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# The impact of microwave energy on the results of silica gel hydrothermal modification

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**Abstract** Two series of the hydrothermally treated (HTT) silica gel samples using the microwave reactor or the classical autoclave have been prepared. The HTT modification processes have been performed under the liquid water layer or in the water vapour. The initial and HTT silica samples were examined by means of adsorption ($N_2$), thermogravimetric (TG) and infra red (FTIR-ATR) methods. On the basis of the obtained results it was stated that even a short time of HTT modification using microwaves is enough to make distinct changes in the porous structure of silica. The time and pressure are the most influential parameters during HTT using microwaves. However, in the case of the samples modified in the classical autoclave the most important factors are temperature and time. The hydrothermally modified silica samples possess different concentration of intraglobular water dependently on applied treatment conditions and water state.

**Keywords** Silica gel · Hydrothermal treatment · Microwaves · Water vapour · Porous structure

## 1 Introduction

Silica is one of the most often applied oxide materials widely used as efficient adsorbents and selective absorbents, active phase carriers in catalysis, fillers in polymer systems, adsorbents and supports for gas and liquid chromatography, thickeners for dispersion media and others (Iler 1979). Various problems related to silica characteristics are encountered in different areas of science and technology: physics, chemistry and physical chemistry, agriculture, soil science, biology and medicine, some fields of geology, etc. Such a wide range of silica applications requires the preparation of materials of different porous structure and various physicochemical characteristics. Hydrothermal treatment (HTT) is one of the most effective methods of porous structure adsorbents modification. During the hydrothermal treatment of silica the depolymerization (decondensation) of small particles to orthosilicic acid occurs according to the following reaction

$$(SiO_2)_n + 2H_2O \leftrightarrow (SiO_2)_{n-1} + Si(OH)_4$$

and next there appear the processes of deposition of this acid (recondensation) on large particles of silica. In this way the direction of recondensation process is opposite to decondensation one.

The results of HTT depend on many factors such as the initial structure of adsorbent (Leboda et al. 1995a, 1998), temperature and time of the process (Leboda et al. 1995b, 1995c), gas or liquid phase (Leboda et al. 2000) and pH of medium (Leboda et al. 1995d). During the hydrothermal modification of silica gel, simple mathematical relations allowing to determine the extent of hydrothermal treatment effect on structural parameters (sizes and volumes of pores and specific surface areas (Leboda et al. 1995c)) can be obtained. Such HTT processes are usually performed by using of high pressure autoclaves heated in traditional furnaces. However, this method possesses some shortcomings of both technical and substantive nature. One of them is suitable high duration time to reach the required temperature of the system and the other one is the possibility of occurrence of temperature gradients (in the starting stage of process) especially in the large dimension autoclave. As a result the material of heterogeneous porous structure can be obtained

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(Mendyk et al. 1992). In this case the consumption of large energy is also very important.

A very interesting and useful source of thermal energy are microwaves. This form of energy has been applied since the 50s of 20th century in home equipment in the form of microwave cookers. The advantages of using microwaves in many organic syntheses has been known since the 80s but in inorganic ones since the 90s (Berlan 1995). This technology makes it possible to carry out chemical reactions which could not be performed under traditional conditions in such a short time or with such a high yield (Vanetsev et al. 2002; Khollam et al. 2001). The results of large investigations over the application of microwaves in hydrothermal modification of carbon-silica adsorbents are presented in paper (Skubiszewska-Zięba 2008). There are a few requirements which have to be fulfilled to use the microwaves as a source of thermal energy. The most important is polar character of heated substance, i.e. its dielectric constant $\varepsilon'$ and especially the dielectric losses $\varepsilon''$. The higher the $\varepsilon''$ value the better the effectiveness of microwave energy transformation. Water is one of the polar substances which have the possibility of microwave energy transformation into the heat. Its dielectric looses $\varepsilon''$ value is 0.123. It should be noted that e.g. for ethanol and methanol these values are 0.941 and 0.659 respectively. It means that these reagents are good heating media in microwave energy utilization. The aim of the present work is to study the influence of different conditions of hydrothermal modification of silica gel on its porous structure parameters and surface chemistry by using microwave energy as a source of heat. During the action of microwave radiation the process of sample heating starts from its inner part which may be the additional factor allowing faster achievement of suitable temperature and consequently, more homogeneous porous structure formation. For comparison the experiments under similar conditions of time and temperature by using the classical steal autoclave were performed. The initial and modified silica adsorbents were studied by means of adsorption ($N_2$), thermogravimetric (TG) and infra red (FTIR) methods.

## 2 Experimental

### 2.1 Materials

The commercial mesoporous silica gel Si-60, chromatographic grade (Merck, Germany), $d = 0.3$–$0.5$ mm, $S_{\mathrm{BET}} = 464.5\ \mathrm{m}^2/\mathrm{g}$, and $V_{\mathrm{por}} = 0.85\ \mathrm{cm}^3/\mathrm{g}$ was used as an initial adsorbent. The modifications were performed in a microwave reactor, 300 W power (NaNo 2000, Plazmatronika, Poland). Silica samples were hydrothermally modified (HTT) by two ways, i.e. under liquid water layer and under the conditions of saturated water vapour. Before experiments initial silica gel was dried at 200 °C to remove physically adsorbed water. In the case of modifications under the liquid water layer the weighted portion of dry silica gel (2 g) was put on the bottom of a special teflon cuvette (100 $\mathrm{cm}^3$) of the microwave reactor and mixed with 40 $\mathrm{cm}^3$ of distilled water. But in the case of saturated water vapour the silica sample was placed into the special quartz vessel which next was put into the teflon cuvette containing 40 $\mathrm{cm}^3$ portion of previously added water. The HTT processes were carried out at different duration times (from 5 to 100 minutes), different pressure limits (from 20 to 70 atm) and at different temperatures (from 220 to 290 °C).

For comparison the experiments in the classical steal autoclave (0.3 $\mathrm{dm}^3$) under the suitable conditions of temperature and time, as in the case of samples modified by using of microwaves were performed. The prepared samples were named as follows: Si-$60_{\mathrm{ini}}$ (initial silica gel), Si-$\mathrm{N}_{\text{m-vap}}$ (microwave-vapour), Si-$\mathrm{N}_{\text{m-liq}}$ (microwave-liquid), Si-$\mathrm{N}_{\text{a-vap}}$ (autoclave-vapour), Si-$\mathrm{N}_{\text{a-liq}}$ (autoclave-liquid).

### 2.2 Nitrogen adsorption

Low-temperature (77.4 K) nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2405N (USA) adsorption analyzer. The specific surface area $S_{\mathrm{BET}}$ was calculated using the standard BET equation (Gregg and Sing 1982) at $p/p_0$ between 0.06 and 0.2, where $p$ and $p_0$ denote the equilibrium and saturation pressures of nitrogen, respectively. The pore volume $V_{\mathrm{p}}$ was estimated at $p/p_0 \approx 0.98$ converting the volume of adsorbed gas nitrogen to the volume of fluid. The average pore diameter ($D_p$) was calculated for a model of cylindrical pores, $D_p = 4V_p/S_{\mathrm{BET}}$. Pore volume distributions in the function of their radius were calculated by using the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951).

### 2.3 TG measurements

The thermal behavior of studied silicas was performed on heating in air atmosphere from 20 to 1000 °C (heating rate 10 deg/min) using a Derivatograph C (Paulik, Paulik & Erdey, MOM, Budapest). Total concentration of OH groups ${}^{\mathrm{tot}}\delta_{\mathrm{OH}}$ ($\mathrm{OH/nm}^2$) was determined on the basis of sample mass loss of dry silica sample in the range of 200–1000 °C according to the de Boer equation (Linsen 1970): ${}^{\mathrm{tot}}\delta_{\mathrm{OH}} = 2/3 \cdot 10^3 \cdot \Delta\mathrm{m} \cdot \mathrm{S}^{-1}$, where $\Delta$m denotes the sample mass loss (% w/w), and $S$ the specific surface area. Concentration of OH groups ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$ derived from the presence of structural (intraglobular) water inside the silica particles was calculated by subtracting the value of 4.6 $\mathrm{OH/nm}^2$ (corresponding to the concentration of the surface OH groups for maximally hydroxylated silica, $\alpha_{\mathrm{OH}}$) from the value of experimentally determined: ${}^{\mathrm{V}}\delta_{\mathrm{OH}} = {}^{\mathrm{tot}}\delta_{\mathrm{OH}} - \alpha_{\mathrm{OH}}$ (Zhuravlev 2000). The silica globule diameter $D_{\mathrm{g}}$ was determined according to the equation: $D_{\mathrm{g}} = 6 \cdot 10^4/\rho \cdot S$ where $\rho$ is the density of silica (2.2 $\mathrm{g/cm}^3$) and $S$ the specific surface area (Karnaukhov 1979).

**Table 1** Preparation conditions and structural parameters of silica adsorbents modified in the microwave reactor or in the autoclave

| Sample (microwave) | $t$ min | $p_{\text{m}}$ atm | $T$ °C | $S_{\text{BET}}$ m$^2$/g | $V_{\text{por}}$ cm$^3$/g | $D_{\text{por}}$ nm | Sample (autoclave) | $p_{\text{a}}$ atm | $S_{\text{BET}}$ m$^2$/g | $V_{\text{por}}$ cm$^3$/g | $D_{\text{por}}$ nm |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Si-60$_{\text{ini}}$ | – | – | – | 464.5 | 0.85 | 7.3 | – | – | – | – | – |
| Si-1$_{\text{m-vap}}$ | 5 | 60 | 275 | 94.4 | 0.39 | 16.7 | – | – | – | – | – |
| Si-1$_{\text{m-liq}}$ | 7 | 60 | 290 | 88.6 | 0.60 | 27.3 | – | – | – | – | – |
| Si-2$_{\text{m-vap}}$ | 40 | 60 | 270 | 77.7 | 0.27 | 14.1 | Si-2$_{\text{a-vap}}$ | 54 | 183.4 | 0.84 | 18.2 |
| Si-2$_{\text{m-liq}}$ | 40 | 60 | 270 | 83.0 | 0.30 | 15.3 | Si-2$_{\text{a-liq}}$ | 54 | 188.1 | 0.88 | 18.6 |
| Si-3$_{\text{m-vap}}$ | 60 | 70 | 280 | 44.0 | 0.10 | 9.1 | Si-3$_{\text{a-vap}}$ | 63 | 66.6 | 0.26 | 15.4 |
| Si-3$_{\text{m-liq}}$ | 60 | 70 | 280 | 57.0 | 0.20 | 12.7 | Si-3$_{\text{a-liq}}$ | 63 | 122.9 | 0.56 | 18.1 |
| Si-4$_{\text{m-vap}}$ | 70 | 40 | 220 | 72.6 | 0.26 | 14.5 | Si-4$_{\text{a-vap}}$ | 23 | 308.0 | 0.86 | 11.2 |
| Si-4$_{\text{m-liq}}$ | 70 | 40 | 230 | 78.3 | 0.30 | 14.9 | Si-4$_{\text{a-liq}}$ | 28 | 226.8 | 0.91 | 16.0 |
| Si-5$_{\text{m-vap}}$ | 100 | 20 | 230 | 125.0 | 0.73 | 23.5 | Si-5$_{\text{a-vap}}$ | 28 | 106.3 | 0.31 | 11.7 |
| Si-5$_{\text{m-liq}}$ | 100 | 20 | 230 | 105.0 | 0.63 | 23.9 | Si-5$_{\text{a-liq}}$ | 28 | 110.3 | 0.24 | 8.8 |
| Si-6$_{\text{m-vap}}$ | 100 | 60 | 270 | 63.0 | 0.21 | 13.2 | Si-6$_{\text{a-vap}}$ | 54 | 37.7 | 0.09 | 10.0 |
| Si-6$_{\text{m-liq}}$ | 100 | 60 | 270 | 66.5 | 0.20 | 12.6 | Si-6$_{\text{a-liq}}$ | 54 | 36.3 | 0.05 | 6.0 |

Note: $t$—time; $p_{\text{m}}$—pressure created in microwave reactor; $T$—temperature; $S_{\text{BET}}$—specific surface area; $V_{\text{por}}$—total pore volume; $D_{\text{por}}$—average pore diameter; $p_{\text{a}}$—pressure of saturated vapour steam in autoclave at corresponding temperature of modification (Physicochemical Handbook, 1962)

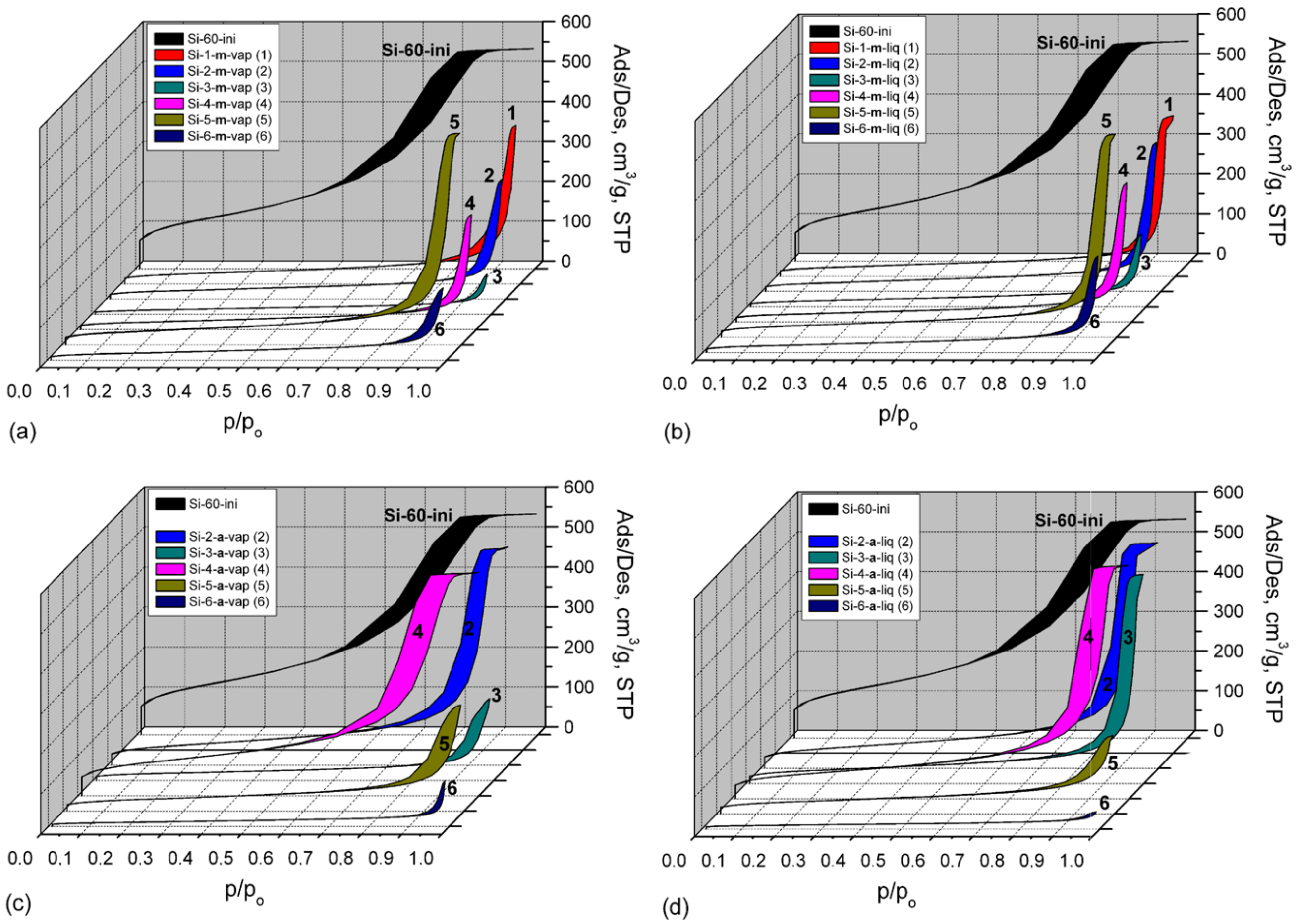


**Fig. 1** The low-temperature adsorption-desorption isotherms of nitrogen for initial silica gel Si-60 and hydrothermally treated samples in the microwave reactor (**a**, **b**) or in the autoclave (**c**, **d**)

### 2.4 FTIR spectra

The IR spectra of silica samples were recorded over the range of 4000–400 $cm^{-1}$ by means of the attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR), using a FTIR spectrometer NICOLET 8700 (Thermo Scientific, USA) equipped with Diamond Smart Orbit ATR. Before the FTIR measurements the samples were dried at 200 °C for 2 hours.

## 3 Results and discussion

Table 1 presents the preparation conditions of silica samples modified in the microwave reactor and autoclave. In both cases the values of time and temperature were the same. However, the values of pressure were slightly different. It results from the fact that during microwave heating it is possible to set the maximum pressure which, consequently, determines the maximum of temperature. But in the case of modification in the autoclave the saturated water pressure refers to temperature of the system (Physicochemical Handbook 1962).

Comparing structural parameters of the samples (Table 1) modified in the microwave reactor, it is clearly seen that even a very short time of HTT modification is enough to make distinct changes in porous structure of silica. Just already 5 and 7 minutes of modification allows decrease the specific surface area from 464.5 $m^2/g$ (Si-$60_{ini}$) to 94.4 $m^2/g$ (Si-$1_{m\text{-}vap}$) and 88.6 $m^2/g$ (Si-$1_{m\text{-}liq}$). A longer time influ-

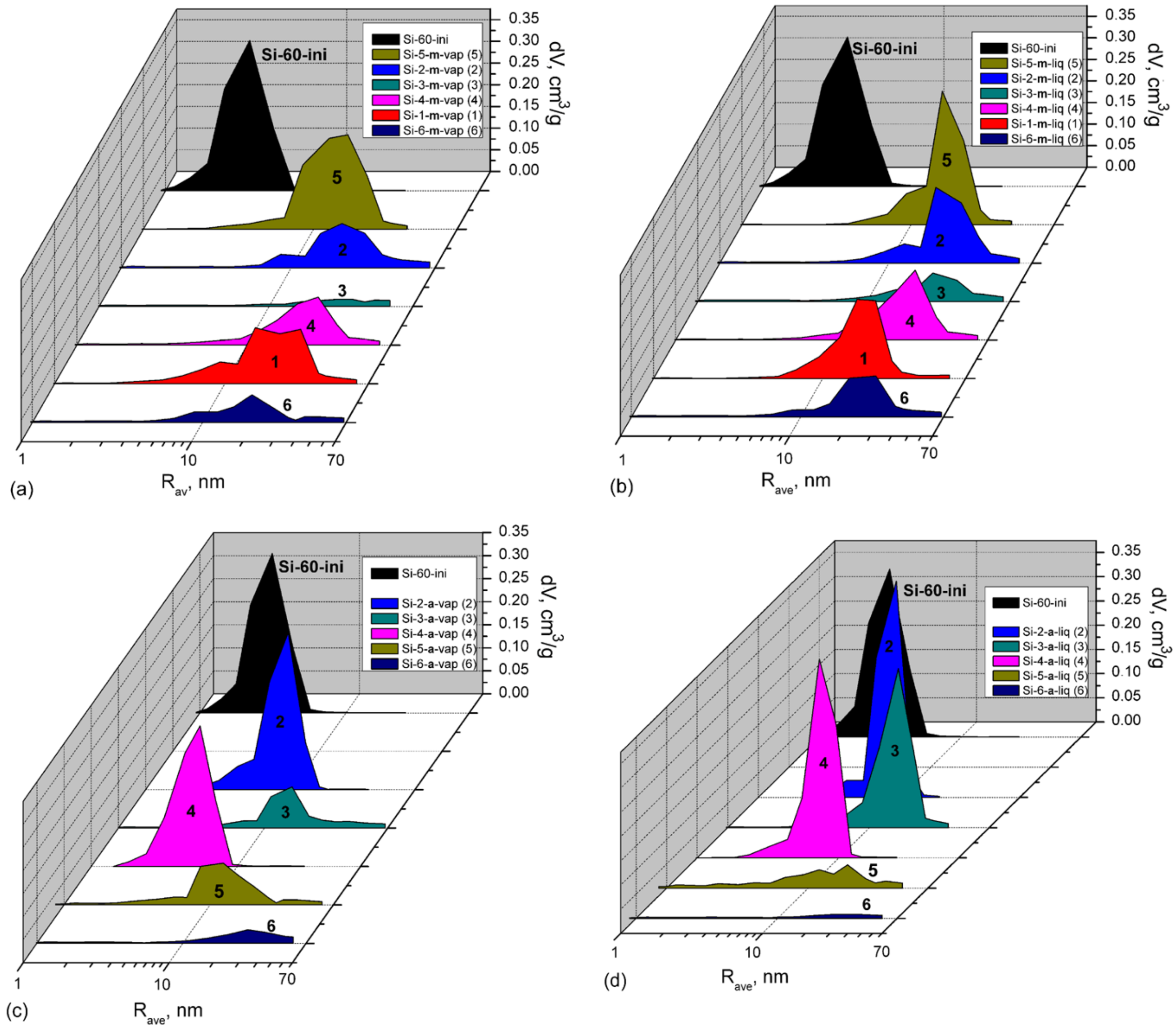


**Fig. 2** The pore volume distribution functions in respect of their radius for initial silica gel Si-60 and hydrothermally treated samples in the microwave reactor (**a**, **b**) or in the autoclave (**c**, **d**)

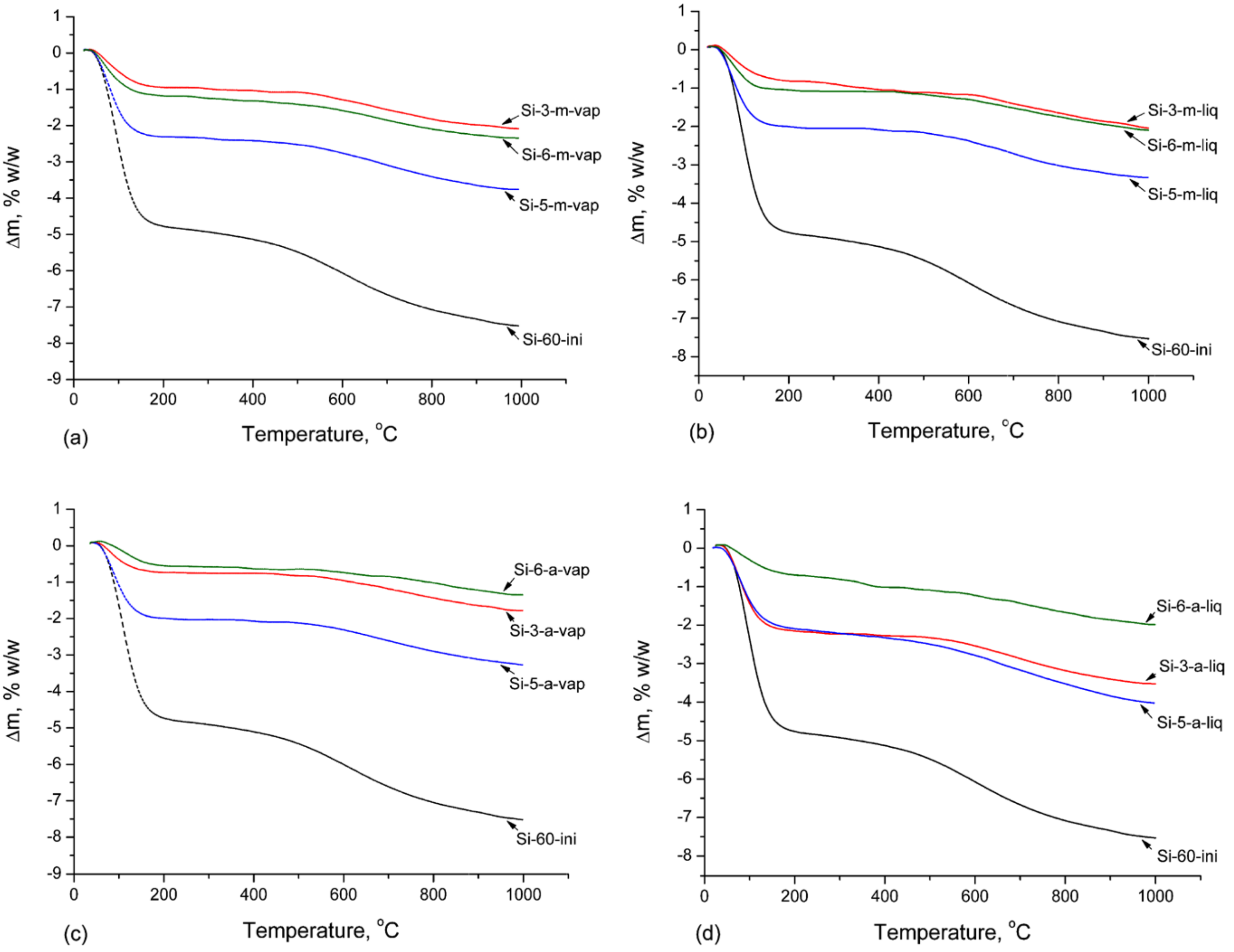


**Fig. 3** TG curves of initial silica gel Si-60 and hydrothermally treated samples in the microwave reactor (**a**, **b**) or in the autoclave (**c**, **d**)

ences the extent of modification that is evidenced in the case of samples Si-2$_{\text{m-vap}}$, Si-2$_{\text{m-liq}}$ (270 °C, 40 min) and Si-6$_{\text{m-vap}}$ and Si-6$_{\text{m-liq}}$ (270 °C, 60 min). However, the most influential parameter is pressure. The higher the pressure the lower the specific surface area of the modified sample. These observations are well visible in the case of the samples modified at the same temperature (230 °C) but under different values of pressure, i.e. Si-5$_{\text{m-vap}}$, Si-5$_{\text{m-liq}}$ (20 atm) and Si-4$_{\text{m-vap}}$ and Si-4$_{\text{m-liq}}$ (40 atm).

In the case of the samples modified in the autoclave the most important factors are the temperature and time. It is clearly seen in the case of the samples Si-2$_{\text{a-vap}}$, Si-2$_{\text{a-liq}}$ ($S_{\text{BET}}$, 183.4 and 188.1 m$^2$/g), and Si-6$_{\text{a-vap}}$ and Si-6$_{\text{a-liq}}$ ($S_{\text{BET}}$, 37.7 and 36.3 m$^2$/g) modified at the same temperatures and pressures (270 °C, 54 atm) but at different duration times (40 and 100 min). The longer the treatment time the higher the extent of modification. Comparing the samples Si-2$_{\text{m-vap}}$, Si-2$_{\text{m-liq}}$ ($S_{\text{BET}}$, 77.7 and 83 m$^2$/g) and Si-2$_{\text{a-vap}}$, Si-2$_{\text{a-liq}}$ ($S_{\text{BET}}$, 183 and 188 m$^2$/g) modified under similar conditions but in different reactors one can see that during modification in the autoclave the time of 40 minutes is too short to obtain similar structural parameters comparing to those of the samples modified by applying microwave heating. It should be also noted that for some samples modified in the microwave reactor and autoclave in spite of similarity of specific surface area the total volumes of pores differ significantly. It is in the case of the samples Si-$_{\text{m-vap}}$, Si-$_{\text{m-liq}}$ and Si-$_{\text{a-vap}}$, Si-$_{\text{a-liq}}$. The above discussed data are confirmed by the courses of adsorption-desorption isotherms presented in Fig. 1 and pore volume distributions shown in Fig. 2. Here we can see that the shapes of isotherms depend both on the state of water (vapour or liquid) and type of reactor (microwave or autoclave). The hysteresis loop for the initial silica gel belongs to H2 type according to the IUPAC classification (Gregg and Sing 1982). Such a kind of loop suggests the presence of globular mesoporous structure with wide distribution of pores (Fig. 2). Hydrothermal modification of initial silica gel in the microwave reactor both in vapour and liquid phases leads to formation of more homogeneous structure of pores giving hysteresis loops of H1

**Table 2** Results of quantitative analysis of TG measurements

| Sample | TG mass losses (wt%) at different temperature ranges (°C) | | | | | | ${}^{\mathrm{tot}}\delta_{\mathrm{OH}}$ | $D_g$ | ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 20–200 | 200–400 | 400–600 | 600–800 | 800–1000 | 200–1000 | OH/nm$^2$ | nm | OH/nm$^2$ |
| Si-60$_{\mathrm{ini}}$ | 4.80 | 0.37 | 0.75 | 1.25 | 0.47 | 2.85 | 4.1 | 5.9 | – |
| Si-3$_{\mathrm{m\text{-}vap}}$ | 0.94 | 0.08 | 0.24 | 0.55 | 0.32 | 1.19 | 18.0 | 62.0 | 13.4 |
| Si-3$_{\mathrm{m\text{-}liq}}$ | 0.80 | 0.24 | 0.11 | 0.48 | 0.44 | 1.27 | 14.9 | 47.8 | 10.3 |
| Si-5$_{\mathrm{m\text{-}vap}}$ | 2.30 | 0.12 | 0.37 | 0.67 | 0.34 | 1.50 | 8.0 | 21.8 | 3.4 |
| Si-5$_{\mathrm{m\text{-}liq}}$ | 1.90 | 0.08 | 0.30 | 0.65 | 0.32 | 1.35 | 8.6 | 26.0 | 4.0 |
| Si-6$_{\mathrm{m\text{-}vap}}$ | 1.19 | 0.13 | 0.29 | 0.52 | 0.26 | 1.20 | 12.7 | 43.3 | 8.1 |
| Si-6$_{\mathrm{m\text{-}liq}}$ | 1.03 | 0.08 | 0.18 | 0.44 | 0.58 | 1.28 | 12.8 | 41.0 | 8.2 |
| Si-3$_{\mathrm{a\text{-}vap}}$ | 0.74 | 0.02 | 0.20 | 0.46 | 0.36 | 1.04 | 10.4 | 41.0 | 5.8 |
| Si-3$_{\mathrm{a\text{-}liq}}$ | 2.20 | 0.11 | 0.27 | 0.66 | 0.35 | 1.39 | 7.5 | 22.2 | 2.9 |
| Si-5$_{\mathrm{a\text{-}vap}}$ | 1.98 | 0.09 | 0.30 | 0.60 | 0.36 | 1.35 | 8.5 | 25.7 | 3.9 |
| Si-5$_{\mathrm{a\text{-}liq}}$ | 2.10 | 0.22 | 0.50 | 0.74 | 0.54 | 2.00 | 12.1 | 24.7 | 7.5 |
| Si-6$_{\mathrm{a\text{-}vap}}$ | 0.54 | 0.02 | 0.05 | 0.52 | 0.40 | 0.98 | 16.1 | 72.3 | 11.5 |
| Si-6$_{\mathrm{a\text{-}liq}}$ | 0.70 | 0.12 | 0.15 | 0.28 | 0.30 | 0.91 | 24.4 | 75.5 | 19.8 |

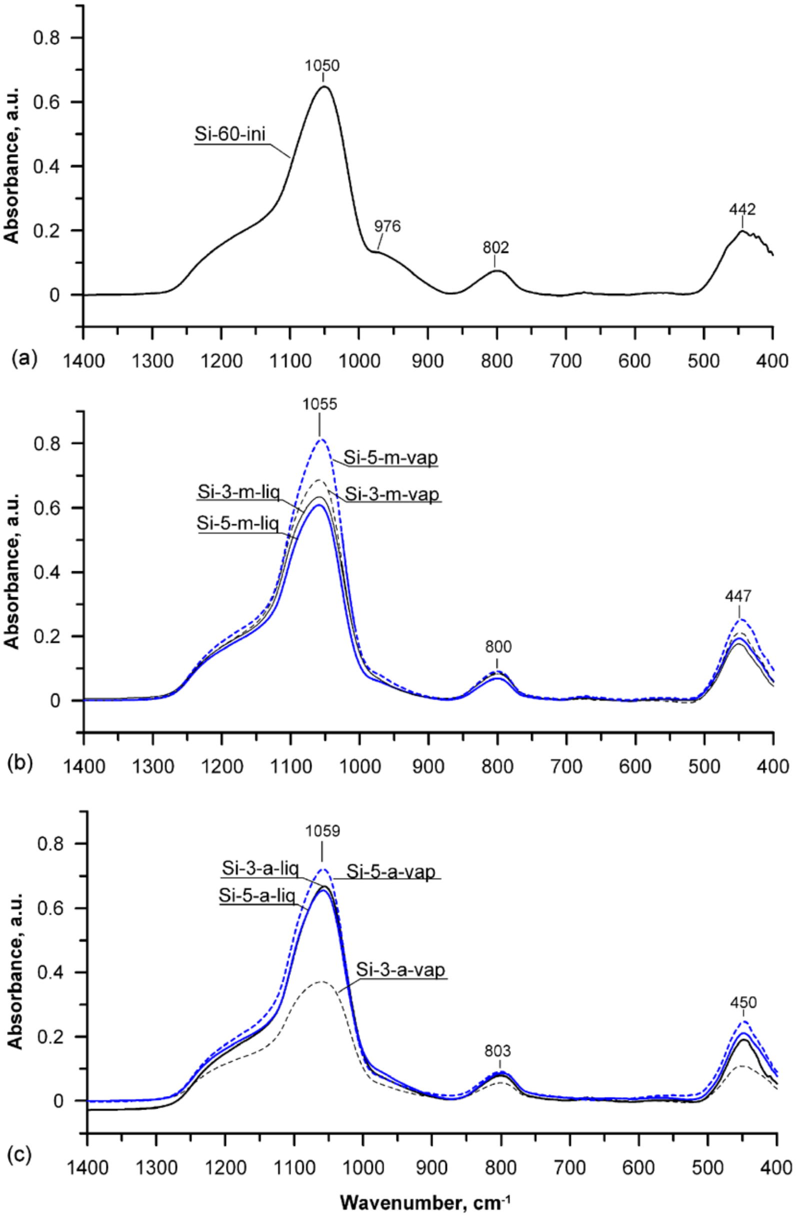
Note: ${}^{\mathrm{tot}}\delta_{\mathrm{OH}}$—is the total concentration of OH groups; $D_g$—is globule diameter; ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$—is the concentration of OH groups derived from the presence of structural (intraglobular) water

type (Figs. 1a, b). Their adsorption-desorption branches are upright and shifted both along the axis of relative pressures and that of adsorption. Moreover the hysteresis loops of microwave modified samples are sufficiently narrow. But in the case of the samples modified in the autoclave their hysteresis loops are wider and for samples Si-4$_{\mathrm{a\text{-}vap}}$ and Si-4$_{\mathrm{a\text{-}liq}}$ are of H2 type (Figs. 1c and 1d) similarly to the initial silica gel. These observations find reflection in the course of pore volume distribution functions presented in Fig. 2. Here one can see that for the samples modified in the microwave reactor independently on the water state all peaks of $dV(R)$ function are shifted towards larger pores (Figs. 2a, b). But in the case of the samples modified in the autoclave only for the samples treated for 100 minutes (Si-5$_{\mathrm{a\text{-}vap}}$, Si-5$_{\mathrm{a\text{-}liq}}$ Si-6$_{\mathrm{a\text{-}vap}}$ Si-6$_{\mathrm{a\text{-}liq}}$) their peaks of $dV(R)$ function are shifted towards larger pores. Comparing all curves of $dV(R)$ functions presented in Fig. 2 it can be generally stated that depending on the water state used during modification their shapes differ and it seems that the pore volume distribution functions for all samples modified under the liquid layer are slightly narrower.

In Fig. 3 the TG curves of chosen silica samples are presented. Comparing the shapes of these curves some differences can be observed. Here two distinct steps of mass loss can be seen. The first step, in the range of 20–200 °C, is connected with dehydration process (removing physically adsorbed water) but the second one, from 200 to 1000 °C, corresponds to condensation of all types of surface OH groups and that present inside the $SiO_2$ skeleton (intraglobular). During heating these hydroxyls are removed in different ranges of temperature. First, up to 400 °C the isolated, geminal and vicinal surface silanols are removed and internal OH groups gradually disappear with an increase of temperature. At 900 °C there are only isolated single (free) and geminal (free) OH groups on the surface, but the internal (inraglobular) OH groups disappear completely. At the temperatures above 900 °C the degree of surface coverage by isolated (free) OH groups gradually decreases up to their complete removal (Zhuravlev 2000; Ek et al. 2001; Huhn 1988). The second stage of mass loss can be used for determination of total concentration of hydroxyl groups contained in silica. In Table 2 the results of such calculations for the studied samples are presented.

Analysing the data presented in Table 2 one can observe that for the hydrothermally modified silica gel samples the total concentration of hydroxyl groups ${}^{\mathrm{tot}}\delta_{\mathrm{OH}}$ calculated on the basis of TG data is much higher than that of the surface silanol groups $\alpha_{\mathrm{OH}}$ (approximately equal to 4.6 OH/nm$^2$) of completely hydroxylated silica (Zhuravlev 2000). It results from the fact that these samples contain not only the surface OH groups $\alpha_{\mathrm{OH}}$ but also structurally bound water inside the skeleton of bulk silica, marked here as ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$ (Linsen 1970; Zhuravlev 2000; Ek et al. 2001; Huhn 1988). In the case of the samples modified in the microwave reactor the ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$ values corresponding to hydroxyls contained within the bulk of silica globules are directly proportional to the temperature of HTT modification. The samples Si-5$_{\mathrm{m\text{-}vap}}$ and Si-5$_{\mathrm{m\text{-}liq}}$ modified at 230 °C have the lowest ${}^{\mathrm{V}}\delta_{\mathrm{OH}}$ value (3.4 and 4.0 OH/nm$^2$) but Si-3$_{\mathrm{m\text{-}vap}}$ and Si-3$_{\mathrm{m\text{-}liq}}$ modified at 280 °C have the highest one (13.4 and 10.3 OH/nm$^2$). However, in the case of the samples modified in the autoclave these values increase with the increasing duration time. The samples Si-3$_{\mathrm{a\text{-}vap}}$ and Si-3$_{\mathrm{a\text{-}liq}}$ modified at 280 °C

**Fig. 4** FTIR-ATR spectra of initial silica gel Si-60 (**a**) and chosen silica samples hydrothermally treated in the microwave reactor (**b**) or in the autoclave (**c**)



for 60 minutes have relatively low $^{V}\delta_{OH}$ value (5.8 and 2.9 OH/nm$^2$) but the samples Si-6$_{\text{a-vap}}$ and Si-6$_{\text{a-liq}}$ modified at 270 °C but for 100 minutes have the highest ones (11.5 and 19.8 OH/nm$^2$). Moreover, in the case of the samples modified in the autoclave with a longer duration time (100 minutes) the $^{V}\delta_{OH}$ values for the samples modified under the liquid water layer (samples Si-5$_{\text{a-liq}}$ and Si-6$_{\text{a-liq}}$, 7.5 and 19.8 OH/nm$^2$) are higher than for those modified under the conditions of saturated water vapour (Si-5$_{\text{a-vap}}$ and Si-6$_{\text{a-vap}}$, 3.9 and 11.5 OH/nm$^2$). Generally speaking the concentration of bulk water $^{V}\delta_{OH}$ (structural hydroxyl groups) is directly proportional to the globule size $D_g$ (Table 2).

The FTIR spectra in the range of 400–1400 cm$^{-1}$ presented in Fig. 4 for the chosen silica samples modified in the microwave reactor at different temperatures (230 and 280 °C), different pressures (20 and 70 atm) and different duration times (60 and 100 minutes) provide additional information of the silica samples under investigation. Here one can see that the intensities of IR bands $\nu_{SiO}$ at about 440 cm$^{-1}$, 800 cm$^{-1}$, and in the range of 980–1260 cm$^{-1}$ related to the bulk of silica depending on the HTT modification conditions differ to some extent. In the spectra of HTT modified samples (Figs. 4b, c) there is lack of band at 976 cm$^{-1}$ in comparison to the initial silica gel (Fig. 4a). Analysing the IR curves presented in Fig. 4b, c one can see that for the samples modified in water vapour at longer time their intensities are higher. However, the intensities of the spectra of the microwave modified samples are higher than those of the samples modified in the autoclave (see Figs. 4b and 4c). But in the case of the samples modified

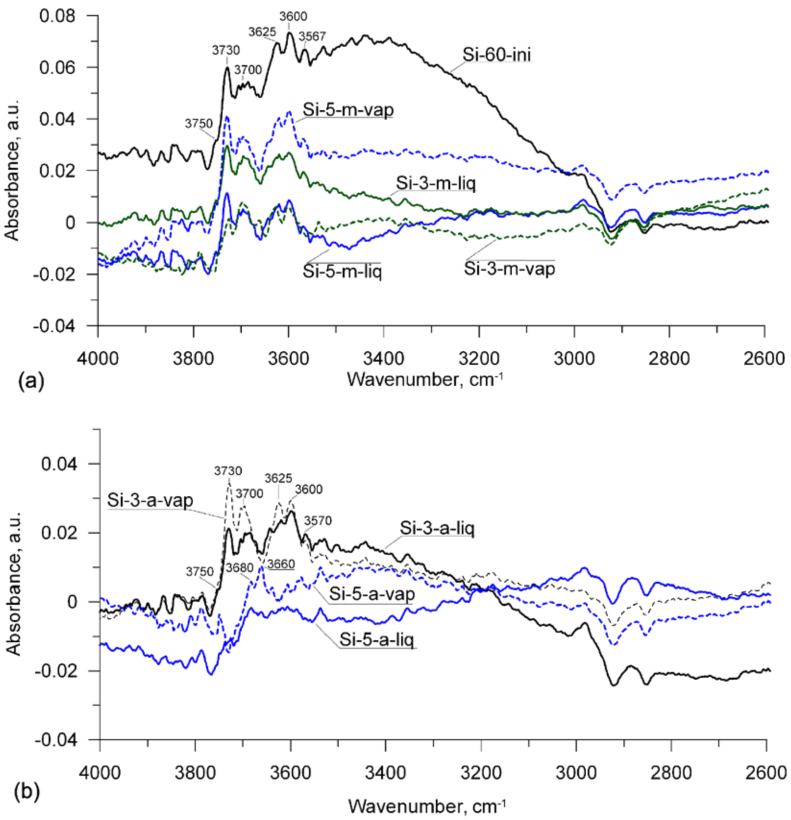


**Fig. 5** FTIR-ATR spectra of initial silica gel Si-60 and chosen silica samples hydrothermally treated in the microwave reactor (**a**) or in the autoclave (**b**)

in the autoclave the longer the modification time the higher the intensities of IR spectra (Fig. 4c, Si-$5_{\text{a-vap}}$ and Si-$3_{\text{a-vap}}$). The relationships observed in Fig. 4 to some extent coincide with the data in Table 2 (column 7) concerning the TG mass losses derived from the dehydroxylation process (condensation of OH groups) of dry silica during heating from 200 °C to 1000 °C.

The additional information about structure of OH functionalities presented on the surface of initial and modified silica samples are shown in Fig. 5. Here we can see the presence of IR bands responsible for occurrence of different kinds of surface silanol groups characteristic for hydroxylated silicas, i.e. in the range of 3650–3750 $\text{cm}^{-1}$ the isolated OH groups, at 3500–3650 $\text{cm}^{-1}$ vicinal and geminal hydroxides and wide spectrum at maximum of 3400 $\text{cm}^{-1}$ responsible for presence of physically adsorbed water molecules. Comparing these spectra (Fig. 5) it could be generally spoken that the intensity of IR bands for samples modified in microwave reactor is much higher in relation to ones obtained for samples treated in autoclave. Moreover the intensity of wide spectrum at 3400 $\text{cm}^{-1}$ characteristic for physisorbed water is much higher for initial silica gel Si-60 in relation to other samples, especially for those modified in microwave reactor.

## 4 Conclusions

Hydrothermal treatment of silica gel using microwave radiation as a source of heat energy is more effective in comparison to such process performed in the autoclave heated in the classical furnace. Even a short time of HTT modification allows to carry out effectively the recondensation/decondensation processes of silica transport both in the saturated water vapour and liquid water. The silica samples hydrothermally treated by using microwaves possess more homogeneous structure of pores than those modified in the classical autoclave. In the case of treatment using microwaves the most important factors are temperature and pressure but the temperature and time are very important parameters in the case of modification in the autoclave. For the hydrothermally modified silica samples total concentration of hydroxyl groups ${}^{\text{tot}}\delta_{\text{OH}}$, calculated on the basis of TG data, is much higher than that of surface silanol groups $\alpha_{\text{OH}}$ of completely hydroxylated silica. It results from the fact that these samples contain not only surface OH groups $\alpha_{\text{OH}}$ but also structurally bound water inside the skeleton of bulk silica. For the samples modified in the microwave reactor the ${}^{\text{V}}\delta_{\text{OH}}$ values corresponding to hydroxyls contained within the bulk of silica globules are directly proportional to the temperature of HTT modification. But in the case of the samples modified in the autoclave these values increase with the increasing time.

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