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Modifying Silicic Acid Xerogels and Accelerating Heterogeneous Reactions with Their Participation with the Use of Microwave Radiation

E. I. Morosanova, A. A. Velikorodnyi, Yu. A. Zolotov, and V. I. Skornyakov

Department of Chemistry, Moscow State University, Leninskie gory, Moscow, 119899 Russia

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Abstract—The use of microwave radiation for drying wet silicic acid gels significantly shortens the time of preparation of dry gels, or xerogels. The specific surface area of xerogels increases from 492 to 963 m^2/g as the power of microwave radiation is increased from 300 to 1000 W. The effect of microwave radiation on the rate of heterogeneous reactions with the participation of analytical reagents incorporated into silicic acid xerogels was studied. It was found that, in a microwave field of a power of 600 W, the reactions between immobilized Bromobenzothiazo and cadmium, immobilized 1-(2-pyridylazo)-2-naphthol and cobalt(II), and immobilized phosphomolybdic heteropoly acid and hydrazine are essentially accelerated. For the reaction of cobalt(II) with 1-(2-pyridylazo)-2-naphthol incorporated into xerogel, microwave radiation accelerates both the outside and inside diffusion. The use of microwave radiation shortens the time of determining metal ions and hydrazine by solid-phase spectrophotometry.

The interaction of microwave radiation with substances manifests itself as both thermal and nonthermal effects. Among the thermal effects is rapid bulk heating due to an increase in the rotational energy of molecules. Nonthermal effects manifest themselves in the electron density redistribution in molecules, the polarization and ionization of molecules, changes in the double electrical layer, and the appearance of free radicals.

Microwave radiation partially removes diffusion restrictions and enhances mass transfer [1, 2]. Microwave radiation is widely used in chemical analysis, mainly for intensifying sample preparation, namely, drying, the dissolution of organic and biological samples, fusion, and dry mineralization [3, 4]. The potentialities of microwave radiation for the acceleration of analytical reactions, including heterogeneous ones, were studied less. Pioneer investigations on intensifying the adsorption preconcentration of platinum metals and chromium(III, IV) were performed in Russia [5–7].

In recent years, much attention has been paid to studies of different analytical reactions and the development of sorption–spectrophotometric analytical methods based on these reactions. A combination of preconcentration and determination improves the sensitivity of determination and the rapidity of analysis. A promising method for the immobilization of analytical reagents is their incorporation into silicic acid xerogels. Heterogeneous reactions with the participation of such modified xerogels were used to determine metal ions, inorganic reductants, and various organic compounds [8–10]. The preparation of modified xerogels includes the step of gel drying. The first attempt at using microwave radiation for gel drying was reported recently [11].

The aim of this work was to study the effect of microwave radiation on the preparation of silicic acid xerogels and the kinetics of heterogeneous reactions with their participation. The studies were performed using reactions between immobilized Bromobenzothiazo (BBT) with cadmium, immobilized 1-(2-pyridylazo)-2-naphthol (PAN) with cobalt(II), and immobilized phosphomolybdic heteropoly acid (HPA) with hydrazine as examples.

EXPERIMENTAL

Xerogels were prepared from tetraethoxysilane of reagent grade and ethanol. To accelerate the gel formation, a 0.1 M solution of $(NH_4)_2SiF_6$ and aluminum fluoride prepared by the dissolution of weighed portions of chemically pure salts in distilled water was added to the reaction mixture [11].

Solutions of 1-(2-pyridylazo)-2-naphthol and Bromobenzothiazo (both of chemically pure grade) were prepared by dissolving weighed portions in ethanol. A solution of phosphomolybdic heteropoly acid (chemically pure grade) was prepared by dissolving a weighed portion in distilled water.

Solutions of cobalt(II), cadmium, and hydrazonium chloride (all of chemically pure grade) were prepared immediately before use by dissolving weighed portions in distilled water.

To prepare nonmodified xerogels, an additive accelerating gel formation was introduced into a mixture of tetraethoxysilane, ethanol, and distilled water (2 : 5 : 2 in volumes), and the gel obtained was dried in a microwave oven at a power of 600–1000 W.

To prepare modified xerogels, ethanolic solutions of reagents 1-(2-pyridylazo)-2-naphthol and Bromobenzothiazo and a saturated solution of phosphomolybdic heteropoly acid in distilled water were added to a mixture of tetraethoxysilane, ethanol, and water in amounts such that the ratio between tetraethoxysilane, ethanol, and water was equal to 2 : 5 : 2; an accelerator of gel formation was introduced; and the resulting gel was dried in a microwave oven at a power of 600 W.

The dried gels were powdered and screened into fractions. We used the fraction 0.25–0.50 mm. The specific surface area of xerogels was determined by the method of low-temperature nitrogen adsorption using a GX-1 gasometer (Russia).

To study the reaction rate, a 30-mL portion of a metal ion or a reducing agent solution with the required pH was added to 0.3 g of a modified xerogel and the absorbance of the xerogel was measured on a KFK-3 spectrophotometer (Russia) in a 0.1-cm cell relative to the nonmodified xerogel of the same fraction after shaking or keeping the xerogel in a microwave oven for a certain time. The cells were filled by the wet method. To reduce light scattering, the cell in the course of measurements was placed in the immediate vicinity of the light detector.

The samples were stirred with a mechanical shaker. A Pluton microwave oven (Russia) and a Milestone programmed microwave analyzer (Italy) were used.

RESULTS AND DISCUSSION

In the sol–gel method, the preparation of a modified xerogel implies the preparation of a modified gel followed by its drying [12]. We studied the effect of the power of microwave radiation on the time of drying and the physicochemical properties of the resulting xerogels. As the radiation power was increased from 300 to 1000 W, the specific surface area of xerogels significantly increased (Table 1), and the time it took to bring wet gels to a constant mass shortened. Thus, at a power of 1000 W, a xerogel can be prepared for only 8 min. Note that, in the methods for xerogel preparation reported in the literature, xerogels were dried at 40°C for two weeks. The rapid heating of the entire gel sample during its drying in a microwave field and, probably, the polarization of and orientation of ethanol molecules are responsible for the significant intensification of the process and an increase in the specific surface area of the resulting xerogels.

The average pore diameter is of great importance for the subsequent use of modified xerogels as adsorbents and indicator powders. It may be anticipated that, with an increase in the average pore diameter, diffusion lim-

Table 1. Effect of the power of microwave radiation on the physicochemical properties of xerogels. Concentration of ammonium hexafluorosilicate 0.010 M

Power of microwave radiation, W	Time of drying, min	Specific surface area, m^2/g	Pore diameter, Å
300	120	492	3.0
600	40	584	3.4
800	12	787	3.5
1000	8	963	4.4

Table 2. Effect of the nature and concentration of an additive accelerating gel formation on the physicochemical properties of xerogels

Additive accelerating gel formation	Concentration of additive accelerating gel formation, M	Specific surface area, m^2/g	Pore diameter, Å
Ammonium fluoride	0.002	1141	12
	0.006	1063	13
	0.011	772	22
Ammonium hexafluorosilicate	0.017	435	37
	0.022	393	54
	0.002	396	11
	0.006	403	13
	0.011	493	9
	0.017	534	9
	0.022	443	10

itations in the heterogeneous processes will be removed. The power of microwave radiation in the studied range had no effect on the average pore diameter. The physicochemical properties of xerogels strongly depended on the conditions of gel preparation, primarily on the nature and concentration of the accelerating additive, ammonium fluoride or the recently proposed ammonium hexafluorosilicate [11]. By varying the concentration of ammonium fluoride in the hydrolyzed mixture, we could obtain xerogels with different average pore diameters (Table 2). The gels were dried under microwave radiation at a power of 600 W.

In the preparation of xerogels modified with 1-(2-pyridylazo)-2-naphthol, Bromobenzothiazo, and phosphomolybdic heteropoly acid, ammonium fluoride was added to accelerate gel formation, and the power of microwave radiation was 600 W. Special experiments have shown that, under these conditions, the analytical reagents did not decompose and were well retained on xerogels [8–10].

We studied the effect of microwave radiation on the rate of heterogeneous reactions between cobalt(II) and PAN, cadmium and BBT, and hydrazine and the HPA.
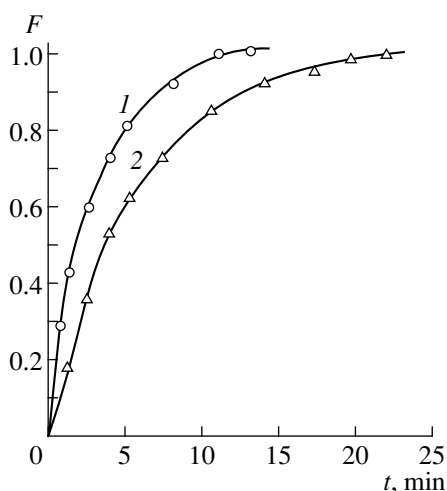
Fig. 1. The degree of attaining equilibrium as a function of the time of phase contact in the reaction of silicic acid xerogel modified with 1-(2-pyridylazo)-2-naphthol with a 5×10^{-5} M solution of cobalt(II) (*1*) in a microwave field at a power of 600 W and (*2*) under conventional conditions with mechanical stirring. c = 4.2 µmol/g; pH 5.0; mass of modified xerogel, 0.3 g; volume of solution, 30 mL.

The heterogeneous reaction in a vigorously stirred solution usually proceeds as a series of consecutive steps: the diffusion of the component from the bulk of the solution to the adsorbent surface, including its diffusion through the surface layer adjacent to the adsorbent (Prandtl layer); diffusion in the adsorbent particles; and chemical reaction with the immobilized reagent. When chemical reaction is the rate-determining step, the rate of the process (W) is described by the equation $W = KS \prod_i c_i^{ni}$, where K is the rate constant of chemical reaction, S is the surface area of the solid phase, c_i is the surface concentration of the immobilized reagent, and n_i is the reaction order with respect to the ith component [13]. At a high rate of chemical reaction, the heterogeneous reaction can be considered as a purely diffusion process. In this case, the rate-determining step may be the diffusion in the film around a solid particle (outside diffusion) or the diffusion in the solid particle (inside diffusion).

It was found for heterogeneous ion-exchange reactions that, if the reaction rate is determined by outside diffusion, the time dependence of the degree of attaining equilibrium (F) is as follows:

$$-\ln(1 - F) = K_1 t,$$

where K_1 is the rate constant of outside diffusion. If the reaction rate is controlled by inside diffusion, the time dependence of the degree of attaining equilibrium at $F < 0.05$ is

$$F = K_2 t^{1/2},$$

where K_2 is the rate constant of inside diffusion [14].

The degree of attaining equilibrium is determined as the ratio between the component concentration in the solid phase at moment t to its equilibrium concentration.

By plotting the experimental data as $-\ln(1 - F)$ against t or F against $t^{1/2}$, one can determine the kinetics of the heterogeneous reaction. If the rate-determining step is outside diffusion, the plot of $-\ln(1 - F)$ vs. t must be linear, and the slope of the plot is equal to the rate constant of outside diffusion. If the rate-determining step is inside diffusion, the dependence of F on $t^{1/2}$ for small values of F should have a linear portion, and the slope of this portion is equal to the rate constant of inside diffusion. By the value of the rate constant one can judge the intensity of one or another diffusion process. If the rate constants of outside and inside diffusion are comparable, the rate of heterogeneous reactions is controlled by both diffusion steps, and mixed diffusion is observed. If the experimental plot cannot be rectified in each of the above system of coordinates, the rate-determining step is chemical transformation.

The kinetics of heterogeneous reactions between cobalt(II) and PAN, cadmium and BBT, and hydrazine and the HPA was studied by solid-phase spectrophotometry. The analytical reagents were immobilized by incorporation into silicic acid xerogels. The experimental conditions are listed below.

System	λ, nm	pH (acidity of solution)
Co(II)–PAN	600	5.4
Cd–BBT	620	10.0
Hydrazine–HPA	680	0.4 M H_2SO_4

The absorbance of xerogels was measured at absorption maxima of the products of heterogeneous reactions at certain time intervals until equilibrium was attained. The degree of attaining equilibrium was determined as $F = A_i/A$, where A_i and A are the absorbances of xerogel at the given moment and at equilibrium. The experimental time dependences of the degree of attaining equilibrium are shown in Figs. 1–3. The rate of the process was characterized by the reaction half-period, which was determined as the time it takes to attain $F = 0.5$. The half-periods of reactions and the time it takes to attain equilibrium under conventional conditions and in a microwave field at a power of 600 W are listed in Table 3. All the heterogeneous reactions studied were significantly accelerated in the microwave field. In this case, the spectrophotometric properties of reaction products obtained in the microwave field were identical to those of compounds synthesized under conventional conditions.

The time dependence of the degree of attaining equilibrium for complexation reactions between cadmium and immobilized BBT and for the reduction of immobilized HPA with hydrazine was rectified neither
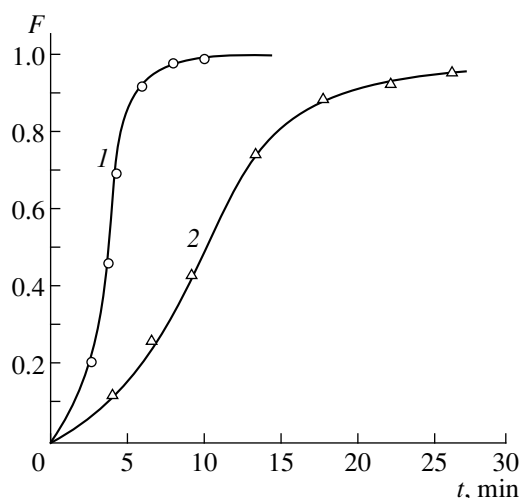
Fig. 2. The degree of attaining equilibrium as a function of the time of phase contact in the reaction of silicic acid xerogel modified with Bromobenzothiazo with a 5×10^{-5} M solution of cadmium (*1*) in a microwave field at a power of 600 W and (*2*) under conventional conditions with mechanical stirring. $c = 2.5$ µmol/g; pH 9.0; mass of modified xerogel, 0.3 g; volume of solution, 30 mL.
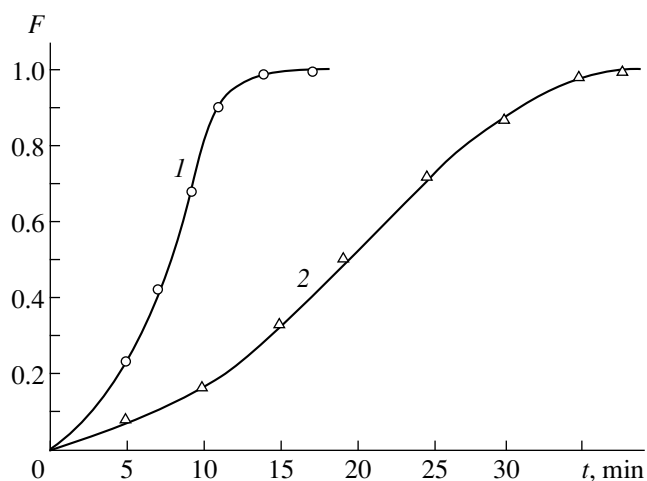

Fig. 3. The degree of attaining equilibrium as a function of the time of phase contact in the reaction of silicic acid xerogel modified with a phosphomolybdic heteropoly acid with a 3×10^{-5} M solution of hydrazine (*1*) in a microwave field at a power of 600 W and (*2*) under conventional conditions with mechanical stirring. $c = 5.8$ µmol/g; 0.4 M H_2SO_4; mass of modified xerogel, 0.3 g; volume of solution, 30 mL.

on the coordinates $-\ln(1-F)$ vs. t nor on the coordinates F vs. $t^{1/2}$. This suggests that the rate-determining step of these reactions both under conventional conditions and in the microwave field is chemical transformation.

The experimental data for the reaction between cobalt(II) and immobilized PAN were rectified in the coordinates $-\ln(1-F)$ vs. t and F vs. $t^{1/2}$, and the correlation coefficients were close to unity. This suggests that this reaction is diffusion-controlled both under conventional conditions and in the microwave field. The rate constants of outside and inside diffusion under conventional conditions and in the microwave field are given below.

	Constant of outside diffusion, min^{-1}	Constant of inside diffusion, min^{-1}
Conventional conditions	0.16	0.07
Microwave field, 600 W	0.27	0.14

Thus, microwave radiation significantly accelerates reactions and enhances both outside and inside diffusion.

The kinetics of reaction between cobalt(II) and immobilized PAN was studied more comprehensively. We studied the effect of the concentration of PAN in xerogel on the time it takes to attain equilibrium. For this purpose, we prepared xerogels containing from 0.42 to 16.7 µmol/g PAN by varying the concentration of PAN in the hydrolyzed mixture (Table 4). For these

xerogels, the time it takes to attain equilibrium was independent of the concentration of PAN in the xerogel. Therefore, under these conditions, the rate of reaction between cobalt(II) and immobilized PAN is not controlled by the rate of chemical interaction, and the rate-determining step is diffusion.

It is known that the diffusion intensity depends on the specific surface area and the pore diameter of the

Table 3. The time it takes to attain equilibrium and the half-period of the reaction under conventional conditions and in a microwave field at a power of 600 W. Pore diameter, 45 Å. $\overline{PAN}$, xerogel modified with 1-(2-pyridylazo)-2-naphthol; $\overline{BBT}$, xerogel modified with Bromobenzothiazo; $\overline{HPA}$, xerogel modified with a phosphomolybdic heteropoly acid

System	Time it takes to attain equilibrium, min		Half-period of reaction, min	
	conventional conditions	microwave field	conventional conditions	microwave field
Co(II)–$\overline{PAN}$	28	9	3.50	1.75
Cd–$\overline{BBT}$	25	6	10.00	3.75
Hydrazine–$\overline{HPA}$	35	13	19.25	7.50

Table 4. Concentration of 1-(2-pyridylazo)-2-naphthol in the xerogel as a function of its concentration in the hydrolyzed mixture

Concentration of 1-(2-pyridylazo)-2-naphthol	
in hydrolyzed mixture 10^5, M	in xerogel, μmol/g
3.1	0.42
6.3	0.83
18.8	2.50
31.3	4.20
125	16.7

Table 5. Experimental conditions for the preparation of xerogels modified with 1-(2-pyridylazo)-2-naphthol with different physicochemical properties. Concentration of PAN in xerogels 4.2 μmol/g

Concentration of ammonium hexafluorosilicate in the hydrolyzed mixture, M	Specific surface area, m^2/g	Pore diameter, Å
0.002	370	11
0.010	328	18
0.020	317	20
0.030	166	39
0.040	106	58

Table 6. Effect of pore diameter in xerogels modified with 1-(2-pyridylazo)-2-naphthol on the kinetics of reaction with cobalt(II). Concentration of PAN in xerogels 4.2 μmol/g. Shaking for 30 min

Pore diameter, Å	Time it takes to attain equilibrium, min	Rate constant, min^{-1}	
		inside diffusion	outside diffusion
58	23	0.14	0.23
39	33	0.13	0.19
20	42	0.07	0.18
18	43	0.08	0.16
11	47	0.06	0.16

solid phase, other conditions being the same. To study the effect of the above parameters on the rate of reaction between cobalt(II) and PAN incorporated into xerogel, xerogels were prepared with a constant concentration of PAN differing in specific surface area and average pore diameter. Xerogels with an average pore diameter of 11–58 Å were prepared by varying the concentration of ammonium fluoride in the hydrolyzed mixture (Table 5).

The average pore diameter was calculated as the ratio between the specific pore volume and the specific surface area of the xerogel powder. The specific pore volume was determined by subtracting the net volume of the xerogel powder and the void volume between the powder particles from the bulk volume of the powder. The bulk volume of the powder was measured by thoroughly filling a graduated test tube (least division of ±0.1 mL) with a weighed portion of the xerogel. The void volume for the studied xerogel fraction was $0.5V_{bulk}$. The net volume of the xerogel powder was determined as the difference between the powder volume that became transparent after the addition of a given (known precisely) volume of chloroform and the volume of chloroform added.

Thus, the effect of the average pore diameter on the rate of reaction between cobalt(II) and immobilized PAN was studied. The rate constants of outside and inside diffusion were estimated from the constructed kinetic curves, the calculated degree of attaining an equilibrium F, and the plots of $-\ln(1-F)$ vs. t and F vs. $t^{1/2}$ (Table 6). The results obtained point to the mixed diffusion mechanism of the reaction with a greater contribution of inside diffusion.

The results of this study demonstrate that the use of microwave radiation is promising for the preparation of xerogels with required analytical properties (nature and concentration of the immobilized reagent, pore diameter, etc.) and for the intensification of heterogeneous reactions with the participation of analytical reagents immobilized on xerogels. The intensification of analytical reagents is, probably, due to both the removal of diffusion limitations and the acceleration of the chemical reaction itself.

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