthesis and characterization of carbo-aerosils

Synthesis and some sorptive and electric properties of new type carbon-silica adsorbents - carbo-aerosils prepared from fumed silica and products of methylene chloride pyrolysis at 500 °C - were first studied in the paper [3]. Highly-dispersed carbon-silica powders with specific surface area about 150 m²/g, particle diameter 18.5 nm, and carbon contents in a range 5-36 wt % were prepared. An effect of the amount of carbon deposited on the silica surface on the adsorption and electric properties and pore structure of the samples synthesized were determined. It was demonstrated that carbo-aerosils are characterized by increased adsorption activity compared with pristine fumed silica, and provide new electric properties.

The adsorption properties of hydroxylated silica gel as well as carbon-silica adsorbents (Carbosils) containing 5 and 18 wt % carbon, both treated hydrothermally with hydrogen peroxide solution, towards Methylene Blue were compared in the paper [14]. The equilibrium adsorption of Methylene Blue solutions of $6.5 \cdot 10^{-4}$ mol/L concentration and its dependence on pH were studied. At this concentration, ca 30% of the adsorbent surfaces investigated were covered with Methylene Blue molecules under optimal adsorption conditions. Though an introduction of a small amount of carbon deposit on the silica surface may generate mosaic structures, such modification did not lead to a decrease in the adsorption capacity of Carbosils relative to that of hydroxylated silica. But the adsorption mechanism of Methylene Blue at equilibrium in individual systems of the adsorbent type investigated can differ significantly. On the one hand, this mechanism is associated with the differing behaviour of silica over a wide range of pH relative to treated and untreated Carbosils and on the other hand with the specific properties of Methylene Blue molecule (its affinity for both carbon and silica adsorbents, its occurrence in a cationic form, the possibility of various forms of interaction depending on the pH value of the solution, etc.). However, it was demonstrated that such modifying carbon deposits increased the resistance of the adsorbent towards the action of alkalis. Oxidation of the carbon deposit in the hydrothermal treatment process caused a further increase in this resistance.

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