

Determination of hydroxyls density in the silica-mesostructured cellular foams by thermogravimetry

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Abstract

Thermogravimetry was applied to determine the surface hydroxyls coverage in the mesostructured cellular foams (MCFs) calcined at different temperatures and then rehydroxylated by contacting with water vapor or liquid. The TG measurements were performed by heating MCFs in air stream using a three-step temperature program: (i) at rate of $5\text{ }^{\circ}\text{C min}^{-1}$ from 25 to $200\text{ }^{\circ}\text{C}$; (ii) held at $200\text{ }^{\circ}\text{C}$ for 30 min; and (iii) heating at rate of $10\text{ }^{\circ}\text{C min}^{-1}$ up to $1100\text{ }^{\circ}\text{C}$. The hydroxyls content was calculated from weight loss during third step. The hydroxyls density appeared to depend strongly on the calcination temperature and the subsequent contact with water vapor. When MCFs were exposed for a short period (ca. 1 min) to moist air the hydroxyls content increased rapidly, more in the samples calcined at $300\text{ }^{\circ}\text{C}$ than $500\text{ }^{\circ}\text{C}$, to attain surface densities of 4.75 and 1.6 OH nm^{-2} , respectively. The 2-h contact with water vapor resulted in slower further increase of hydroxyls densities, to values of 5.45 and 2.9 OH nm^{-2} , for samples calcined at 300 and $500\text{ }^{\circ}\text{C}$, but longer contacts had no significant effect. A similar trend was also observed when sample was treated with liquid water.

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1. Introduction

Mesostructured silica cellular foams (MCFs) are a new class of mesoporous materials [1,2] with very promising properties for sorption and catalysis and hence attracting considerable attention in recent years [3–5]. Pure silica MCFs have specific surface area up to $1000\text{ m}^2\text{ g}^{-1}$ and cage-like uniform mesopores of diameter 20–40 nm, interconnected by windows with diameter 10–15 nm. Porous structure of these materials is templated by the oil-in-water (O/W) microemulsion droplets, typically composed of trimethylbenzene (oil) and amphiphilic three-block copolymer PEO–PPO–PEO, acting as stabilizing agent. After synthesis, organic template is removed by calcination or extraction. Functionalization of MCFs with organic groups or transition metals is necessary to obtain the specific sorption or catalytic properties. An active component can be introduced either by a direct method or by post-synthesis procedure [6,7]. During the latter the precursor of an active compound reacts with sur-

face silanols to form links between silica surface and functional moieties. These links depend on several parameters, but the hydroxyls concentration on the silica surface is deemed to be critical; they are responsible for the reactivity of the silica surface [8–13].

The silica surface consists of a combination of silanol groups of different type and of siloxane bridges whose relative concentration depends on calcination temperature, ambient humidity and storage time [14]. Hydrogen-bonded water molecules or physisorbed water may also be adsorbed onto all types of surface silanols. Thermal treatment before functionalization is necessary to remove physisorbed water and weakly bonded hydroxyls.

According to Zhuravlev [15,16], the threshold temperature corresponding to the completion of dehydration and the beginning of dehydroxylation is estimated to be $190 \pm 10\text{ }^{\circ}\text{C}$. It has been shown by NMR techniques [17] that drying at $110\text{ }^{\circ}\text{C}$ also removes some of the hydroxyls weakly bonded to the surface. So, the weight loss above $200\text{ }^{\circ}\text{C}$ accounts for the removal of hydroxyls strongly bonded to the surface and bulk hydroxyls.

Thermogravimetry is recognized [14,18,19] as efficient and inexpensive method to determine the hydroxyls density in silica on the basis of water loss due to the condensation of silanol

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groups, assuming that no other entities are released from the sample.

The aim of this work was to investigate by means of thermogravimetry the surface density of hydroxyls in MCFs, calcined at different temperatures and afterwards hydroxylated by treating in saturated water vapor or liquid water. These may be of importance for the development of the MCF-based specific adsorbents and catalysts.

2. Experimental

2.1. Synthesis and characterization of MCFs

MCFs were synthesized as proposed in [1,2]. The compounds used: Pluronic PE 9600 was from BASF, 1,3,5-trimethylbenzene (>99%) and tetraethoxysilane (TEOS) (99%) were from Aldrich, NH_4F (pure p.a.) and HCl (36–38%, pure p.a.) from POCH (Poland). In typical procedures surfactant Pluronic (0.4 mmol) was dissolved in 1.6 M HCl (75 ml) at room temperature. 1,3,5-Trimethylbenzene (17 mmol) and NH_4F (0.6 mmol) were added under vigorous stirring and the mixture was heated to 60 °C. Following 1-h stirring TEOS (4.4 g) was added. The mixture was stirred for 2 h, then stored at 60 °C for 20 h and further at 100 °C for 24 h. After cooling to room temperature, the precipitate was isolated by filtration, dried at room temperature for 4 days and calcined at 300, 400 or 500 °C to give MCF samples.

Specific surface area (S_{BET}) and pore-size distributions of calcined MCFs were obtained using nitrogen adsorption method. Nitrogen isotherms were measured at 77 K using a Micromeritics ASAP 2000 instrument.

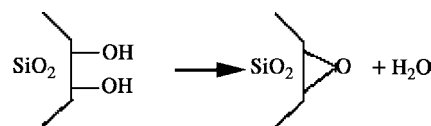
2.2. Thermogravimetric measurements

Thermogravimetric measurements were made with a Mettler Toledo thermobalance (Star 851, LF/1100) using standard platinum crucibles (70 μl) and sample size of 10–15 mg. Uncalcined MCFs were heated at a rate of 5 °C min^{-1} from 25 to 600 °C in air flow of 60 ml min^{-1} to determine the temperature at which all organic template was removed from MCFs. Three-step heating procedure was applied to determine the hydroxyls density in MCFs: (i) first heated at rate of 5 °C min^{-1} from 25 to 200 °C (T_1); (ii) then held at 200 °C for 30 min; and (iii) finally heated at rate of 10 °C min^{-1} up to 1100 °C (T_2). All measurement were performed under air stream of 60 ml min^{-1} . Calcined samples (ca. 50 mg) were stored in vessels with saturated water vapor at room temperature for 2 or 12 h. Selected samples were mixed with water for 2 and 12 h at room temperature to check the effect of a direct liquid water exposure on the hydroxyls site concentration.

Water released during heating forms in the condensation of silanols present on the silica surface (Scheme 1) [14,19].

The OH amount in MCFs was calculated from the weight loss in third step (Δm) and specific surface area (S_{BET}) after calcinations:

$$\text{OH}(\text{nm}^{-2}) = \frac{\Delta m 2N_{\text{A}}/M_{\text{H}_2\text{O}}}{S_{\text{BET}}m} \quad (1)$$



Scheme 1. Mechanism of water formation during heating of samples.

where m is the weight of samples at 200 °C, N_{A} the Avogadro's constant and $M_{\text{H}_2\text{O}}$ is the molecular weight of water.

3. Results and discussion

Fig. 1 shows TG, DTG and SDTA curves from MCF sample prior to calcination. Two weight-loss steps can be seen in the thermogram. The first one (ca. 4%) is due to the removal of water remaining after synthesis, whereas the second one, considerably larger (ca. 45%), comes from the removal of organic template (oil plus surfactant). This step is accompanied by a sharp exothermic peak on SDTA curve. Thus, all organic templates were removed below 300 °C.

The studied MCF materials were amorphous powder with average diameter of particles ca. 10 nm. As can be seen from Table 1 the specific surface area of calcined MCFs depended on the temperature of heat treatment. The S_{BET} values decreased from 655 to 600 $\text{m}^2 \text{g}^{-1}$ with the rise of that temperature from 300 to 500 °C. The mesopores of diameter ca. 20 nm appeared to be interconnected by 12 nm windows (Fig. 2). Mesopore volume of sample calcined at 500 °C was 2.2 $\text{cm}^3 \text{g}^{-1}$. Low-pressure nitrogen adsorption tests ($p/p_0 > 10^{-7}$) showed that

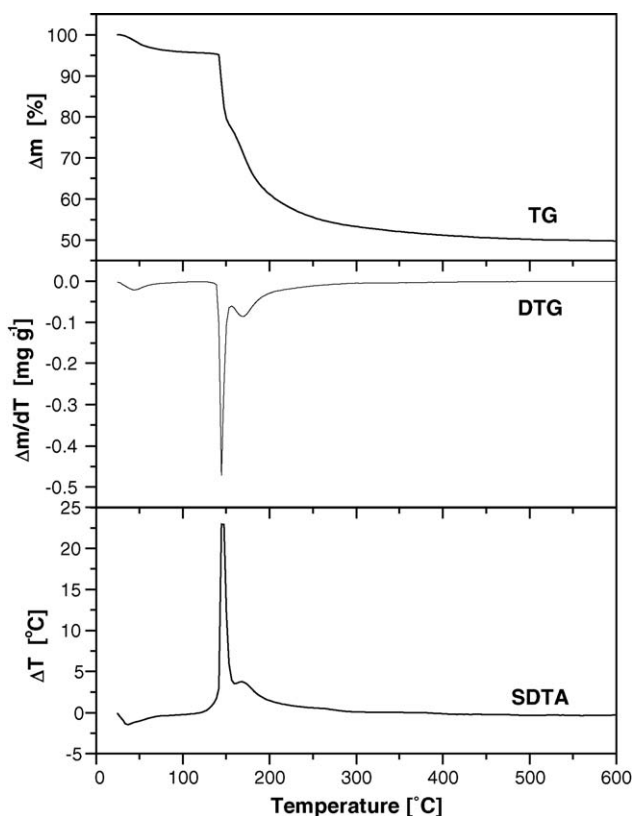


Fig. 1. TG, DTG and SDTA curves from the uncalcined MCF.

Table 1
Hydroxyls coverage in MCFs as a function of calcination temperature and time of water vapor treatment after calcinations

No.	T_{calc} (°C)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$t_{\text{H}_2\text{O}}$ (h)	$\text{H}_2\text{O}_{\text{ads}}$ (%)	OH concentration (mmol/g SiO_2)	OH concentration (OH nm^{-2})
1	300	655	0	1.8	2.59	4.75
2	300		2	24.3	2.98	5.45
3	300		12	45.2	3.04	5.58
4	400	607	0	1.5	1.60	3.16
5	400		2	17.6	2.09	4.14
6	400		12	38.1	2.12	4.20
7	500	600	0	0.83	0.80	1.60
8	500		2	16.6	1.46	2.92
9	500		12	37.1	1.53	3.06
10	500		2 ^a	–	1.81	3.59
11	500		12 ^a	–	1.84	3.65

T_{calc} , calcination temperature; $t_{\text{H}_2\text{O}}$, time of water vapor treatment of MCF; $\text{H}_2\text{O}_{\text{ads}}$, physically adsorbed water; and S_{BET} , specific surface area.

^a Time of liquid water treatment of MCF.

no micropores were present in this material. The calcination temperature (300–500 °C) had little effect on the pore-size distribution of investigated materials (Fig. 2).

Fig. 3 shows TG curve from the sample calcined at 300 °C and stored in a humid air for 2 h. First stage of weight loss equalled ca. 24% (up to about 110 °C) is due to physisorbed water. Very small weight loss (ca. 0.2%) was observed in the temperature range of 110–200 °C and almost negligible loss (0.1%) during heating at 200 °C for 30 min. The TG profiles from samples calcined at 400 and 500 °C were similar (not shown here). The values of physisorbed water $\text{H}_2\text{O}_{\text{ads}}$ (weight loss in the range of 25–200 °C) on all samples are given in Table 1. As expected, the amount of adsorbed water depended on the calcination temperature and the time of contact with water vapor. The amount of physisorbed water increased with time of contacting with water vapor and decreased with calcination temperature. Samples calcined at 300 °C adsorbed notably more of water than those treated at 400 and 500 °C, the difference between which

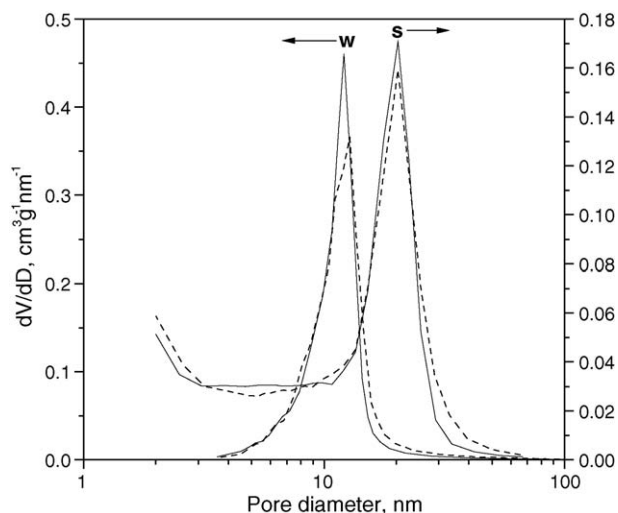


Fig. 2. Pore size distributions of cages(s) and windows(w) in MCF calcined at 300 °C (solid line) and 500 °C (dashed line).

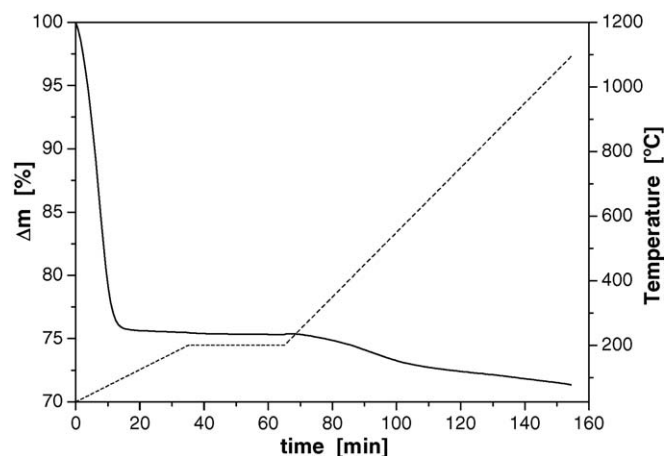


Fig. 3. TG curve (solid line) from MCF calcined at 300 °C and treated with water vapor for 2 h; temperature profile (dashed line).

was quite small. Notwithstanding the large porosity of MCFs, the process of water uptake was not completed even before 12 h. This may be due to a number of factors. Firstly, the materials had pore volume, ca. $2.2 \text{ cm}^3 \text{ g}^{-1}$, i.e. considerably larger than in conventional porous silicas. It determines the upper bound on water uptake capacity and extends the time of achieving it. Secondly, the MCF texture is predominantly mesoporous, with little macropores, and this poses severe diffusion limitations on water transport into particles. A similar trend was also previously observed for silica-based composite adsorbents of water vapor [20,21]. Small amounts of water (0.8–1.8%) detected in samples not treated with water vapor were ascribed to the very rapid adsorption of moisture during their preparation for measurements (<1 min).

Fig. 4 shows TG curves from MCFs calcined at 300, 400, 500 °C and treated with water vapor for 2 or 12 h. Weight losses during heating from 200 to 1100 °C were normalized to the corresponding weights at 200 °C. The values of OH concentration, calculated from weight loss in this temperature range, are given in Table 1. As can be seen, the OH concentration strongly depends on the calcination temperature and on the contact time with water vapor. The sample calcined at 300 °C, even without water vapor treatment, appeared to have three times more hydroxyls (4.75 OH nm^{-2}) than that calcined at 500 °C (1.6 OH nm^{-2}). As could be expected, the 2-h contact of samples with water vapor resulted in the increase of hydroxyls concentration, more notable in silicas calcined at higher temperatures (e.g. from 1.6 to 2.92 OH nm^{-2} in that calcined at 500 °C). Extending this time from 2 to 12 h resulted in a fairly small further increase of hydroxyl concentration. Still the largest increase was in a sample calcined at 500 °C. After exposure of samples to liquid water for 2 and 12 h the hydroxyls concentration increased up to 3.59 and 3.65, respectively (Table 1). The increase of exposure time had little influence on the hydroxyls concentration, similarly as observed for water vapor. The rehydroxylation of silica surface due to transformation of siloxane bridges Si-O-Si to silanol groups caused by the presence of water vapor is a complex, not completely reversible process above 400 °C. Normal unstained siloxanes are hydrophobic [22] and strongly resist to

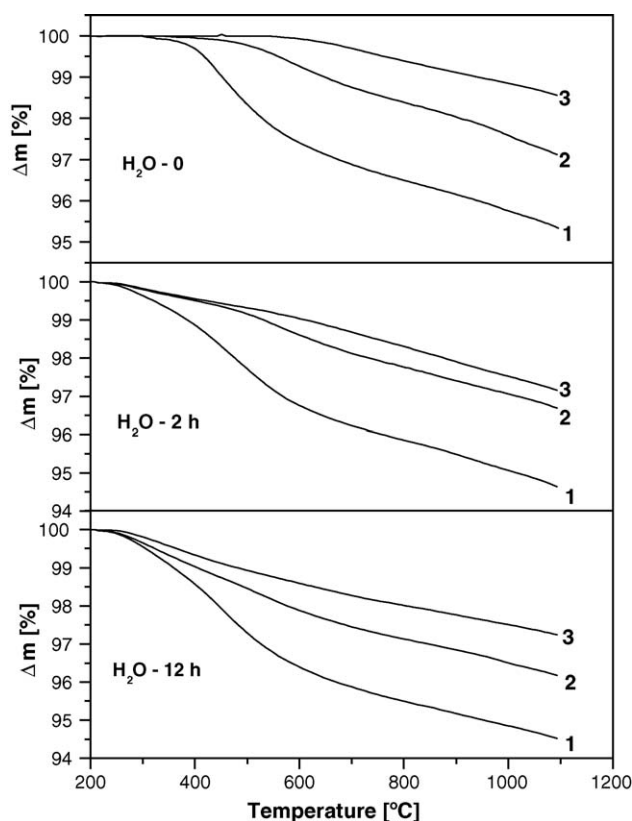


Fig. 4. TG curves from MCFs calcined at (1) 300; (2) 400; and (3) 500 °C and treated with water vapor for 2 and 12 h (normalized to the weight of samples at 200 °C).

dissociation via hydrolysis to form silanols. However, due to surface heterogeneity effects, the siloxane sites located close to strong, residual silanols present on highly dehydroxylated silica and surface sites of edge-shared silicate tetrahedra are believed to be quite reactive and easily hydrolysable.

The observed trend of hydroxyls variation and the calculated values of OH concentration are in good agreement with those reported by Zhuravlev [23,11], where the hydroxyls concentration of fully hydroxylated silica was found to be in the range of 4.2–5.7 OH nm⁻² in over 100 different silica samples.

Thermogravimetric study does not allow to distinguish between the types of silanols, but as was shown in [11,24] the ratio of isolated silanols to those of hydrogen-bonded increases with the increase in temperature of thermal treatment. This observation was recently successfully applied to obtain very effective Ti-modified silica MCF catalysts with highly reactive and selective isolated sites [5].

4. Conclusions

The concentration of hydroxyls in silica MCFs strongly depends on the calcination temperature applied to remove organic templates and on the time of contact with water vapor

or liquid, especially if less than 2 h. Density of hydroxyls in MCFs exposed to moist air for a short period of time was three times larger in a sample calcined at 300 °C than at 500 °C. Transformation of siloxane bridges to silanol groups due to dissociative chemisorption of water on the MCFs surface occurs more easily in the samples calcined at higher temperatures. The results obtained clearly demonstrate that concentration of strong silanols needed for the controlled modification of MCFs surface with functional organic groups or transition metals can be achieved by a suitable selection of calcination temperature and the period of exposure to water vapor or liquid water followed by further thermal treatment.

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