

Synthesis and Characterization of Ordered Mesoporous Silica Materials

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Introduction

Mobil scientists [1] proposed a new technique of synthesis of molecular sieves of larger diameters between micropores and macropores. It was based on usage of self-organized surfactant solutions as template agents. Introducing a silica source to such a solution it is possible to obtain a well-organized material with uniform system of pores. The structure of these materials depends on a type of used template (various surfactants, polymers, liquid crystals), the synthesis conditions or a post-synthesis treatment. The MCM-41 silicas were created by applying low-molecular surfactants, however, the SBA-15 or MCF of wider mesopores are the polymer-templating materials [2-8]. The group of materials with wider pore diameters received much attention because of the possibility of engineering new classes of sorbents or catalysts which may be used in the processes involving large molecules. Among such adsorbents the cage-like ordered silicas seem to be very interesting because of application reasons [9-12].

In the paper, the investigations on synthesis and characterization of mesoporous silicas of various porous structures are presented. As the pore creating agent the Pluronic triblock copolymer was applied. Changing the conditions of synthesis process a group of materials was obtained with divergent pore characteristics. The obtained materials were characterised by using gas adsorption and XRD methods in order to compare their structure properties. The effect of temperature of aging process and concentration of pore expanding agent on the character of formed silica structures was analyzed.

Experimental

Material preparation. The series of mesoporous silicas were prepared using the non-ionic triblock copolymer Pluronic PE 9400 - (EO)₂₁(PO)₄₇(EO)₂₁ - as a template (BASF, Poland) and tetraethylorthosilicate (TEOS) as silica source according to a procedure being a modification of the method described in the papers [13,14]. The syntheses were carried out in strong acidic conditions (1.6M HCl). The weighed amount of copolymer was dissolved in 180 ml of HCl solution, placed in thermostat and vigorously stirred for 45 min. at 308 K. Then, the weighed amount of TEOS was added and the mixture was stirred for 20 hrs. In all conducted syntheses the molar ratio of TEOS to copolymer template was constant and equal to 75:1. Some silica samples were synthesized with addition of 1,3,5-trimethylbenzene (TMB) as pore expanding agent (the molar proportion of TMB:polymer was varied: 38:1, 77:1, 115:1). The aging was conducted for 24 hrs at elevated temperatures (343, 353, 363, 373, 393 K) in autoclave. Finally, the synthesized product was thoroughly washed with bi-distilled water, dried and calcined at 873 K for 6 hrs.

Material characterisation. In order to characterise the properties of synthesised materials gas adsorption and XRD techniques were applied.

To confirm the regularity of sorbent structure XRD patterns were recorded by the modified diffractometer DRON 3 (Russia) using CuK α radiation.

In order to estimate the values of parameters characterising the mesoporous structure of synthesised materials the nitrogen adsorption/desorption at 77 K were determined volumetrically using ASAP 2405N analyser (Micromeritics Corp., USA). Before the experiment the adsorbents were outgassed ($\sim 10^{-2}$ Pa) at 493 K.

The adsorption data were used to evaluate the BET specific surface area, S_{BET} (from the linear BET plots) and the total pore volume, V_t (from the adsorption at the relative pressure $p/p_0=0.98$) [15]. To estimate the values of the external (macropore) surface area, S_{ext} , and the primary mesopore volume, V_p , the α_s plot method was applied [16]. This method is based on the comparison of nitrogen isotherm on a studied porous solid with the standard isotherm on a reference nonporous adsorbent. This standard reduced isotherm α_s is defined as the ratio of adsorption value corresponding to a given relative pressure p/p_0 and the adsorption value at the point $p/p_0=0.4$ (p is the gas pressure, p_0 is the saturation pressure, $p/p_0=0.4$ is a starting point of isotherm hysteresis loop for nitrogen adsorption). As a reference adsorbent the macroporous silica gel LiChrospher Si-1000 was used [16]. The calculations of pore size distributions (PSD) followed the Barrett, Joyner and Halenda (BJH) procedure. [15]. The mean hydraulic pore diameters were calculated from the BET surface areas and pore volumes $D=4V_t/S_{BET}$.

Results and discussion

The first group of silicas was synthesized without 1,3,5-trimethylbenzene. The synthesis mixtures were aged at different temperatures: 70°C, 80°C, 100°C, and 120°C. For the obtained samples the nitrogen adsorption/desorption isotherms were measured. In Fig. 1 these isotherms are compared for four samples. The sorbent PE9400-70 obtained at the lowest temperature reveals the character similar to microporous adsorbents. With increasing temperature some mesoporous structures grow (the region $p/p_0>0.4$), whereas, at lower relative pressures the isotherms differ only slightly. However, the dramatic change of the isotherm character for the highest aging temperature proves that the fundamental change of structure occurs in this case.

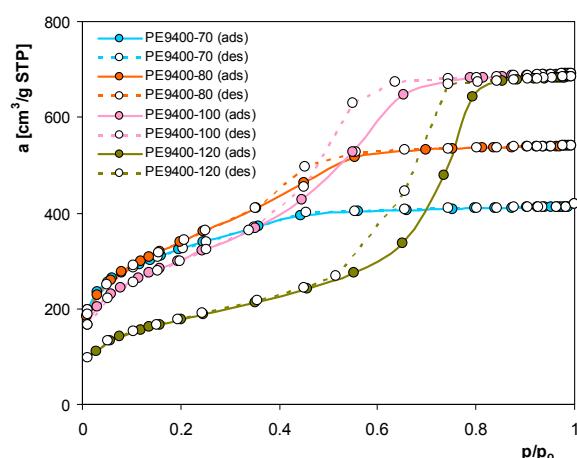


Fig. 1. Adsorption/desorption isotherms

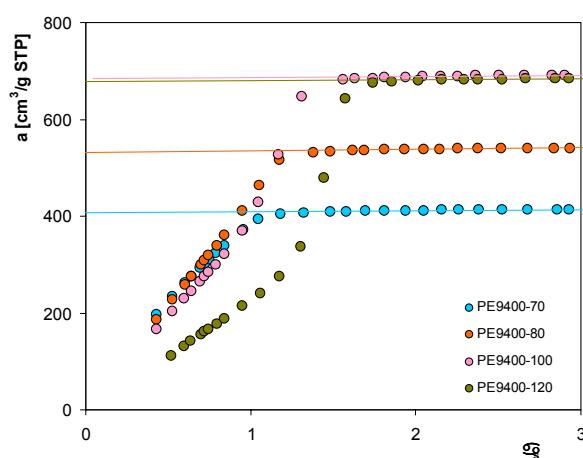


Fig. 2. α_s plots

The shape of isotherm for PE9400-120, with unchanged total pore volume (as compared to the material heated at 100°C) proves that at 120°C the internal walls of small pores are dissolved and the structure is rebuilt into an almost purely mesoporous one. In Fig. 2 the α_s -plots are drawn for four synthesised samples. The shape of this curve for the sample PE9400-70 is similar to the α_s -plot typical for microporous adsorbents. However, in Fig. 3 the pore size distributions are compared for three of the studied materials. For PE-9400-70 the PSD was not calculated because the BJH method can not be applied to microporous materials. The pore size distributions for the materials heated at elevated temperatures are shifted toward higher pore diameters. It is especially visible for PE9400-120, what confirms a drastic change of porous structure for this sample.

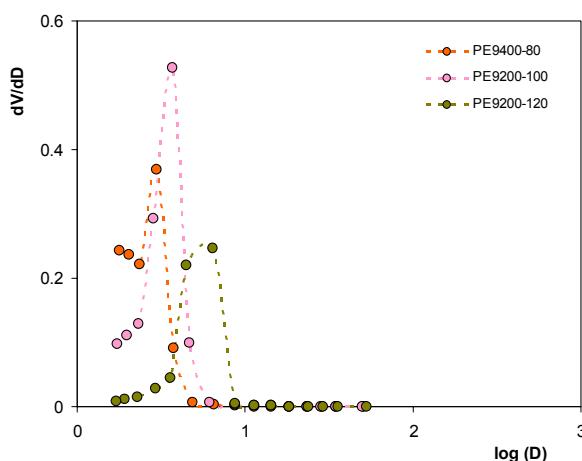


Fig. 3. Pore size distributions obtained from desorption data

The next group of sorbents was synthesized with addition of 1,3,5-trimethylbenzene as pore expanding agent. The molar proportions of the reacting mixture were: TEOS:TMB:polymer=75:38:1. In order to understand the effect of temperature on developing the pore structure the nitrogen isotherms for the materials aged at lower and higher temperatures are compared pair wise in Figs. 4 and 5 and all are presented in Fig. 6. The characteristic feature of all these isotherms – with the sole exception of the sample obtained at the highest temperature – is a very wide hysteresis loop, which indicates that the obtained sorbents have a cage-like structure. Almost identical adsorption branch courses up to the same onset of capillary condensation (at approx. $p/p_o = 0.85$) for the samples aged at 70 – 100°C proves that they have a similar structure in the range of and internal curvatures of mesopores. The sample synthesized at 120°C has similar, though much lower course, and the same total adsorption volume. However, the total volume of mesopores increases. Low temperature samples display very similar and almost vertical desorption branch of hysteresis loop at the same $p/p_o=0.45 - 0.55$. However, for high synthesis temperatures it becomes much less steep and for 100°C it is in the range 0.45 – 0.65 and for 120°C it appears even higher at 0.55 – 0.75.

All that together suggests that the samples obtained at low temperatures have almost constant volume of small pores, and large share of cage-like mesopores. With the increase of aging temperature the mesopore volume increases without significant changes of the shape and size or change of small pores. However, when aging temperature increases up to 100°C the pore openings become wider and total pore volume increases as the wall material is dissolved and rebuilt. Further increase of aging temperature to 120°C brings about a partial collapse of walls between small pores creating more and larger mesopores at a cost of small pores without actual decrease of total pore volume.

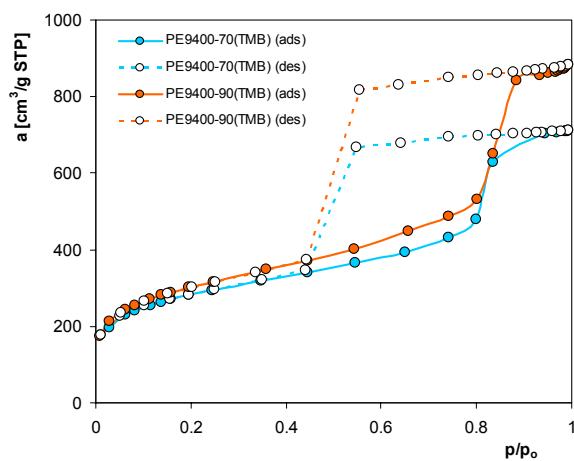


Fig. 4. Adsorption/desorption isotherms

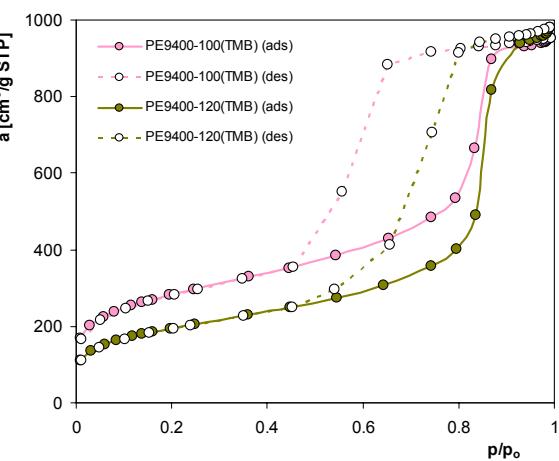


Fig. 5. Adsorption/desorption isotherms

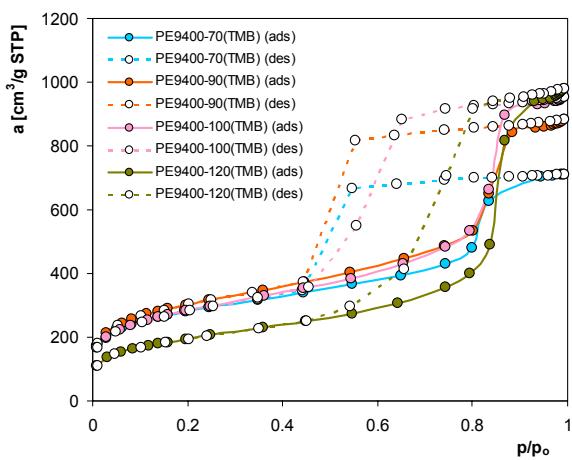


Fig. 6. Adsorption/desorption isotherms

The α_s plots for these materials presented in Fig. 7 further confirm these conclusions. In Fig. 8 the PSD calculated from adsorption branch of nitrogen isotherms are compared for all samples. They are similar and they reveal only a small shift toward higher pore diameters in the case of the samples heated at elevated temperatures.

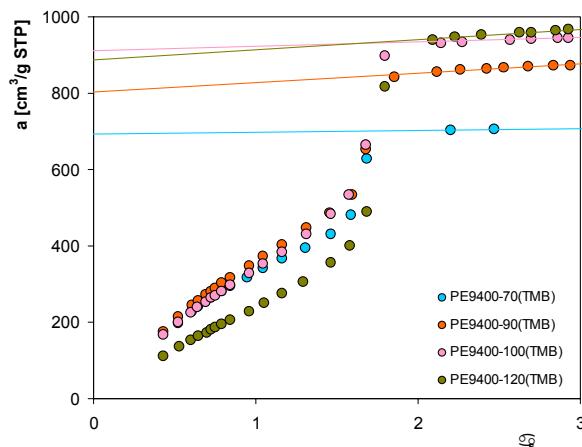


Fig. 7. α_s plots

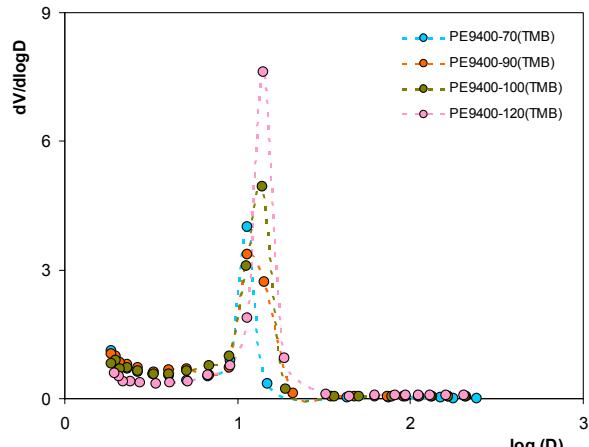


Fig. 8. Pore size distributions obtained from adsorption data

The following figures present the nitrogen isotherms (Fig. 9) and PSD-s (Fig. 10) for a series of samples obtained at low aging temperature (70°C) for the increasing ratio of TMB to other synthesis components: TEOS:TMB:polymer = 75:38:1, 75:77:1 and 75:115:1 (the initial TMB amount – denoted TMB - was doubled and tripled for the other samples – denoted 2TMB and 3TMB, correspondingly). The highest pore size and the highest total pore volume was obtained for PE9400-70(2TMB). For the sample PE9400-70(TMB), with the smallest amount of 1,3,5-trimethylbenzene, smaller pore size and pore volume is quite logical, however, the reason why similar effect appeared with larger amount of TMB pore expander doesn't seem so clear (at the same time quantity of small pores increased slightly from TMB to 2TMB and finally 3TMB). Most probably the colloidal structure wasn't stable for a too big TMB:polymer ratio and amount of silica available wasn't enough to create large pores with wall thick enough to withstand synthesis conditions. As a result some large pores collapsed what brought about smaller total pore volume without diminishing the volume of small pores. The pore size distribution for the sample PE9400-70(2TMB) is shifted toward higher values of diameters in contrast to two other materials.

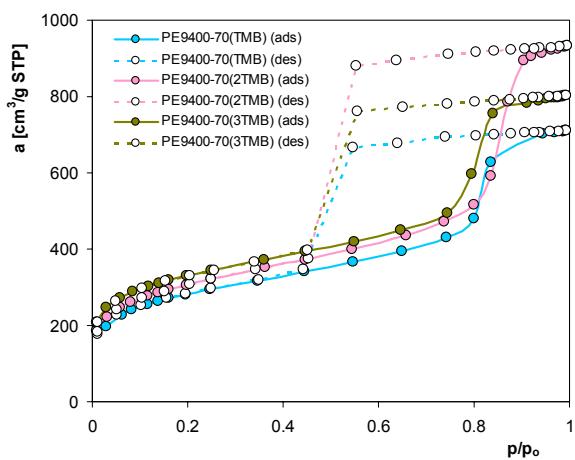


Fig. 9. Adsorption/desorption isotherms

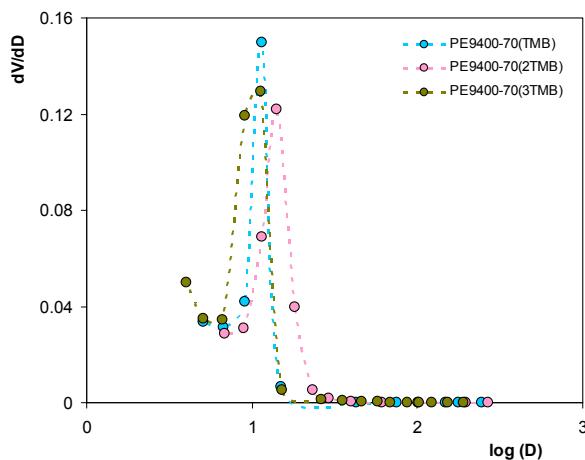


Fig. 10. Pore size distributions obtained from adsorption data

The analysis of low angle XRD spectra with a prominent peak at $2\theta=1.2^{\circ}$ suggests that the existing cage-like mesopores are organized in some super-structure.

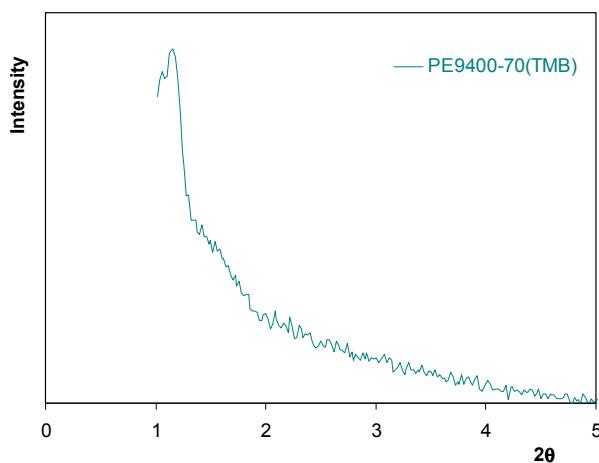
Fig. 11 XRD pattern for the sample synthesized with TMB and aged at 70°C .

Table 1. Parameters characterizing porous structure of the synthesized materials

Sorbent	Aging temp. [°C]	S_{BET} [m ² /g]	V_t [cm ³ /g]	V_p [cm ³ /g]	S_{ext} [m ² /g]	D [nm]
PE9400-70	70	1154	0.64	0.63	5	2.2
PE9400-80	80	1215	0.84	0.82	8	2.7
PE9400-100	100	1080	1.07	1.06	7	4.0
PE9400-120	120	650	1.06	1.05	4	6.5
PE9400-70(TMB)	70	1015	1.10	1.07	13	4.3
PE9400-90(TMB)	90	1080	1.35	1.24	65	5.0
PE9400-100(TMB)	100	1010	1.46	1.41	33	5.8
PE9400-120(TMB)	120	695	1.49	1.37	74	8.6
PE9400-70(2TMB)	70	1100	1.44	1.39	24	5.2
PE9400-70(3TMB)	70	1180	1.24	1.20	22	4.2

Temperature of ageing process strongly influences the character of porous structure of synthesised materials. It is reflected in the shape of adsorption/desorption isotherms and pore size distributions. In Table 1 the values of parameters characterising the porous structure of obtained materials are compared. Analysing the values of structure parameters presented in Table 1 one can find that the increase of temperature results in growing pore size and pore volume. The silicas obtained over the temperature range 70 - 100°C are characterized by similar values of specific surface area, however, for the adsorbent aged at 120°C a distinct decrease of its value is observed. These changes are connected with rebuilding of silica skeleton during aging process and its partial dissolution.

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