NEW ROUTE TO MESOPOROUS SILICA VIA A SILSESQUIOXANE PRECURSOR

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The effect of the addition of octakis(tetramethylammonium)-t8-silsesquioxane (octaanion) on the modification of the porous structure of the silica gel obtained by the sol-gel method catalysed by acetic acid was studied. The obtained silica gel was characterised by the low-temperature nitrogen adsorption/desorption method (BET), powder diffraction (XRD), thermogravimetry (TG) and microscopic observations (TEM). The octaanion was found to act as a textural promoter, as evidenced by almost a 25 % increase in the surface area of the obtained silica. As a result of the stabilisation in the porous structure of the silica gel, the tetramethylammonium groups of the octaanion show higher thermal stability than the groups present in the octaanion structure or those introduced in the form of tetramethylammonium hydroxide. Tetramethylammonium ions were proved to show increased thermal resistance, which is related to the porous properties of the SiO_2 matrix.

INTRODUCTION

The quaternary ammonium ion shows strong structure-determining properties, therefore it can be applied for the dissolution of silica by the generation of cage structures, Q_x, where x = 6, 8, 10 [1]. The addition of quaternary ammonium hydroxides to a reaction mixture increases its pH. The use of hydroxides of different alkyl chains can lead to obtaining materials of different degrees of organisation and ordering [2]. One of the methods for the generation of polyanionic cage structures Q_x is the dissolution of silica characterised by a high surface area in the solutions of tetraalkylammonium hydroxides of concentrations higher than 0.2 M [1]. On the other hand, tetraalkylammonium hydroxides are used in the synthesis of ordered porous materials, mainly zeolites [3] and mesoporous materials [4]. The process of selective extraction of the Si–O–Si lattice in the silica is known as desilication or basic leaching and has been widely used for obtaining hierarchic materials, e.g., zeolites [5-9]. The leaching agent, which is quaternary ammonium hydroxide, has a specific effect on the kinetics of the process. The rate of silica dissolution in tetrabutylammonium or tetrapropylammonium hydroxide is much lower than in NaOH, which means that the

process of dilution can be better controlled in the former two hydroxides. The size of the alkylammonium cation and strength of the hydroxide determine the porosity of the obtained material [4]. The final stage of the material's processing is the decomposition of the alkylammonium cation by thermal treatment in oxidising conditions, leading to the formation of the protonated form of the porous material which can subsequently be subjected to an ionic exchange [10].

Besides the kinetic effect, tetraalkylammonium cations also have an impact on the preferred stabilisation of the symmetric cage structures in the solution. If the solution concentration is $[OH^-]:[Si] \geq 1:1$, the preferred formation of the silicate anion $Si_8O_{20}^{8-}$ stabilised by 8 tetramethylammonium (TMA⁺) cations is observed. The cations of ammonium hydroxides make a stabilising hydrophobic shell protecting the anion core against hydrolysis [11]. The study reported in this paper was undertaken to establish the impact of the introduction of an octaanion into a stable silica gel solution (obtained by the sol-gel method) on the final structure and texture of the obtained adsorbing material. For the sake of comparison, the analogous adsorbing material was synthesised with the equivalent amount of tetramethylammonium hydroxide introduced into the same amount of silica gel.

EXPERIMENTAL

Synthesis of SiO_2

Modified silica systems were synthesised by the aqueous sol-gel method. The synthesis was based on our previous experience with similar system preparations [12-14].

A glass reactor of 1 l in capacity, equipped with a reflux, dropping funnel, mechanical stirrer and heating mantle, was charged with 500 ml H_2O (27.7 mol) of water, 35 ml acetic acid (0.333 mol) and 100 ml tetraethoxysilane (TEOS – 0.48 mol Si). The mixture was heated at 80°C for 24 h. The obtained iridescent gel was mixed for the next 24 h at room temperature. As a result of hydrolysis and condensation, an SiO_2 gel was obtained and evaporated under reduced pressure (p = 500 hPa) at 90°C. The silica obtained in this way was labelled as SiO_2.

Synthesis of octakis(tetramethylammonium)-t8-silsesquioxane (octaanion)

A glass reactor of 1 l in capacity, equipped with a reflux, dropping funnel, mechanical stirrer, was charged with 177.6 ml, 25 % w/w water solution of tetramethylammonium hydroxide (0.48 mol, TMAH), 90.8 ml (2.27 mol) of methanol and 68.4 ml (3.8 mol) of water. The mixture was cooled to 0°C and then 100 ml of tetraethoxysilane (TEOS – 0.48 mol Si) was added dropwise upon vigorous stirring. The solution was stirred for 24 h at room temperature. The reaction gave a solution of the octaanion. The solvent was evaporated under reduced pressure (p = 500 hPa) at 90°C. The octakis(tetramethylammonium)-T8-silsesquioxane sample was labelled as OCTA.

Synthesis of SiO_2 with the octaanion addition

Portions of 7.14 g of octaanion (SiO_2 = 0.033 mol, the sample denoted as Si-OCTA1) or 20.74 g of octaanion (SiO_2 = 0.098 mol, the sample denoted as Si-OCTA2) were added to the SiO_2 gel (0.48 mol Si), obtained according to the procedure described in chapter "Synthesis of SiO_2". (prior to evaporation) at room temperature. Further steps of the preparation method: the evaporation and drying were the same as that for SiO_2.

Synthesis of SiO_2 with the TMAH addition

Portions of 177.6 ml of tetramethylammonium hydroxide (Aldrich, 25 % w/w methanol solution) (0.48 mol TMAH) the sample labelled as Si-TMAH, or 36.27 ml of tetramethylammonium hydroxide (Aldrich, 25 % w/w methanol solution) (0.098 mol TMAH), the sample labelled as Si-TMAH2, were added to SiO_2 (0.48 mol Si) obtained according to the procedure described in in chapter "Synthesis of SiO_2". (prior to evaporation) at room temperature. In the latter Si-TMAH2 sample, the amount of TMAH added is equimolar with the OCTA introduced to the synthesis of Si-OCTA2. Further steps of the procedure: the evaporation and drying were the same as that for SiO_2.

All obtained sample labelling and molar compositions are presented in Table 1.

Table 1. Sample labelling and molar composition of the silicon obtained by the acetate method to the silicon contained in the tetramethylammonium hydroxide.

Sample code	Si_{TEOS} (mol. %)	Si_{TMAH} (mol. %)	Si_{OCTA}/Si_{gel}
OCTA	–	100	–
SiO_2	100	–	–
Si-OKTA1	93.6	6.4	0.0688
Si-OKTA2	83.1	16.9	0.2042
Si-TMAH2	83.1	16.9	0.2042
Si-TMAH	–	100	–

Thermal treatment

The samples were dried at 90°C and then calcined in a tube furnace in an air atmosphere, at 500°C for 6 hours.

Characterisation of the porous structure

Prior to the determination of the porous structure, the samples were calcined at 500°C (see Thermal treatment). The porous structure was determined by low temperature (-196°C) nitrogen adsorption/desorption measurements carried out with an Accelerated Surface Area and Porosimetry System model 2010 V2.00 D made by Micromeritics, using 200 - 300 mg of the samples with a grain size fraction between 0.1 - 0.2 mm. Prior to the nitrogen adsorption, all the samples were outgassed at 400°C at 0.4 Pa till a constant weight. Both the adsorptive and desorptive branches of the isotherm were recorded in the range of p/p_0 0 - 1.

XRD analysis

The X-ray powder diffraction patterns of the samples (after thermal treatment -500°C in an air atmosphere for 6 hours) were taken on a Philips PW1050 diffractometer, with Ni filtered CuKα radiation. The reflections position, half bandwidth as well as the intensity were calculated by the APD Philips programme.

Thermal analysis

The thermal transformation of the gel samples was carried out on a TA Q50 (TA) under the same conditions. A ca. 20 mg sample was placed in a platinum dish

and heated at a rate of 20°C·min⁻¹ up to 800°C. For all the experiments, we used the fraction of grain size below 0.1 mm. The TG traces were recorded in an air atmosphere. For the thermal analysis, we used vacuum dried samples (90°C) with an excess of encapsulated solvents removed from the gel by evaporative drying.

TEM analysis

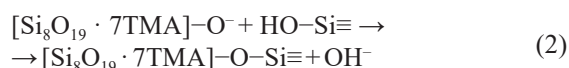The gel structures were characterised by transmission electron microscopy (JEOL 200 CX *Jeol*).
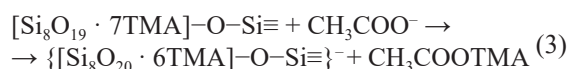
RESULTS AND DISCUSSION

In our study, octaanion was used as a modifier of the structure of the SiO_2 gel obtained by the standard sol-gel method [12-14]. The octaanion can react with the acetic acid present in the SiO_2 gel:

$$[Si_8O_{20} \cdot 8TMA] + CH_3COO^- \rightarrow$$
$$\rightarrow [Si_8O_{19} \cdot 7TMA]{-}O^- + CH_3COOTMA \qquad (1)$$
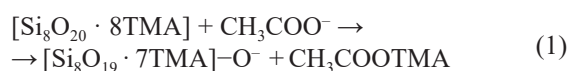
the ion formed $[Si_8O_{19} \cdot 7TMA]{-}O^-$ undergoes a condensation reaction with the silanol groups present in the SiO_2 gel structure:

$$[Si_8O_{19} \cdot 7TMA]{-}O^- + HO{-}Si\equiv \rightarrow$$
$$\rightarrow [Si_8O_{19} \cdot 7TMA]{-}O{-}Si\equiv + OH^- \qquad (2)$$

and further reactions with acetic acid:

$$[Si_8O_{19} \cdot 7TMA]{-}O{-}Si\equiv + CH_3COO^- \rightarrow$$
$$\rightarrow \{[Si_8O_{20} \cdot 6TMA]{-}O{-}Si\equiv\}^- + CH_3COOTMA \qquad (3)$$

The gel samples dried at 90 °C were subjected to a thermogravimetric study (Figure 1). The mass loss curve recorded for the initial silica gel (curve B) showed a maximum corresponding to the removal of water at 103°C and an inflection point in the range ~160 - 170°C, assigned to the removal of the residues of acetic acid.

For the OCTA sample, three mass loss maxima

Figure 1. The thermogravimetric curves and weight losses of the silica gel systems in an air atmosphere.

were recorded (Curve A). The decomposition of the pure octaanion runs as follows:

$$[Octaanion \cdot H_2O] \rightarrow [Octaanion] \rightarrow SiO_2 \qquad (4)$$

The theoretical mass loss related to the removal of all TMA+ groups should be 57.8 %. It corresponds to the sum of two separate mass loss events at 156°C and 188°C, which is 56.1 %. The former one corresponds to the removal of water and amounts to 16.8 % corresponding to 16.53 of H_2O molecules per one molecule of the octaanion.

The TG curves recorded for the SiO_2 samples modified with the octaanion (Si-OCTA1 and Si-OCTA2) show two peaks, assigned to the removal of water at 103°C and to the removal of TMA⁺ ions above 200°C. A shift of the TMA⁺ decomposition temperature towards higher values for the mixed systems with respect to that of pure OCTA is related to the ions' stabilisation in the closed structures and their greater resistance to temperature. This effect has also been observed for TMA⁺ ions confined in a zeolite cage [15]. The confined ions are more resistant to decomposition. In the, the situation is the reverse: TMA⁺ ions are directed outwards from the structure, so their thermal resistance is lower, as confirmed by the DTG results. The effect of stabilisation weakens with the increasing content of TMA⁺. After the addition of a considerable amount of the octaanion, the high-temperature peak is shifted towards the lower temperatures of 266°C for Si-OCTA1 and 253°C for Si-OCTA2. It should be noted that above 300°C no mass loss was observed, irrespective of using octaanion or TMAH as a modifier. The thermal stabilisation of the TMA⁺ ions is greater than that of the pure octaanion and smaller than that of the zeolites. Moreover, the stability of the TMA⁺ ions is higher for the systems whose precursor is an octaanion, so these systems should have a structure closer to that of zeolites, however the XRD results indicated no ordered structure (as presented and discussed below).

Silica gels modified with the octaanion and TMAH were subjected to calcination at 500°C in order to get SiO_2. As follows from low-temperature nitrogen adsorption/desorption studies, the initial SiO_2 has a microporous character (Figure 2a) and a surface area of 319 m²·g⁻¹, Table 2. The use of an octaanion as the agent promoting texture development leads to an increase in the surface area to 444 or 377 m²·g⁻¹ depending on the amount of the promoter added (Table 2). For the sake of comparison, the texture of the octaanion subjected to calcination 500°C was characterised. The material obtained had a low surface area of 27 m²·g⁻¹ and a pore diameter of about 10 nm, which means that it is mesoporous. The addition of greater amounts of OCTA to the SiO_2 gel causes a decrease in the surface area, which was observed for the Si-OCTA1 and Si-OCTA2 samples.

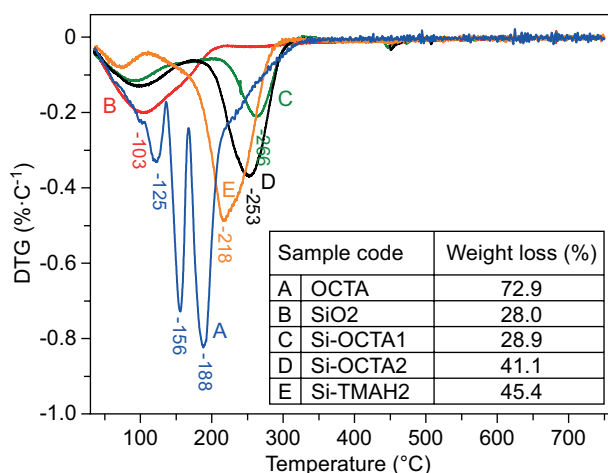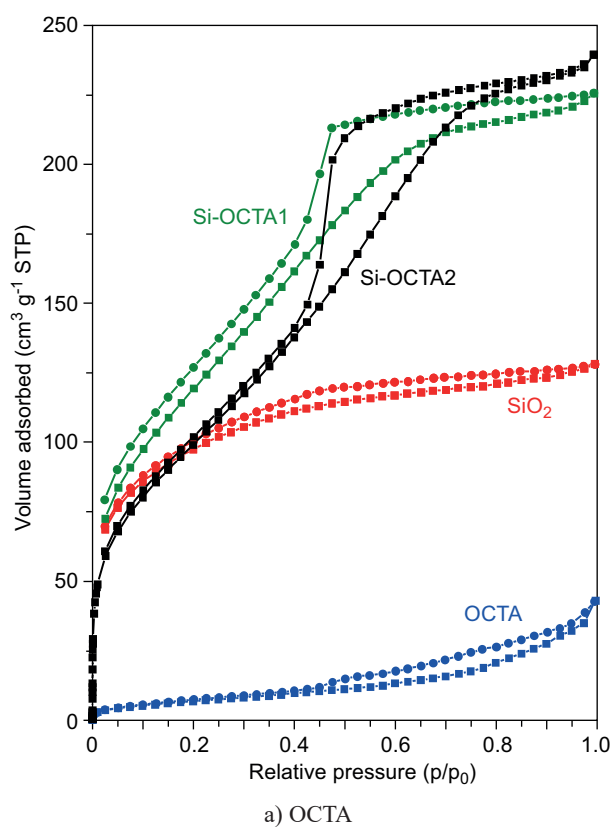Textural changes in the samples after the addition of

a) OCTA

OCTA are particularly well pronounced in the character of the low-temperature nitrogen adsorption/desorption, Figure 2a. The isotherm obtained for the initial silica (SiO_2) is of type I(b) according to the recent IUPAC classification [16] and is typical of materials having a pore size distribution over a broader range including wider micropores and possibly narrow mesopores ($< \sim 2.5$ nm). Poorly marked, but a visible hysteresis loop, occurs in practically the whole range of partial pressures p/p_0 which confirms the presence of wide micropores and capillary condensation taking place in the very narrow mesopores. The pore size distribution covers the range from 3 to 5 nm, with no distinct maximum (Figure 2b).

The use of octaanion as a texture promoting agent in the process of the silica gel synthesis provokes significant changes, not only in the surface area, but also in the pore structure, as manifested by the shape of the isotherm typical of Type IV(a) and the shape of the hysteresis loop described as H2(a), in particular, for the sample with a higher content of octaanion (Si_{TMAH} = 16.9 %) – Si-OCTA2. The H2(a) loop is typical of mesoporous materials with a pore system for which network effects are important. The very steep desorption branch, which is a characteristic feature of H2(a) loops, can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. The hysteresis loop recorded for Si-OCTA1
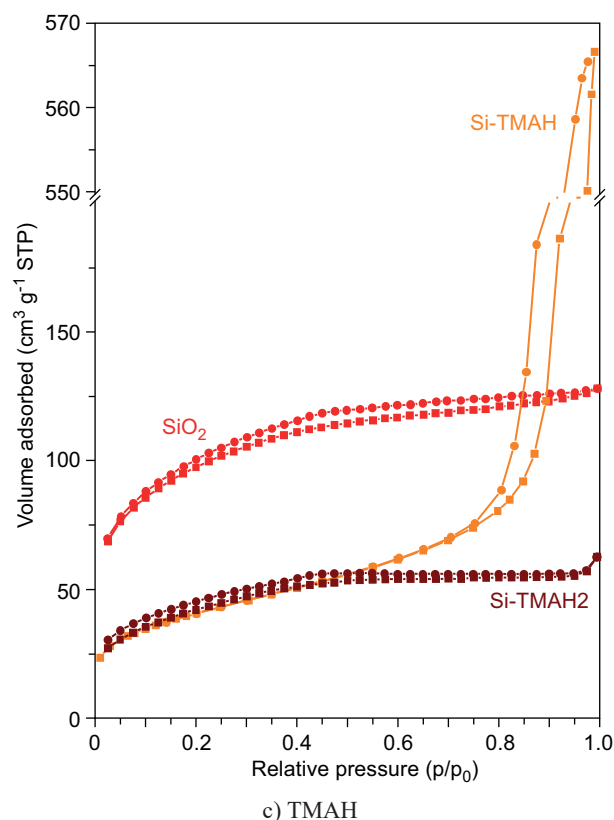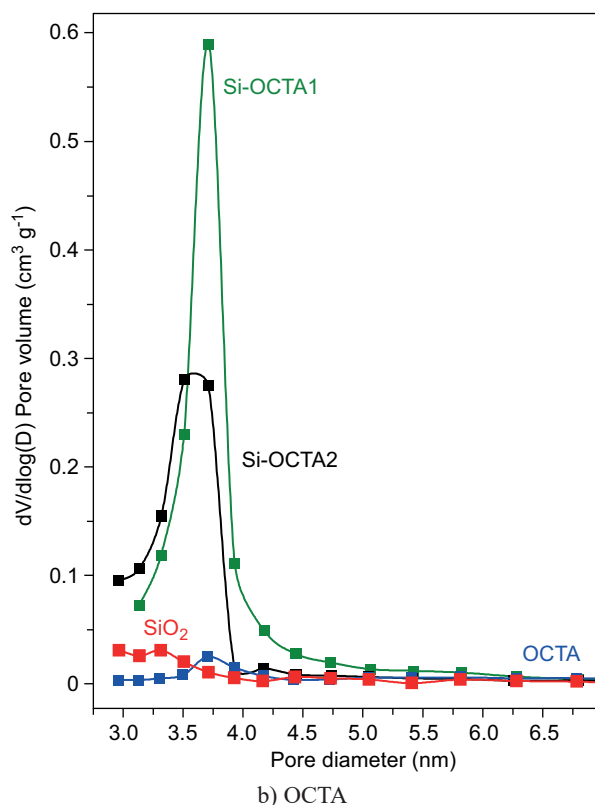

b) OCTA

c) TMAH

Figure 2. Low temperature nitrogen adsorption isotherms and pore size distribution of SiO2 modified by the octaanion (OCTA) (a and b) and tetramethylammonium hydroxide (TMAH)

(Si_{OCTA}/Si_{gel} = 0.0688) can also be classified as H2(a), however, the not fully-closed hysteresis loop occurring in the p/p_0 range from 0 to 0.5 is the evidence of the presence of wide micropores of average size of 3.1 nm, which means that the materials borders on micro- and mesoporous ones, Figure 2b and Table 2. Samples Si-OCTA1 and Si-OCTA2 are characterised by very narrow pore size distribution, the majority of them have diameters between 3 and 4.5 nm, the mean pore diameter is 3.1 and 3.9 nm, respectively.

For SiO_2, the type of structural promoter added in

Table 2. Textural characteristics of the samples after calcination in air at 500°C for 6 h.

Sample code	BET surface area ($m^2 \cdot g^{-1}$)	Average pore diameter* (nm)
OCTA	27	9.9
SiO2	319	2.5
Si-OCTA1	444	3.1
Si-OCTA2	377	3.9
Si-TMAH2	147	2.6
Si-TMAH	144	23.2

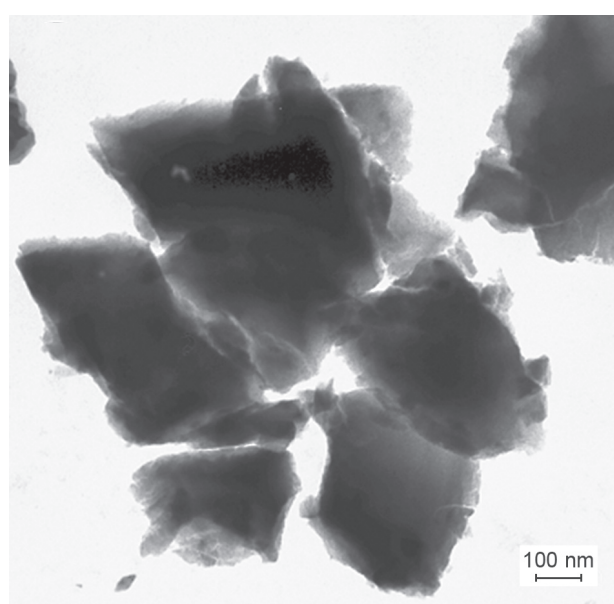** calculated by BJH from the desorption branch of the isotherm*

the process of the material synthesis had a great effect on the surface area and structure of the pores in the materials. The addition of OCTA resulted in an increase in the surface area, while the addition of TMAH caused its decrease, Table 2. The introduction of TMAH, in the amount equimolar to OCTA, directly into the gel of acidic character (Si-TMAH2) leads to a different porous structure, Figure 2c. The isotherm of nitrogen adsorption/

desorption recorded for the system Si-TMAH2 does not show a hysteresis loop related to the capillary condensation in the mesopores. Apart from the reduction in the surface area from 319 $m^2 \cdot g^{-1}$ for SiO_2 to 147 $m^2 \cdot g^{-1}$ for Si-TMAH2, the average pore size remained practically the same and was ~2.6 nm. The isotherm recorded for Si-TMAH2 was of a I(b) type, which is characteristic of materials having a pore size distribution over a broader range including wider micropores and possibly narrow mesopores. The introduction of greater amounts of tetramethylammonium hydroxide (Si-TMAH) led to a typical mesoporous material whose nitrogen adsorption/desorption isotherm had clear features of a Type IV(a) one [16]. The appearance of a Type H1 hysteresis loop indicates the presence of mesopores of a narrow diameter range and bottle pores with a neck size distribution similar to the width of the pore/cavity size distribution.

The microporous character of the initial silica has been confirmed by the transmission microscope images (TEM) – Figure 3a, clearly revealing a homogeneous structure of micropores. A small addition of octaanion to the silica gel (Si-OCTA1 – Si_{OCTA}/Si_{gel} = 0.0688) resulted in a considerable increase in the surface area (444 $m^2 \cdot g^{-1}$ – Table 2) however, the morphology of this system remained very similar to that of standard silicas. No inhomogeneous areas were observed and the structure had features of an amorphous system (Figure 3b).

The TEM image of the octaanion (Figures 4a-d) is more complex, which indicates the diversity of its structure and the occurrence of ultramicroporous regions (Figure 4a, d) along with the areas of a cluster structure typical of silicas obtained with the use of basic catalysts (Figure 4b, c) [17, 18].

An increase in the amount of the octaanion intro-

a) SiO_2 gel sample
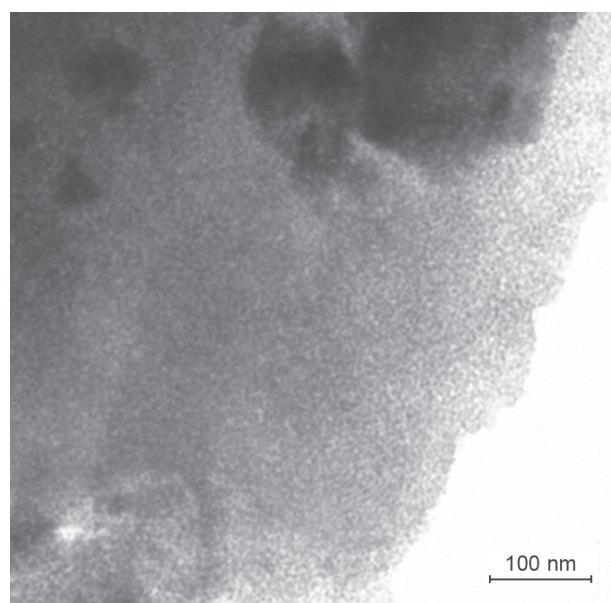
b) Si-OCTA1

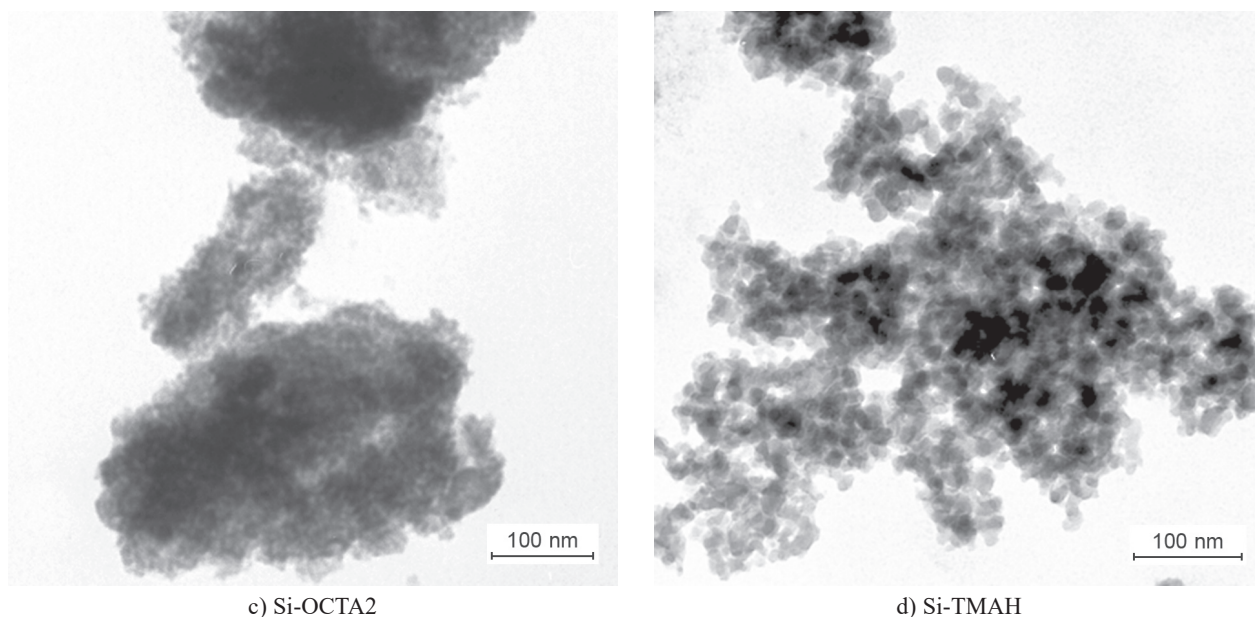Figure 3. TEM images: a) SiO_2 gel sample, b) Si-OCTA1. *(Continue on next page)*

c) Si-OCTA2

d) Si-TMAH

Figure 3. TEM images: c) Si-OCTA2, d) Si-TMAH.

duced into the basic gel obtained by the acidic method (Si_{OCTA}/Si_{gel} = 0.2042) results in the weakening of the effect of textural promotion, however, the surface area of this material is still much larger than that of the reference material (377 $m^2 \cdot g^{-1}$ for Si-OCTA2). With the increasing content of the octaanion, the system begins to lose the features characteristic of the systems synthesised over acidic catalysts (Figure 3c), the appearance of distinct domains is observed which can become clusters characteristic of the systems synthesised over the basic catalysts on the increasing content of the hydroxide [19]. The microporous character of Si-TMAH2 indicated by the

results of nitrogen adsorption/desorption measurements was confirmed by the TEM images, Figure 3d.

The information on the structure of the materials obtained was supplemented with the XRD studies. In a small-angle range (2Θ = 0.5 - 5), no reflections assigned to the order mesoporous structure were detected. In the range 2Θ = 5 - 100, only the octaanion, not subjected to calcination, has a crystalline structure (Figure 5). The other systems show an amorphous structure indicated by a lack of reflections besides a broadened one, typical of silica in the range of 2Θ = 21 - 26.
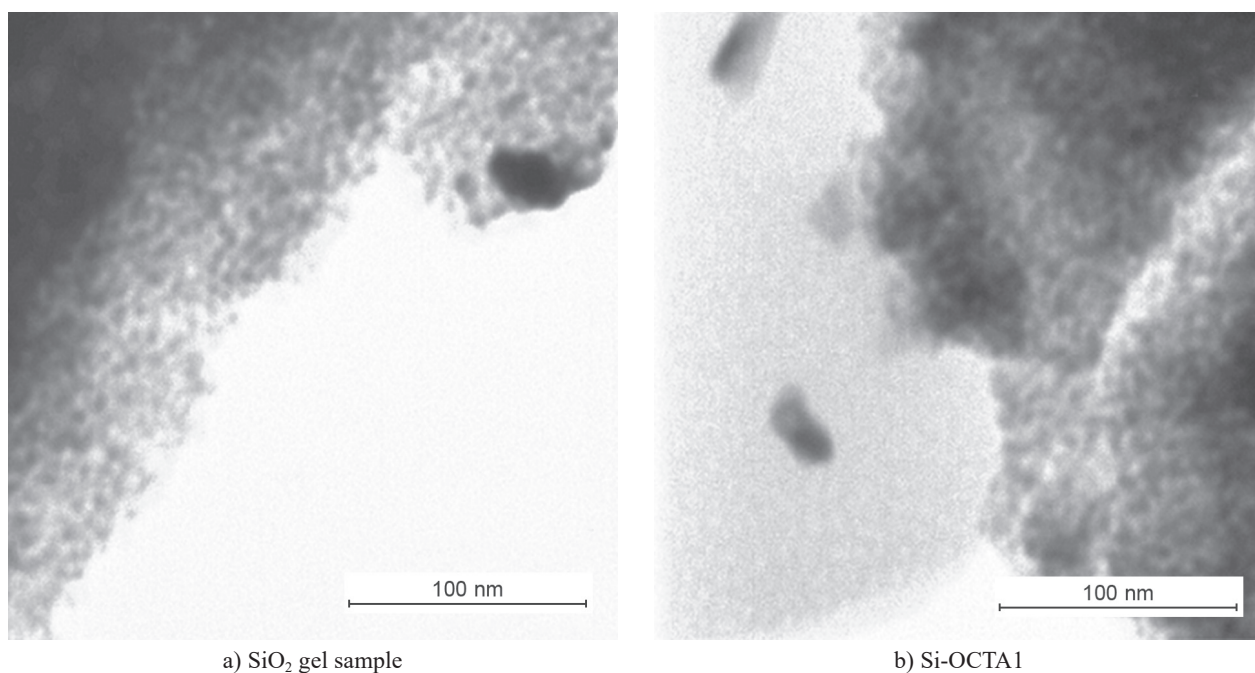

a) SiO$_2$ gel sample

b) Si-OCTA1

Figure 4. TEM images of the calcinated octaanion: a) SiO$_2$ gel sample, b) Si-OCTA1. *(Continue on next page)*

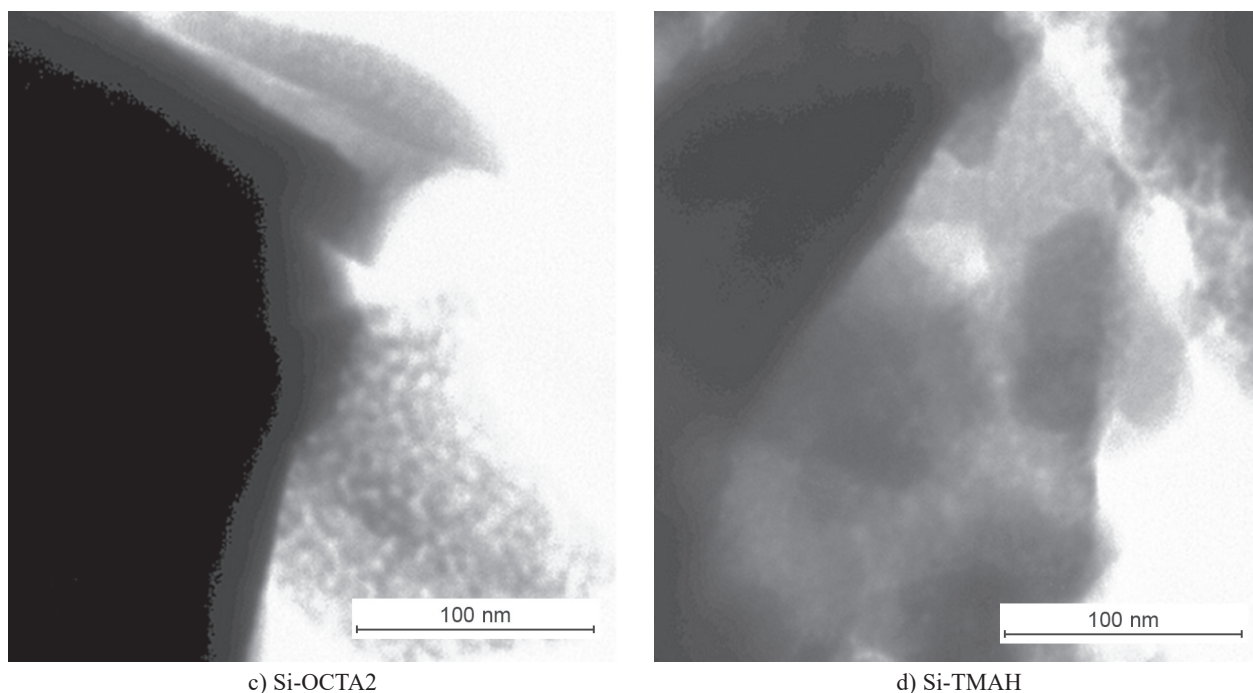c) Si-OCTA2   d) Si-TMAH

Figure 4. TEM images of the calcinated octaanion: c) Si-OCTA2, d) Si-TMAH.

CONCLUSIONS

- The addition of oktakis(tetramethylammonium)-T8--silsesquioxane (OCTA) to silica has a considerable effect on the development of its surface area, in contrast to a small effect of the direct addition of tetramethylammonium hydroxide (TMAH).

- The materials with the addition of OCTA show much greater thermal stability of the tetramethylammonium groups relative to that of the silica materials with TMAH.

- The thermal decomposition of OCTA leads to a material of small surface area containing a mixture of structures of diverse morphologies.

- The use of TMAH in the amount equilibrium to that of OCTA leads to a silica material of pore diameters close to 2.5 nm, so similar to the unmodified silica, but of much smaller surface area.

- The addition of OCTA results in a change in the shape of the adsorption isotherm from a I(b) type characteristic of microporous materials, typical of a narrow-pore silica, to a IVa type (with a hysteresis loop H2a), typical of mesoporous materials.
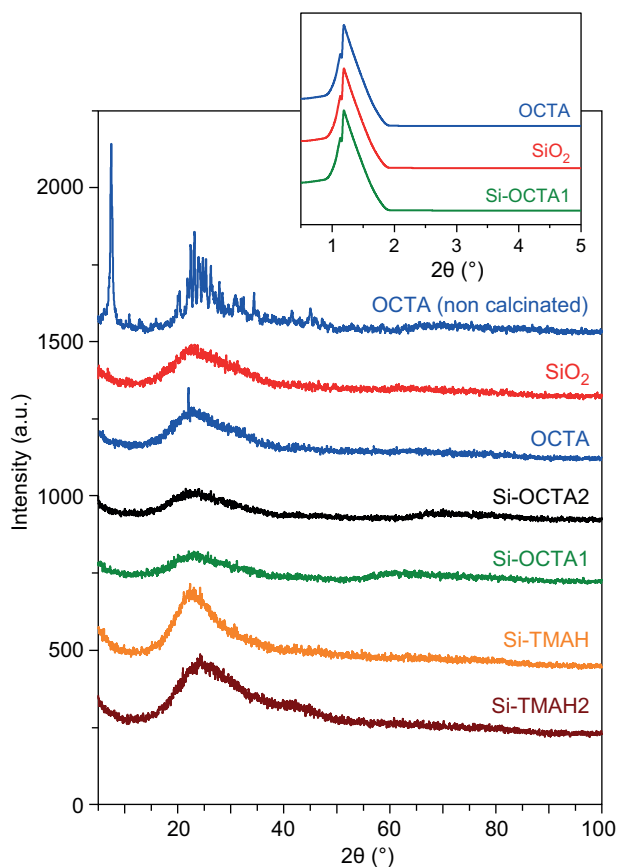

Figure 5. The XRD patterns for the porous gel systems.

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