

Plugged Hexagonal Mesoporous Templated Silica : A unique micro- and mesoporous material with internal silica nanocapsules.

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Following the development of purely mesoporous templated silicas, it is a desirable next step to create innovative catalytic support materials, consisting of a stable composite matrix with combined micro- and mesoporosities and a sufficient stability to withstand most industrial treatments.

We show in this paper the development of a hexagonal plugged material, with combined micro- and mesopores and a tunable amount of both open and inkbottle mesopores. The ratios of these different pore types are variable in a wide range. The obtained materials are much more stable than the conventional micellar templated structures known so far.

1. INTRODUCTION

Following the pioneering publications on the synthesis of mesoporous, semi-crystalline silicas [1-4], intensive research efforts have been devoted to the development of new mesoporous support materials of ordered structure. The research is motivated by the fact that such materials fill the gap in catalytic chemistry between the crystalline microporous zeolites and amorphous, disordered mesoporous supports like silica gel [5]. Due to their controlled pore size and a very narrow pore size distribution, the ordered mesoporous materials have a large potential as catalytic support in fine chemistry [5], pharmaceutical industry [7], as well as for the production of special polymer materials [6]. Heterogenizing the synthetic procedures in these fields of chemistry forms an important tool in achieving the goals of green, sustainable production processes and end-of-pipe waste reduction [7]. It is desirable to create innovative catalytic support materials, consisting of a stable composite matrix with combined micro- and mesoporosities. Such materials will offer significant supplementary advantages of an improved diffusion rate for transport in catalytic processes (faster reactions); better hydrothermal stability [8]; synthesis of multifunctional catalysts, which can process a large variety of feedstocks; capabilities of encapsulated waste in the micropores; controlled leaching rates for a constant and gradual release of an active component, etc. Here, we present a very simple synthesis procedure of a plugged hexagonal mesoporous material with very thick walls, high stability and controllable and tunable micro- and mesoporosities.

2. EXPERIMENTAL

A plugged MTS material is prepared by dissolving 4 g of Pluronic P123 (non-ionic triblock copolymer, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) in an acidic water/HCl solution. Subsequently, an amount of TEOS (between 5 and 25 g) is added. The solution is stirred for 4-8 hours at a fixed temperature between 40 and 80°C and subsequently aged at ambient pressure for 17 h at 80-120°C. The white solid was filtered, washed and calcined at 550°C. Detailed experimental conditions can be found in [9].

X-Ray Diffractograms were recorded on a Philips PW1840 powder diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation. Porosity and surface area studies were performed on a Quantachrome Autosorb-1-MP automated gas adsorption system. The calcined samples were degassed for 17 h at 200°C. TGA measurements were recorded on a Mettler TG50 thermobalance.

Mechanical pressing tests were performed in a unilateral press with a typical 13 mm dye (Specac). Hydrothermal tests were performed by placing the sample on a grid in an autoclave, which is filled with liquid water underneath the grid. The entire system is placed in an oven for 17 h in the temperature range 120-160°C, exposing the sample to steam at autogeneous pressure. Other hydrothermal experiments were performed using a fixed bed reactor, using a nitrogen flow, saturated with a certain percentage of water vapor.

3. RESULTS AND DISCUSSION

3.1. Nitrogen isotherms

Changing the synthesis parameters in a controlled way allows the reproducible synthesis of a broad variety of materials. The adsorption-desorption isotherms of three distinctly different materials are shown in Figure 1. The isotherm in figure 1A is typical for the SBA-15 material [3], a two-dimensional p6mm structure formed by open cylindrical mesopores > ca. 5 nm in diameter. The desorption isotherm corresponds to the vapor pressure of the equilibrium meniscus in the open cylindrical pore, while the adsorption isotherm corresponds to the limit of stability of the adsorption film [10]. It should be noted that the material contains significant amounts (up to 30% of the porosity) of intrawall micropores (< ca. 3 nm) located in the pore walls, as evaluated by the NLDFT method [11]. The isotherm in Figure 1C shows the isotherm of a material with regular cylindrical pores that are accessible only through permeable microporous plugs. This is evident from the desorption branch of the isotherm and the shape of the hysteresis loop. If a pore is plugged, desorption is delayed until the vapor pressure is reduced below the desorption pressure from a pore aperture (ink-bottle effect). However, if the pore aperture is below a critical diameter, decrease in the vapor pressure causes the fluid in the larger pores to become thermodynamically unstable before the desorption pressure for the pore aperture is reached [12]. For nitrogen at 77 K this instability occurs at p/p_0 : 0.42-0.45. The isotherm in Figure 1B is remarkable. It exhibits the following characteristic features: 1) adsorption in intrawall micropores at low relative pressures; 2) multilayer adsorption in regular mesopores and capillary condensation in narrow intrawall mesopores; 3) a one-step capillary condensation, indicating uniform mesopores; 4) a two-step desorption branch indicating the pore blocking effects (sub-step at the relative pressure of ca. 0.45). The adsorption-desorption behavior is consistent with a structure comprising both open and closed cylindrical mesopores. This interpretation is fully supported by the non-local density functional theory (NLDFT) of adsorption and hysteresis in cylindrical pores [10]. The mesopore size distribution and the total amount of micropores are calculated from the

adsorption branch of the isotherm by the NLDFT method [11]. The fractions of open and closed mesopores, as indicated schematically in Figure 2, have been determined from the pore size distributions (see Table 1). Details of calculations will be presented elsewhere.

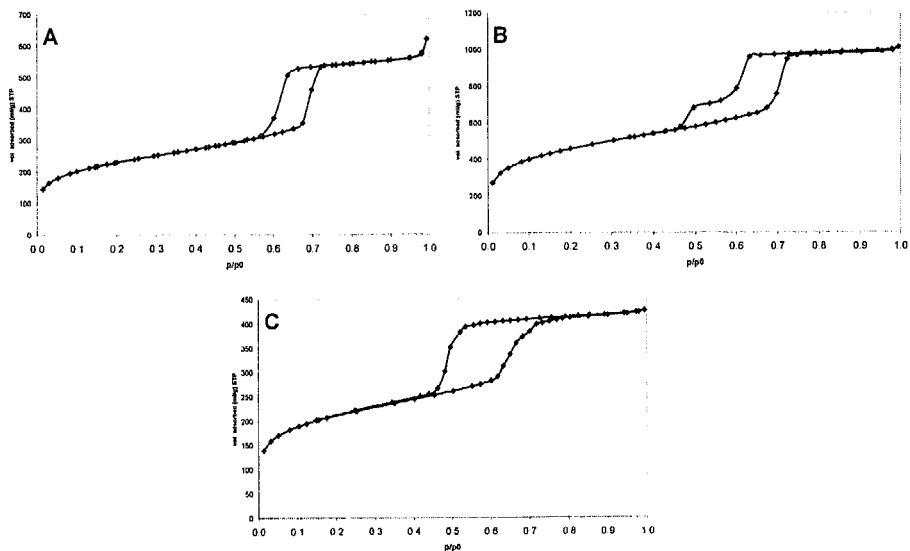


Figure 1 : Nitrogen adsorption-desorption isotherms of (A) SBA-15, all open mesopores, (B) plugged material, with combined open and closed mesopores and (C) material with exclusively closed mesopores.

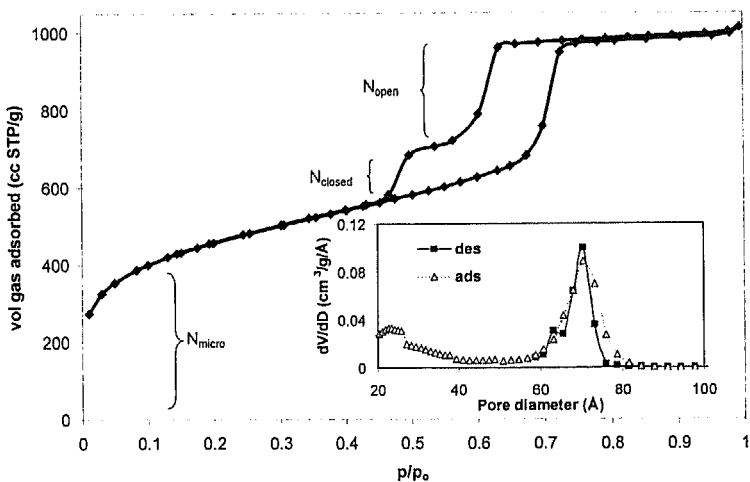


Figure 2. Nitrogen adsorption-desorption isotherm (77K) of a plugged hexagonal mesoporous templated silica and the mesopore size distribution calculated by the NLDFT method [10].

3.2. X-Ray Diffractogram

The X-Ray Diffraction pattern in Figure 3 shows the characteristic reflections for a 2D hexagonal pore ordering in the $p6mm$ space group [3]. The plugged mesoporous material therefore has the same structure as the SBA-15 hexagonal material.

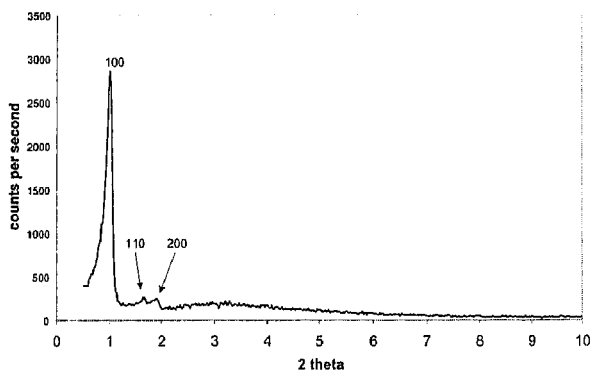


Figure 3 : X-Ray Diffractogram of the plugged hexagonal mesoporous silica sample.

3.3. Plugged hexagonal mesoporous templated silica

The data in Figures 1-3 point towards a composite material with a combined micro- and mesoporosity, as schematically represented in Figure 4. The rather thick walls (~ 4 nm) of the large cylindrical mesopores are perforated with micropores. Moreover, the cylindrical mesopores themselves are 'plugged' with amorphous silica nanocapsules, which are also microporous. These nanocapsules are created by large excess of the silica source (TEOS) that is used in the synthesis and by rapid hydrolysis of the silicon alkoxide at the very low pH used in the synthesis. The micropores in the silica walls can be explained by the penetration of hydrophilic poly(ethyleneoxide) chains of the triblock copolymer in the silica wall, as already suggested by Kruk et al [13]. The microporosity of the plugs may have a different origin. It is known that Pluronic triblock copolymers are in fact polydisperse mixtures of several triblock copolymers with a wide range of molecular weights, and that they contain appreciable amounts of diblock copolymers and even free PO chains. Some of these components, especially the low molecular weight ones, may not be involved in the actual templating of the mesopores, but still act as templates for the disordered nanocapsules, inducing a complementary porosity. The mesopores themselves are created by the so-called charge compensating templating mechanism of the entire triblock copolymer.

The most important characteristics of these materials are summarized in Table 1. The table evidences the large variety in sample characteristics that can be obtained. The thickness of the mesoporous walls is typically 3-4 nm, which is excellent, compared to a typical wall thickness of 1 nm for the well-known MCM-41 structure. Extremely high total pore volumes can be obtained. The contribution of micropores (with contributions of both micropores in the walls and micropores in the silica nanocapsules) has an unprecedented high value. Micropore volumes up to $0.3 \text{ cm}^3/\text{g}$ can be obtained (40% of the total pore volume), which is

considerably higher than the micropore volumes of any composite material known so far. Both the ratio micropore/mesopore volume as the ratio open/closed mesopores is tunable in a wide range.

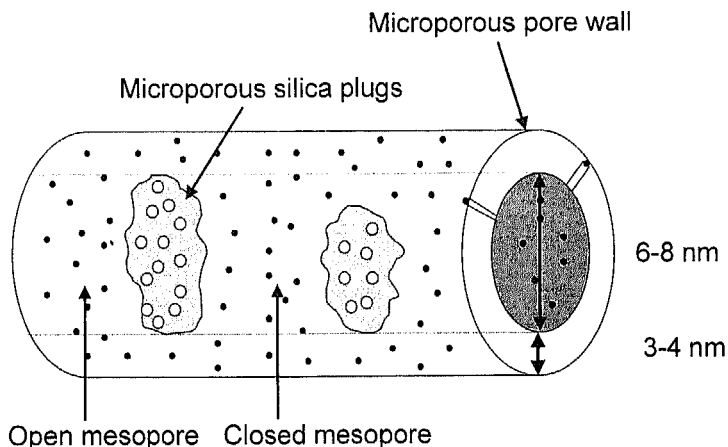


Figure 4 : Schematical representation of the plugged hexagonal mesoporous templated silica (PHMTS)

Table 1:

Structural characteristics of 4 selected samples, PHMTS : Plugged Hexagonal Mesoporous Templated Silica, a_0 – lattice spacing, V_{tot} – total pore volume (micropores and mesopores), V_{mi} – micropore volume, V_{me} – mesopore volume, D_{ads} – pore diameter from the adsorption branch, D_{des} – pore diameter from the desorption branch, D_{geom} – pore diameter from geometrical considerations using V_{mi} , V_{me} and 2.2 g/cm^3 for the silica skeleton density, h_w – pore wall thickness, $h_w = a_0 - D_{ads}$; $V_{me}(\text{open})$ – volume of open mesopores, $V_{me}(\text{closed})$ – volume of closed mesopores

Sample	a_0 (nm)	V_{tot} (cm^3/g)	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	D_{ads} (nm)	D_{des} (nm)	D_{geom} (nm)	h_w (ads) (nm)	$V_{me}(\text{open})$ (cm^3/g)	$V_{me}(\text{closed})$ (cm^3/g)
SBA-15	11.31	1.25	950	0.14	1.11	7.3	7.59	7.76	4.01	1.11	0
PHMTS-1	11.08	1.03	1040	0.29	0.74	6.79	7.03	7.12	4.30	0.23	0.51
PHMTS-2	9.58	0.71	880	0.26	0.45	6.08	no	5.89	3.50	< 0.01	0.45
PHMTS-3	10.16	0.83	945	0.30	0.53	7.03	7.03	6.94	3.13	0.38	0.15

3.4. Transmission electron microscopy

Using a Philips CM200 microscope, we have investigated extensively the PHMTS and SBA-15 samples in bright field transmission mode. In figure 5 we show representative images for these materials. Both micrographs provide side-on views of the ordered mesopore system. While the mesopores in SBA-15 run smoothly over several micrometers of length, the PHMTS displays smaller domain sizes for the ordered mesopores. Moreover, the wall thickness varies more strongly for the latter material, which may be caused by the presence of silica plugs inside the mesopores. Most recently, 3D-TEM techniques have been developed to image mesopores in three dimensions [14,15]. In a future paper, we will present evidence from 3D-TEM for the different pore systems in SBA-15 and our novel material PHMTS [9].

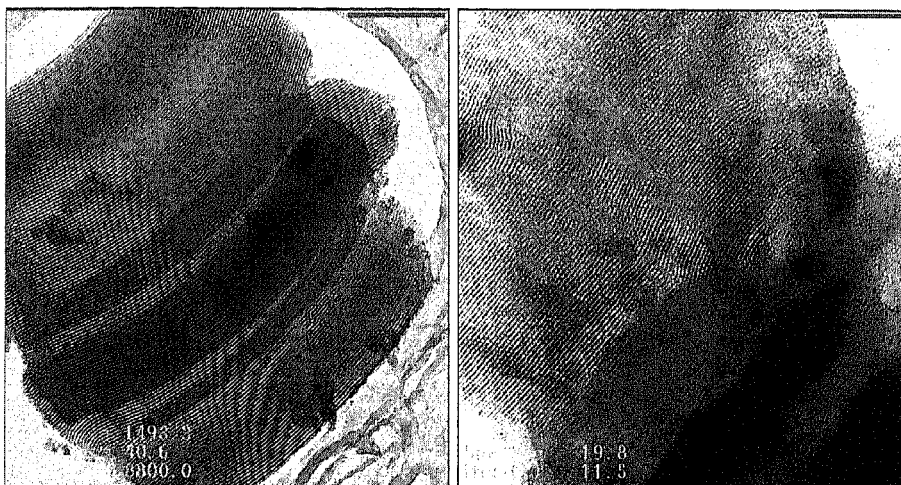


Figure 5 : TEM images of SBA-15 (left) and PHMTS (right).

3.5. Stability

Table 3 presents the intrinsic thermal, mechanical and hydrothermal stabilities of some of the most important MTS materials [16]. Table 3 reveals that all materials are poorly resistant to (mild) hydrothermal treatments. The SBA-15 is the best resistant of the conventional mesoporous silicas ; the PHMTS material is by far the most stable. It still has a very significant surface area and pore volume after 5 days of hydrothermal treatment or after a 24 h treatment in an autoclave in pure steam (sample placed above the water on a grid). Most materials collapse after a thermal treatment at 750°C, with two exceptions : MCM-41 and PHMTS. Resistance toward mechanical (unilateral) pressure is again best for PHMTS, followed by SBA-15. The thick walls of SBA-15 are further stabilized and supported in the PHMTS structure by the silica plugs, resulting in an extremely high mechanical resistance. The reported 10 tons/13 mm² was the highest pressure that could be obtained in our press. Pure silica based materials are obviously stable in neutral and acid conditions, but decompose in alkaline conditions.

Table 3 :

Intrinsic stabilities of MTS materials ; SA = surface area (m²/g), PV = pore volume (ml/g). Thermal stabilities after treatment in furnace, ambient atmosphere for 17 h at indicated temperature. Hydrothermal stability at x% water vapour at y temperature for z hours of treatment. Mechanical pressure, structure is collapsed if the XRD peak < 25% of the original peak and / or the typical diffraction peaks are no longer present. Chemical resistance : stirring for 24 h in an aqueous solution with indicated pH.

¹ : Pressures are expressed as tons per 13 mm² pellet ; 1 ton/13 mm² corresponds to 740 bar.

Treatment	MCM- 41		MCM- 48		HMS		SBA- 15		PHMTS	
	SA	PV	SA	PV	SA	PV	SA	PV	SA	PV
Thermal										
T :550°C	1027	0.90	1433	1.14	1021	0.81	718	0.72	913	0.86
T :650°C	970	0.76	1248	0.73	957	0.58	561	0.63	667	0.66
T :750°C	879	0.68	108	<0.05	213	<0.05	63	<0.05	451	0.48
T :850°C	795	0.53	-	-	-	-	-	-	387	0.39
Hydrothermal										
25%/400/50	892	0.66	1357	1.00	915	0.57	533	0.57	682	0.69
25%/400/120	864	0.59	1318	0.93	830	0.48	445	0.49	687	0.71
100%/100/24	106	<0.05	197	<0.05	228	<0.05	281	0.47	462	0.66
Mechanical										
25% pressure	7 tons ¹		4 tons		5 tons		8 tons		>10 tons	
Chemical										
pH = 1	+		+		+		+		+	
pH = 7	+		+		+		+		+	
pH = 13	-		-		-		-		-	

4. CONCLUSIONS

Using triblock copolymers as surfactant and TEOS as the silicon source, a whole variety of materials can be prepared, varying from pure SBA-15 (hexagonal stacking of pores, all pores are open) to hexagonal systems with exclusively ink-bottle pores and materials with combined open and closed pores, referred to as PHMTS (Plugged hexagonal mesoporous templated silica).

PHMTS is characterized by very large but narrow distributed pores with very thick and microporous pore walls. Moreover, the pores are plugged internally with microporous silica nanocapsules. Their stability (thermal, hydrothermal, mechanical) is extremely high, compared to other commonly used mesoporous silicas. These materials might have unprecedented applications as adsorbers, desorbers and catalytic supports.

Acknowledgements

This research was funded by a grant from the University of Antwerp (Special Research Fund) and by the F.W.O. (Flemish Fund for Scientific Research). The authors are grateful to Mrs. Sandra Kemp for making the TEM images.

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