Effect of Solution pH on the Surface Morphology of Sol−Gel Derived Silica Gel

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Abstract—We have examined the effect of solution acidity on the textural characteristics of silica gels prepared by sol−gel synthesis using tetraethyl orthosilicate (TEOS) as a silica precursor and cetyltrimethylammonium bromide (CTAB) as a template. Using IR spectroscopy, we have studied micellar TEOS solutions and the synthesized silica gel samples. The results demonstrate that, in an alkaline medium in a water−ethanol solution, SiO_2 experiences short-range ordering on the surface of micelles formed by CTAB molecules, whereas in an acid medium the process is not influenced by the presence of CTAB. Nitrogen porosimetry and electron microscopy data indicate that the silica gel obtained at pH 2 is microporous, with an average pore size of 2 nm. In an alkaline medium at pH 10, we obtained mesoporous SiO_2 (18 nm) with a narrow pore size distribution and a specific surface area of 110 m^2/g.

INTRODUCTION

Sol−gel synthesis of silica has been the subject of extensive studies [1−16]. Owing to the existence of silica polymorphs differing in properties, this material has found many engineering applications. Fine silica particles are used in the semiconductor industry, biology, medicine, and optical devices and as fillers of polymers [17]. Surface modification of sol−gel derived amorphous silicas opens up unlimited possibilities for the synthesis of materials for a variety of applications. Silica particles modified with rare-earth ions (Eu^{3+}, Er^{3+}) can be used as matrix elements in nanosensors, microlasers [18], and luminescent markers [19]. The addition of surfactants as templates to sol is favorable for the formation of nanometer mesopores identical in size in xerogels [20, 21]. Such silica gels are used as catalyst supports [22, 23] and are of interest as sorption materials for chromatography [24, 25].

Sol−gel synthesis with the use of silicon alkoxides comprises five main steps: hydrolysis of silicon alkoxides, polycondensation of the hydrolysis products and growth of sol particles, sol aggregation into a gel network, drying, and calcination. Note that each step influences the pore structure of the final product [26].

The hydrolysis of silicon alkoxy compounds, including tetraethyl orthosilicate (TEOS), involves $\equiv Si-OC_2H_5$ bond breaking and the formation of $\equiv Si-OH$ silanols, which are unstable and condense to form $\equiv Si-O-Si\equiv$ siloxane bonds—main structural elements of silica gels. The rates of the hydrolysis and polycondensation reactions and the composition of the forming products depend on solution acidity. According to Shabanova [27], the polycondensation rate is proportional to $[H^+]^{1.2}$ at highly acidic pH values and to $[OH^-]^{0.9}$ at weakly acidic pH, with a minimum rate in the pH range 2−3. According to Sinkó [12], the hydrolysis of alkoxy compounds has the lowest rate at pH 7, whereas the polycondensation rate is lowest at pH 4.5. The discrepancies between the reported pH values corresponding to the maximum polycondensation rate attest to complexity of processes that take place in aqueous solutions of silicic acids, whose kinetics may vary in different steps and depend on external conditions [9, 27, 28].

The purpose of this work was to study the effect of solution pH on the porosity of silica gel prepared by a sol−gel process in the presence of cetyltrimethylammonium bromide (CTAB) molecules.

EXPERIMENTAL

To study the effect of solution pH on the polycondensation of the sols under investigation, we prepared water−alcohol solutions of TEOS using CTAB as a template.

In analyzing the formation of the pore structure of silica gels, Iler [28] differentiates, somewhat arbitrarily, three regions: metastable region (pH from 1 to 2), which contains an isoelectric point; rapid aggregation region (pH form 2 to 7); and region where primary particles
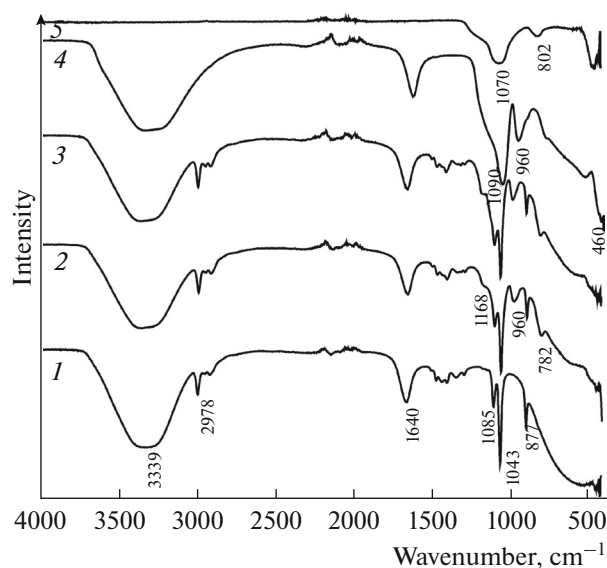
Fig. 1. IR spectra of the pH 2 solutions: (*1*) without TEOS, (*2*) 4 min after the addition of TEOS, (*3*) after 60 min, (*4*) sample dried at 60°C (after 24 h), (*5*) sample calcined at 600°C.

grow without aggregation (pH above 7) [28]. Proceeding from these ideas, in this study we used pH 2, 7, and 10.

Sample 1 was synthesized in an acid medium. The composition of the starting mixture can be represented by the following molar ratio: TEOS : CTAB : H_2O : C_2H_5OH : HCl = 0.66 : 0.005 : 45 : 10 : 0.10. Samples 2 and 3 were synthesized using aqueous ammonia and the following composition of the starting mixture: TEOS : CTAB : H_2O : C_2H_5OH : NH_4OH = 0.66 : 0.005 : 45 : 10 : x, with x = 0.02 and 0.10.

After 24 h of reaction, the mixtures were dried at 60°C using a rotary evaporator. The resultant precursors were washed with distilled water and calcined in a muffle furnace by heating to 600°C at a rate of 1.5°C/min.

The calcination temperature of the silica gel (600°C) was chosen using thermal analysis data obtained with a Netzsch STA 449C thermoanalytical system in the temperature range 25−1000°C at a heating rate of 1.5°C/min in air. This calcination temperature ensured complete CTAB removal.

The evolution of the chemical nature of the TEOS solutions during hydrolysis reactions was followed using infrared spectroscopy. IR spectra were measured on an Agilent Technologies Cary 630 FTIR spectrometer in the range 400−4000 cm^{-1}.

The specific surface area, pore volume, and pore size distribution were evaluated by low-temperature nitrogen adsorption measurements at 350°C using a TriStar II (3020) analyzer. Prior to the measurements, the samples were degassed at 200°C for 2 h. The relative accuracy of the method is 10%.

The surface morphology of the samples was examined by scanning electron microscopy on a Hitachi TM-3000 at an accelerating voltage of 15 kV under conditions preventing surface charging of the sample (electron gun: 5×10^{-2} Pa; sample chamber: 30−50 Pa).

RESULTS AND DISCUSSION

The sol resulting from TEOS hydrolysis at pH 2 has the form of a transparent solution. IR spectroscopy data indicates the formation of Si−OH groups after just 4 min of hydrolysis, as evidenced by an absorption band at 960 cm^{-1}, which is due to the ν_{as}(Si−OH) stretching mode (Fig. 1, spectrum *2*) [29]. In addition, absorption bands emerge at 782 and 1168 cm^{-1}, which correspond to the δ(Si−OH) bending mode and ν_{as}(Si−O−Si) asymmetric stretching mode, respectively, attesting to the formation of a Si−O−Si skeleton (Fig. 1, spectrum *2*) [30]. In the IR spectrum of the dried sol, the 1168-cm^{-1} absorption band is shifted to lower frequencies, 1090 cm^{-1}, because of the growth of the polymer chain. The 460-cm^{-1} band, which is missing in the spectrum of the solution, arises from bending vibrations of the Si−O−Si corner, which contains a bridge oxygen (Fig. 1, spectrum *4*) [29]. The intensity of the 960-cm^{-1} band increases, attesting to an increase in the number of Si−OH groups.

The pH 7 reaction mixture is an oil-in-water emulsion. After 12 min of reaction, a transparent gel-like layer accumulates in the top part of the liquid. After 3 h, the solution turns white. Immediately after the addition of a TEOS solution to the reaction mixture, IR spectra show absorption bands indicating he formation of Si−OH groups at 960 (ν_{as}(Si−OH)) and 783 cm^{-1} (δ(Si−OH)) and Si−O−Si groups at 1168 cm^{-1} (ν_{as}(Si−O−Si)). After 60 min of reaction, the intensity of the absorption bands of the Si−OH groups increases, attesting to an increase in the amount of the hydrolysis product. Moreover, the overlap of the ν(C−O−H) and δ(−CH$_3$) absorption bands of ethanol at 1043 and 1085 cm^{-1}, respectively [30], with the ν_{as}(Si−O−Si) band of the silicate groups forming in solution leads to changes in the shape of the absorption band in this region (Fig. 2, spectrum *3*).

The pH 10 solution becomes turbid 4 min after the addition of TEOS. After 20 min, a white substance precipitates. The IR spectrum of the precipitate contains an absorption band at 1050 cm^{-1}, whose shape and intensity indicate the presence of a large amount of skeletal SiO_2 groups of amorphous silica [31] (Fig. 3, spectrum *3*).

According to data in the literature [9, 28], condensed siloxane groups in a strongly alkaline medium are ionized and repel each other. The polymer chain grows via the attachment of monomers. Because of this, immediately after the formation of a neutral silicic acid molecule as a result of hydrolysis, it
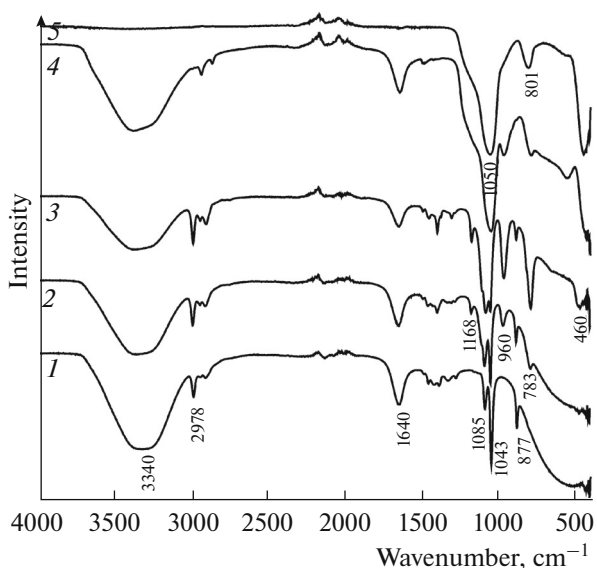
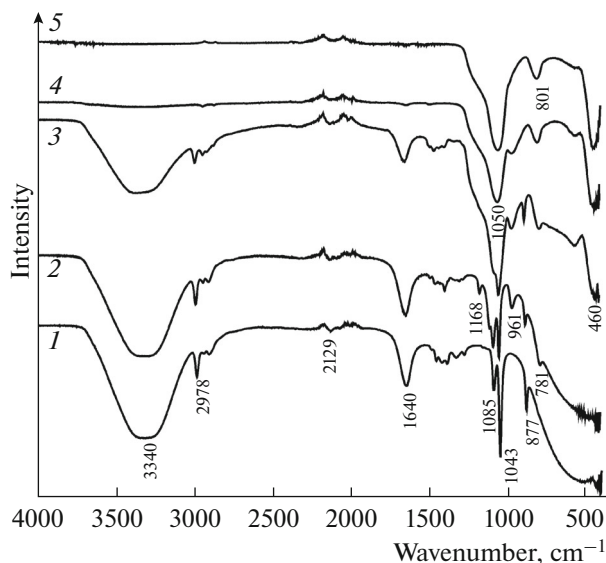**Fig. 2.** IR spectra of the pH 7 solutions: (*1−5*) same as in Fig. 1.

Fig. 3. IR spectra of the pH 10 solutions: (*1−5*) same as in Fig. 1.

becomes incorporated into the polymer chain. The decrease in monomer concentration and increase in chain length are accompanied by polyorganosiloxane cyclization processes, as evidenced by the fact that the IR spectra of the sample dried at 60°C contain no bands of O−H groups (Fig. 3, spectrum *4*).

The bands at 1050, 801, and 460 cm^{-1} in the IR spectra of the calcined samples can be assigned to asymmetric stretching, symmetric stretching, and bending Si−O−Si modes, characteristic of the silicon atoms in SiO$_4$ tetrahedra. At the same time, at pH 2 the 1070-cm^{-1} band is shifted to higher frequencies (Fig. 1, spectrum *5*), attesting to the formation of weakly branched linear SiO$_2$ polymers [28, 30].

The table summarizes the characteristics of the pore structure of the synthesized silica gels. The samples prepared at pH 2 have a specific surface area of 398 m^2/g and average pore diameter of 2 nm. The silica formed at pH 7 has a larger pore size, 10 nm, and a smaller specific surface area: 297 m^2/g. Precipitation in an alkaline medium at pH 10 leads to the formation of SiO$_2$ with a specific surface area of 110 m^2/g and a higher porosity in comparison with the silica gel obtained in an acid medium (18 nm).

Figure 4 shows pore size distributions in the silica gels prepared at different solution pH values. The samples synthesized at pH 2 have a microporous/mesoporous structure. Increasing pH to 7 makes it possible to prepare silica gel with a broad pore size distribution (Fig. 4, spectrum *2*). The samples prepared at pH 10 have a mesoporous structure, with pores ranging in size from 2 to 35 nm (Fig. 4, spectrum *3*).

Scanning electron microscopy data demonstrate that the silica gel prepared in an acid medium consists

of plates with a homogeneous surface. The silicas obtained at pH 7 and 10 consist of spherical particles with a rough surface having many bends and folds.

According to data in the literature, CTAB molecules dissolved in a water−ethanol mixture form micelles with positively charged surfaces [20]. In an alkaline medium, the polymer chain of the TEOS hydrolysis products grows on the surface of the micelles. As a result, the micelles become covered with a hydrated silica polymer layer, forming SiO$_2$−CTAB clusters. With increasing silica concentration, the system becomes colloidally unstable, which leads to coagulation. At pH 10, larger silica gel particles are formed, but the number of particles is smaller [28]. Note that the specific surface area of the calcined sil-
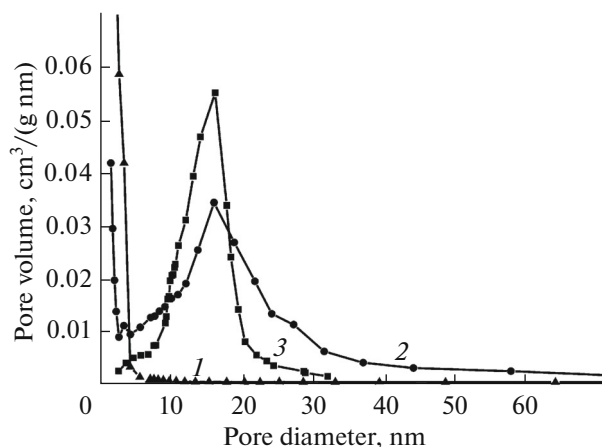

Fig. 4. Differential pore size distributions in the silica gels prepared at pH (*1*) 2, (*2*) 7, and (*3*) 10.
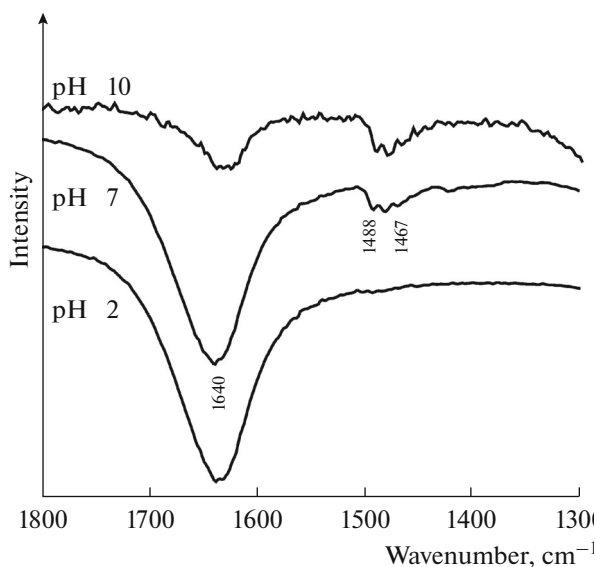
Fig. 5. IR spectra of the silica gels dried at 60°C.

ica gel is considerably smaller than that of the sample synthesized at pH 7, and the average pore size increases to 18 nm. The IR spectra of the silica gels prepared in alkaline media (pH 7 and 10) and dried at 60°C show a vibrational mode of CTAB molecules at 1488 cm^{-1}, $\delta(N-CH_3)$, and the $\delta(CH_2)$ mode at 1467 cm^{-1} (Fig. 5). The spectra of the samples prepared at pH 2 contain no such mode. Therefore, the presence of CTAB has no effect on the formation of silica in the acid medium (Fig. 5).

The observed effect of solution acidity on the formation of the structure of silica gel can be accounted for by the fact that the rates of the hydrolysis and polycondensation reactions are influenced by solution pH [32]. In an acid medium, the hydrolysis process has a high rate, so in the initial stage of the process the sol is supersaturated with molecules containing Si−OH reactive groups. This leads to the formation of linear SiO$_2$ polymers with a large specific surface area and small pore size. In alkaline solutions, silica gel synthesis takes place on the surface of micelles formed by CTAB molecules. The rate of polycondensation reactions exceeds that of hydrolysis reactions, which is favorable for the synthesis of larger SiO$_2$ particles, and

Adsorption properties of the silica gels prepared at different solution pH values

pH	Specific surface area, m^2/g	Total pore volume, cm^3/g	Average pore size, nm
2	398	0.23	2
7	297	0.72	10
10	110	0.51	18

accordingly the resulting silica gel contains large pores.

Thus, one of the key parameters influencing the pore structure of silica gel in the presence of CTAB molecules is solution acidity. SiO$_2$ synthesis at pH 2 is favorable for the formation of microporous silica gel with a specific surface area of 398 m^2/g. Raising pH to 10, we obtained silica samples with a specific surface area of 110 m^2/g and pore size of 18 nm.

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