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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Preparation of Mesoporous Silicon Dioxide with High Specific Surface Area

N. B. Kondrashova, O. G. Vasil'eva, V. A. Val'tsifer, S. A. Astaf'eva, and V. N. Strel'nikov

Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, Perm, Russia

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Abstract—The influence of the reactant ratio on the specific surface area, total pore volume, and mean pore diameter of mesoporous silicon dioxide prepared by the sol–gel method was examined. The optimal reactant ratio for preparing the material with a high specific surface area was determimed.

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Mesoporous synthetic materials with pronounced porous hexagonal structures of the size 2–10 nm and with a high specific surface area (~1000 $m^2\ g^{-1}$) find increasing use in various branches of industry, medicine, and agriculture. Such materials show promise in chemical and biochemical processes as inorganic sorbents, catalysts, and catalyst supports. Therefore, preparation of mesoporous synthetic materials with controllable pore size is a topical problem.

One of the most efficient procedures for preparing nanosized materials with predictable properties of the final product is chemical liquid-phase condensation with the formation of difficultly soluble compounds. By varying the precipitation conditions (temperature, pH, component ratio, component concentrations, addition of surfactants and organic modifiers), it is possible to vary in a wide range the phase composition, size, and shape of the particles formed [1]. Published data on this matter are contradictory, and therefore it is necessary to optimize the conditions of preparation of mesoporous silicon dioxide as support for metal oxide catalysts.

EXPERIMENTAL

As a source of silicon dioxide we used tetraethoxysilane (TEOS). Its hydrolysis yields silica gel in accordance with the following scheme:

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH,$$

$$nSi(OH)_4 \rightarrow (SiO_2)_n + 2nH_2O.$$

Formation of silicon dioxide is accompanied by various physical processes: phase formation, isothermal recondensation, coagulation (preparation of sol), and gelation. The initial synthesis conditions largely determine the process kinetics, properties of the gels, and structure of the final materials.

Many methods used for preparing sols with a narrow particle-size distribution are based on the concepts of phase formation in supersaturated solutions [2–5].

Nuclei of silica particles are formed during the induction period. Their concentration does not change the subsequent steps of particle growth, which is a necessary condition for preparing sols with a narrow particle-size distribution [2]. The induction period decreases with an increase in the total concentration of silica. The process rate is higher in the system with the higher initial concentration of silicic acid when a larger number of nuclei are formed, i.e., when the interface surface area is higher [5].

The sol–gel transition involves formation of a three-dimensional network of chains threading the whole volume of the sol. The gel strength increases with an increase in the silica concentration, but the rate of the gel breakdown increases also [2].

The effect of pH is also strong. Starting from a small supersaturation, the polycondensation in the system occurs only by isothermal recondensation of particles. Its rate is pH-dependent and grows with an increase in pH from 3 to 10 [6]. The higher the pH, the lower the strength of the structure and the earlier it starts to spontaneously degrade. The structure and properties

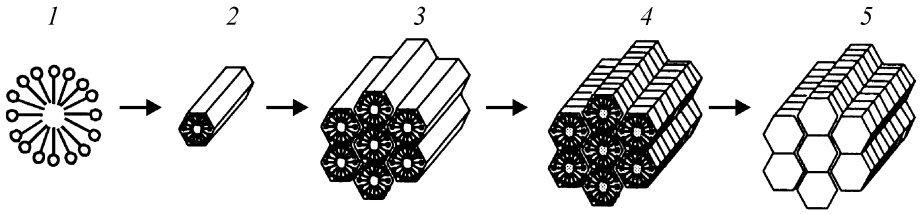

Fig. 1. Scheme of formation of hexagonal porous structures: (*1*) CTAB micelle, (*2*) micellar rod, (*3*) hexagonal matrices, (*4*) inorganic structures, and (*5*) MSM-41.

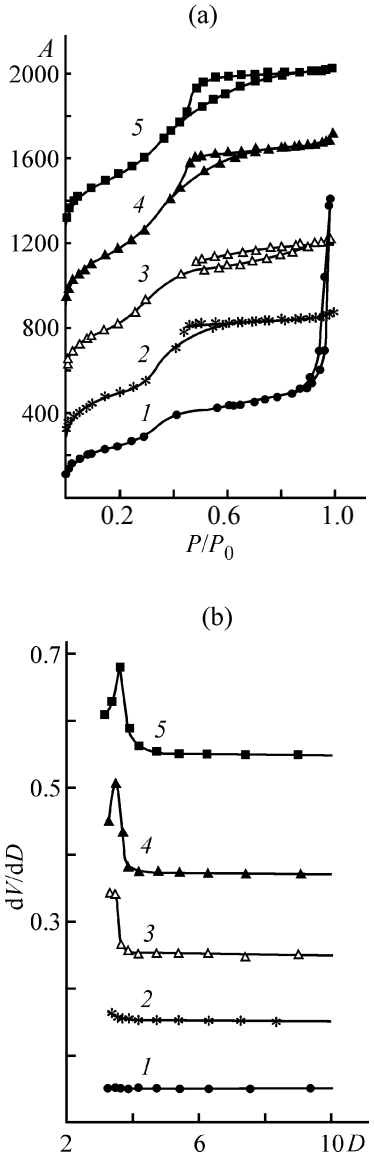

Fig. 2. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution in samples at various CTAB : TEOS ratios used in synthesis of mesoporous silicon dioxide. (*A*) Amount of adsorbed gas, (*V*) pore volume ($cm^3\ g^{-1}$), (P/P_0) relative pressure, and (*D*) pore diameter, nm; the same for Figs. 3 and 4. CTAB : TEOS molar ratio: (*1*) 0.11 : 1, (*2*) 0.22 : 1, (*3*) 0.33 : 1, (*4*) 0.44 : 1, and (*5*) 0.55 : 1.

of gel-like layers on the surface of silica particles also depend on the amount of alkali in the system. Interaction of alkaline hydroxides with silica particles is accompanied by cleavage of siloxane bonds. The same factors give rise to steric repulsion between the particles. In such gels, the system separates in two phases by sedimentation. Thus, sedimentation-unstable dispersions, rather than gels, can be obtained [7, 8].

Enormous role in formation of porous structures is played by surfactants which, when used in the synthesis, act as matrices of a sort. As surfactant we used cationic hexadecyltrimethylammonium bromide (CTAB), $CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$. When a surfactant is dissolved, aggregation of micelles results in formation of so-called hexagonal tubes around which silicates cluster to form inorganic structures reflecting the structure of hexagonal micellar matrices. The length of the hydrocarbon residue of a surfactant is also important: It determines the size of micelles and, as a consequence, the pore size. Removal of a surfactant by calcination or solvent treatment leads to the formation of a mesoporous material (Fig. 1) [9].

Certain procedures for preparing mesoporous silicon dioxide with various ratios of the starting components have been reported in the literature. For example, in [10, 11] the molar ratios of the components were as follows: 1 TEOS : 0.035 CTAB : 0.0175NaOH : 692.5H_2O; 1 SiO_2 : 0.1 CTAB : 0.28 NaOH : 25 H_2O; 1 SiO_2 : 0.33 Na_2O : 0.5 CTAB : 74H_2O, respectively. Therefore, to obtain a material with a higher specific surface area, small pore size, and narrow pore-size distribution, we performed three series of experiments in which we varied the molar ratios of CTAB and TEOS, NaOH and TEOS, and liquid phase (water) and TEOS, respectively.

The texture parameters of the samples were determined by low-temperature nitrogen sorption with an ASAP 2020 device (Micrometrics) after degassing the material in a vacuum at 300°C for 3 h. The specific surface area of the sample was determined by the BET method, and the pore

Effect of the component ratio in synthesis of mesoporous SiO_2 on characteristics of the material

Component ratio	Specific surface area, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$		Pore content, %		Mean pore diameter, nm
		total	micro	D= 1.5-5 nm	D= > 20 nm	
CTAB : TEOS						
0.55:1	1230.6	0.90	0.31	58.64	25.03	3.8
0.44:1	1400.4	0.81	0.35	78.02	11.81	4.2
0.33:1	1207.1	0.49	0.45	77.2	5.95	4.5
0.22:1	1077.8	0.43	0.14	67.45	12.61	5.2
0.11:1	892.6	1.73	0.09	5.55	82.6	21.5
0.055:1	716.9	1.02	0.07	4.84	84.24	23.5
NaOH : TEOS						
0.5:1	1243.0	1.28	0.27	90.54	3.46	4.1
0.4:1	1330.2	1.43	0.31	89.96	2.80	3.8
0.3:1	1119.1	1.45	0.18	58.65	8.64	4.7
0.2:1	1091.4	0.55	0.10	37.48	25.03	5.3
0.1:1	738.6	0.17	0.07	31.06	39.28	5.6
H_2O : TEOS						
80:1	1188	0.85	0.47	83.85	5.70	2.9
100:1	1224	1.07	0.48	88.24	3.33	3.4
200:1	1242	1.40	0.27	93.97	2.15	4.5
300:1	1256	1.46	0.35	88.72	3.40	4.6
400:1	1232	1.26	0.43	81.38	9.32	4.1
500:1	1170	0.83	0.45	32.38	51.10	2.8

size distribution, from the desorption isotherms using the BJH model.

The results of the experiments are given in the table, and the adsorption–desorption isotherms of gaseous nitrogen and pore size distribution patterns, in Figs. 2–4.

The table shows that the best CTAB : TEOS ratios for preparing mesoporous silicon dioxide are 0.55 : 1, 0.44 : 1, and 0.33 : 1. Pores with diameters of 3–4 nm prevailed in samples with surfactant : TEOS molar ratios of 0.44 : 1 and 0.33 : 1. The size of porous formations in the sample with the component ratio of 0.55 : 1 vary in a wide range.

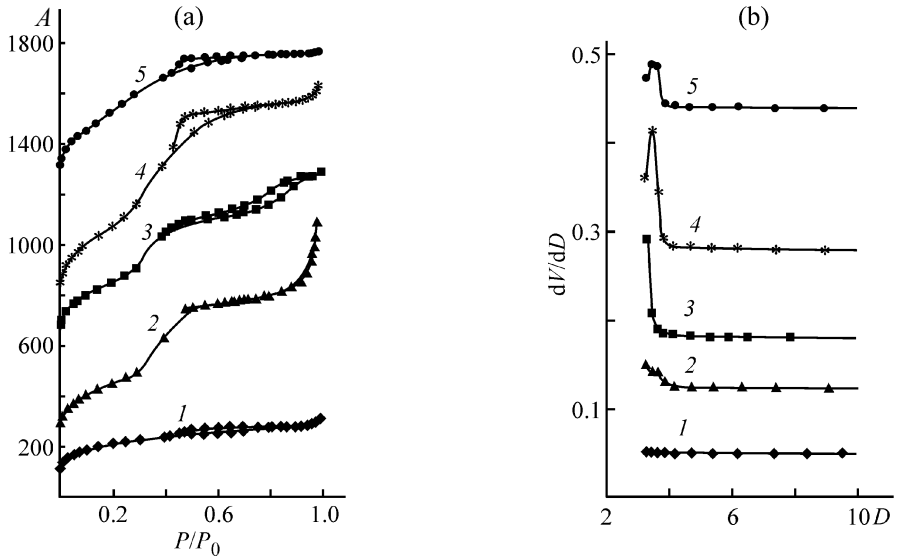

Fig. 3. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution in samples at various NaOH : TEOS ratios used in synthesis of mesoporous silicon dioxide. NaOH : TEOS molar ratio: (*1*) 0.1 : 1, (*2*) 0.2 : 1, (*3*) 0.3 : 1, (*4*) 0.4 : 1, and (*5*) 0.5 : 1.

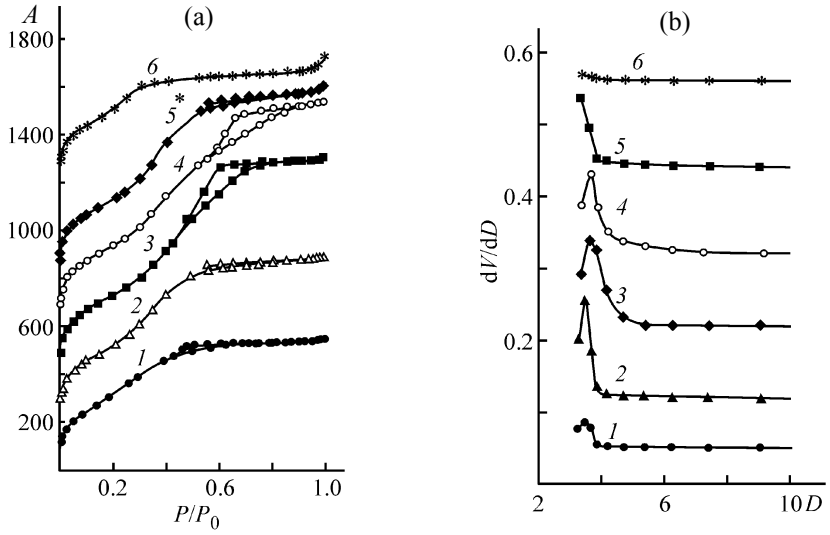

Fig. 4. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution in samples at various H_2O : TEOS ratios used in synthesis of mesoporous silicon dioxide. H_2O : TEOS molar ratio: (*1*) 80 : 1, (*2*) 100 : 1, (*3*) 200 : 1, (*4*) 300 : 1, (*5*) 400 : 1, and (*6*) 500 : 1.

The other samples have coarser pores (25 nm and above). A sharp increase in the total pore volume in samples with surfactant : TEOS ratios of 0.11 : 1 and 0.055 : 1 is due to an increase in the mean pore diameter.

In the second series of the experiments, we examined the effect of the NaOH : TEOS ratio on the texture characteristics of the mesoporous material obtained. The pH of the reaction mixture was varied within 9.35–9.95. Performing the process at higher pH is not appropriate because of the starting dissolution of silicon dioxide formed by hydrolysis.

The table shows that the highest levels of the specific surface area, total pore volume, and amount of porous formations 3–4 nm in diameter are attained in samples with NaOH : TEOS ratios of 0.5 : 1 and 0.4 : 1. Samples prepared at a lower content of alkali have larger mean pore diameter and broader pore-size distribution.

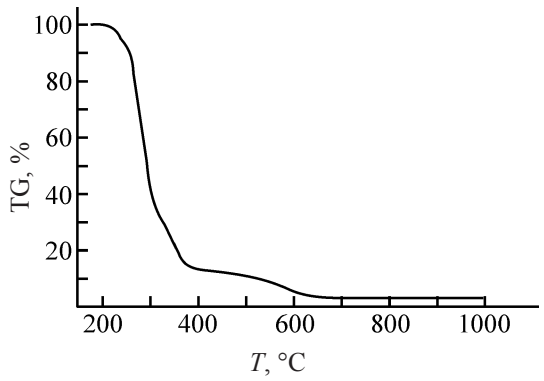

Fig. 5. TG curve of CTAB decomposition. (*T*) Temperature.

The water : TEOS ratio affects the specific surface area and total pore volume less significantly (see table). The best water : TEOS ratio for preparing mesoporous silicon oxide is from 100 : 1 to 300 : 1.

Along with the molar ratios of the reaction components, a strong effect on the quality of the mesoporous material obtained is exerted by the conditions of all the process steps.

To ensure the most complete removal of the surfactant in the step of the xerogel formation, we refined the calcination temperature and time from the results of thermal gravimetric analysis. Thermal oxidative degradation of CTAB was performed with a Q 1500 D derivatograph (MOM, Hungary). Programmed heating was performed at a rate of 10 deg min^{-1} from room temperature to 1000°C.

Figure 5 shows that the decomposition of CTAB is virtually complete at approximately 650°C. Therefore, at this temperature we performed the calcination in the final step of the synthesis of mesoporous silicon dioxide.

CONCLUSION

The optimal molar ratios of the reactants (hexadecyltrimethylammonium bromide, NaOH, tetraethoxysilane) were chosen, and some parameters of the synthesis of mesoporous silicon dioxide were refined. Under these conditions, the material with a high specific surface area (>1400 $m^2 g^{-1}$) and pore diameter of 3–4 nm is obtained.

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