Highly ordered mesoporous silica materials synthesized on non-ionic triblock copolymer templates

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Introduction

The synthesis of hexagonally ordered MCM-41 sorbent conducted by Mobil scientists in 1992 created a possibility of producing well-defined molecular sieves with larger pore structure [1]. A variety of possible applications as supports and catalysts stimulated the interest in synthesis of new materials with uniform structure of pores of diameters between micropores and macropores. The procedures are based on the self-aggregation mechanism of different surfactants used as templates for long-range order adsorbents. Modification of synthesis conditions and surfactant type, as low-molecular-weight surfactants or block copolymers, allows obtaining the materials with near continuously changing structure properties. The polymer-templating syntheses made it possible to create the SBA-15 or MCF mesoporous silicas of wider pores [2].

In the paper the effect of changing synthesis parameters on the properties of obtained mesoporous silicas was studied. The process of synthesis was modified in order to differentiate the pore structure of obtained materials. The effect of surfactant type, substrate concentrations, temperature and time of aging process on the character of silica structure was analysed.

Experimental

The series of mesoporous silicas with various structure properties were prepared using as templating surfactants the non-ionic triblock copolymers Pluronic: PE 9200 - $(EO)_{10}(PO)_{47}(EO)_{10}$, PE 9400 - $(EO)_{21}(PO)_{47}(EO)_{21}$ and PE 10500 - $(EO)_{36}(PO)_{56}(EO)_{36}$ (BASF) and TEOS as silica source by applying a modification of procedure described in the paper [3]. The first step of of synthesis was carried out for 20 hrs. at 310 K in strong acidic conditions (1.6M HCl) and under stirring, with addition of trimethylbenzene as pore expanding agent. Then, the aging procedure at elevated temperatures (343 – 413 K) was conducted for 24 – 72 hrs. in autoclave. In the final step the synthesized product was washed, dried and calcined at 873 K for 6 hrs. Nitrogen adsorption/desorption isotherms at 77 K were determined volumetrically using ASAP 2405 analyzer (Micromeritics, USA). The specific surface areas (S_{BET}) and the total pore volumes (V_t) were obtained by applying the standard methods. The values of parameters characterising mesoporous structure of synthesised materials (the primary mesopore volume, V_p, and the external surface area, S_{ext}) were estimated by using the α_s-method [4]. The calculations of pore dimensions (D) and pore size distributions (PSD) followed the Barret, Joyner and Halenda (BJH) procedure.

Results

In the first part of Figure the nitrogen adsorption/desorption isotherms are compared for the silica material synthesized at two temperatures (343 for 72 hrs. and 393 K for 24 hrs.) by using PE10500 (the samples designated as PE10500-70 and PE10500-120, respectively) surfactant as a template. The second part of Figure presents the pore size distributions for both sorbents. The shape of isotherm hysteresis loops and comparison of adsorption/desorption PSDs evidence bottle-neck character of pore system of synthesized materials. The effect of aging temperature and time on the texture of PE10500 silicas is very strong. It is reflected in isotherm shapes and in widening of PSD. It is in agreement with the results of Hartmann and Vinu [5], who found that up to 393 K the

surface area decreases slightly, while the PSD slightly widens. However, for temperatures 403 K and above the surface area decreases strongly, the pore diameter increases and PSD widens considerably.

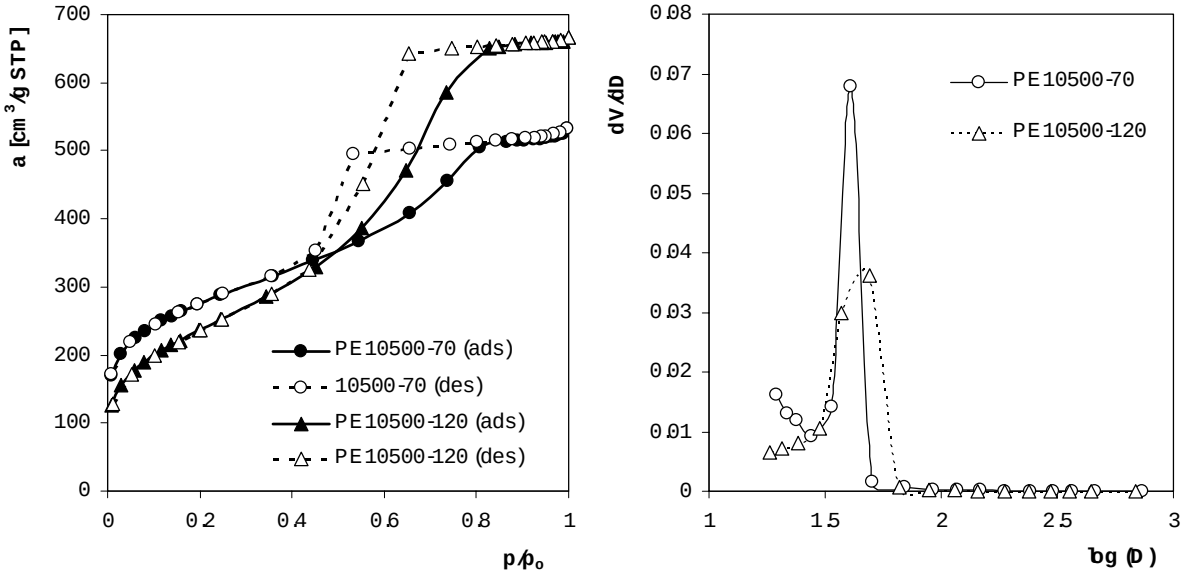

Fig. Adsorption/desorption isotherms of nitrogen and pore volume distributions.

The parameters characterising the structure of synthesized silicas calculated from nitrogen adsorption/desorption isotherm are given in Table. Both sorbents are characterized by high values of specific surface area and pore volumes (total and primary mesopores). However, the higher aging temperature resulted In the increase of pore volume (primary mesopore and total) and pore diameter as well as in the decrease of surface area (BET and external) due to removal of some of the pore wall material. We observed that with increase of aging time the process of structure rebuilding continues and that the longer aging has the effect somewhat similar to the increased temperature. The small pores disappear and larger ones are formed gradually.

Table. Parameters characterizing structure properties of synthesized PE10500 materials.

Sorbent	S_{BET} [m^2/g]	V_t [cm^3/g]	V_{meso} [cm^3/g]	S_{ext} [m^2/g]	D [nm]
PE10500-70	980	0.81	0.76	34	3.3
PE10500-120	845	1.02	0.99	20	4.8

Acknowledgments.

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