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Andrey Ryzhikov, T. Jean Jean Daou, Habiba Nouali, Joël Patarin, Judith Ouwehand, et al.. Periodic mesoporous organosilicas as porous matrix for heterogeneous lyophobic systems. *Microporous and Mesoporous Materials*, 2018, 260, pp.166-171. 10.1016/j.micromeso.2017.10.037 . hal-03544626

HAL Id: hal-03544626

<https://hal.science/hal-03544626>

Submitted on 26 Jan 2022

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Periodic mesoporous organosilicas as porous matrix for heterogeneous

lyophobic systems

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ABSTRACT

Periodic mesoporous organosilicas (PMO) have been studied for the first time as a porous matrix for heterogeneous lyophobic systems (HLS) for absorption and storage of mechanical energy by high pressure intrusion-extrusion of electrolyte solutions. It has been shown that the intrusion of LiCl aqueous solutions in ethane-bridged PMO material is irreversible that corresponds to a bumper behavior. The intrusion pressure increases strongly with the salt concentration - from 13 MPa for 5 M LiCl aqueous solution to 37 MPa for 20 M one. Such a pressure rise of 2.8 times is the highest observed for HLS based on mesoporous materials. Due to high intruded volume (0.63-0.72 mL/g) specific absorbed energy achieves 27 J/g, which is close to the best values ever obtained for HLS based on zeosils and mesoporous silica. The characterization shows that after the intrusion-extrusion

experiments the ordered pore arrangement largely stays intact, but a slight increase of the mesopore volume is observed.

KEYWORDS

Periodic mesoporous organosilicas, high pressure intrusion-extrusion, heterogeneous lyophobic systems, electrolyte solutions

INTRODUCTION

Heterogeneous lyophobic systems (HLS), which consist of a lyophobic porous matrix and a nonwetting liquid, are one of the promising technologies for absorption, storage and low temperature generation of mechanical energy [1-9]. The operating principle is the following: under compression, when the external pressure is equal or higher than capillary pressure, the liquid is intruded into the pores of the matrix with a large increase of the solid-liquid interface. Thus, the mechanical energy is transformed into interfacial energy. When the pressure reduces, the system can induce an expulsion of the liquid out of the pores (extrusion) with recovering of mechanical energy. Depending on the properties of porous material and the nature of nonwetting liquid, the HLS are able to absorb, dissipate or restore the supplied mechanical energy with a more or less significant hysteresis and, as a consequence, they display a bumper, shock-absorber or spring behavior, respectively.

First heterogeneous lyophobic systems developed by V. Eroshenko were based on porous silica and liquid metals [2], then on hydrophobized porous silicas and water as light and environmentally friendly nonwetting liquid [10,11]. Since water became the most used intruded liquid and its high-pressure intrusion was studied for other types of hydrophobic materials such as pure silica zeolites [12-19] and metal-organic frameworks [20-23]. A use of electrolyte solutions was found to be an effective way to improve the energetic performances of HLS by a considerable increase of the intrusion pressure [24-30].

The HLS based on porous silicas demonstrate usually a shock-absorber or a bumper behavior with relatively low values of intrusion pressure (10-50 MPa), but their high intruded volume allows to achieve relatively high absorbed energy. Most part of the works on porous silicas concerns the materials with irregular nanopores of various form and diameter [10,11,28,31,32], but ordered mesoporous silicas with regular pore arrangement were also studied in several reports [33-38]. Nevertheless, a study of new types of hydrophobic porous materials with high pore volume is of considerable interest.

Periodic Mesoporous Organosilicas or PMOs are hybrid nanomaterials which combine an inorganic stable silica matrix with versatile organic functionalities [39]. These organic functionalities are homogeneously distributed throughout the entire material. The synthesis of PMOs shows many similarities with the preparation of ordered mesoporous silicas such as MCMs and SBAs [40-42]. They are synthesized via the hydrolysis and subsequent polycondensation of a polysilsesquioxane around a structure-directing agent (SDA). The silane precursor is generally represented by $(OR')_3Si-R-Si(OR')_3$ with R the organic moiety and OR' a hydrolysable alkoxy function. The presence of the organic bridges can influence the chemical properties of the PMO, *e.g.*, alter the hydrophobicity-hydrophilicity. Currently, research on PMOs is performed for a broad range of applications: as heterogeneous catalysts, adsorbents for metal ions and volatile organic compounds, controlled drugs delivery systems and materials for electronics, however they have never been studied for applications in heterogeneous lyophobic systems.

In this work we present the study of high-pressure intrusion-extrusion of water and electrolyte solutions in an ethane-bridged PMO material with a thorough investigation on its structural and physicochemical properties. The organic moieties contained in the PMO material distinguishes it from the purely inorganic materials studied in the field so far. PMOs are known to be relatively hydrophobic and to have an increased mechanical and hydrolytic stability, compared to mesoporous silica materials [43,44]. These properties should be beneficial in their application as heterogeneous lyophobic systems.

EXPERIMENTAL SECTION

Reagents The reagent, Brij-76 (Polyoxyethylene (10) stearyl ether) was purchased from Sigma Aldrich, whereas, 1,2-bis(triethoxysilyl)ethane (97%) and HMDS (hexamethyldisilazane, 98.5%) were supplied from ABCR. HCl (37%) and chloroform (>99%) were purchased from Carl Roth. All the reagents were used without further purifications.

Synthesis of ethane PMO (PMO 76 ethane)

The ethane-bridged PMO sample (hereafter, PMO 76 Ethane) was synthesized according to the following procedure, adapted from Fernandez and coworkers [45]. An amount of 6 g of Brij-76 surfactant was dissolved in a solution of 20 mL HCl and 280 mL distilled water, followed by stirring at 50°C for 24 h. After adding 19 mL 1,2-bis(triethoxysilyl)ethane, the mixture was stirred for 24 h at the same temperature. The resulting gel was then aged at 90°C for 24 h under static conditions. A white powder was collected by filtration and thoroughly washed with distilled water. In order to remove the surfactant, 1 g of as-synthesized material was stirred in a solution of 1 mL HCl in 50 mL ethanol for 12 h at 80°C. After repeating this process twice, the solid product was recovered by filtration, washed with ethanol and dried under vacuum at 120°C.

Hydrophobization with HMDS

A total amount of 1 g of ethane PMO, dried at 120°C under vacuum, was brought into a schlenk flask under argon atmosphere. 20 ml of HMDS was added and the vial was closed. The mixture was stirred for six hours under argon atmosphere. Then, it was filtered and washed with chloroform. The white solid was stirred in chloroform overnight and filtered. The resulting powder was dried at 120°C under vacuum.

Intrusion–Extrusion Experiments

The intrusion–extrusion experiments of water and LiCl aqueous solutions in preliminary outgassed (90°C, 6 hours under vacuum) PMO 76 Ethane sample were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV) as described in reference 13. The values of the intrusion (P_{int}) and extrusion (P_{ext}) pressures correspond to that of the half volume total variation. Pressure is expressed in Megapascals (MPa) and volume variation in millilitres (mL) per gram of calcined samples. The experimental error on the pressure and on the volume is estimated to be ca. 1 %.

After intrusion–extrusion experiments, the samples intruded with LiCl aqueous solution were filtrated and washed with water to remove traces of LiCl. The absence of chloride in the filtrate was verified by adding few drops of 1 M silver nitrate aqueous solution (no silver chloride precipitate was

observed). Then the samples were dried at 70 °C overnight and hydrated in a 80 % relative humidity atmosphere for 24 h to restore the hydration state. For thermogravimetric experiments one part of the sample intruded with 20 M LiCl aqueous solution was not washed. After filtration, the solid was only dried at room temperature for 24 hours in order to avoid the extraction of the intruded solution from the pores. A similar treatment was performed on the water intruded sample.

Powder X-ray Diffraction

X-ray diffraction pattern of the different samples were recorded using a PANalytical MPD X'Pert Pro diffractometer operating with Cu K α radiation ($\lambda = 0.15418$ nm) in the 2 θ degrees range 0.6–10 and equipped with an X'Celerator real-time multiple strip detector.

Nitrogen Adsorption–Desorption Measurements

Nitrogen adsorption–desorption isotherms were performed at -196 °C using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the samples were outgassed at 90 °C under vacuum during 15 hours. Low outgassing temperature should allow to eliminate physisorbed water, but to avoid the dehydroxylation process. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t-plot methods, respectively.

Thermal Analysis

Thermogravimetric (TG) analyses were carried out on a Mettler-Toledo TG/DSC Star^e System apparatus, under air flow, with a heating rate of 5 °C/min from 30 to 800 °C.

Solid-State NMR Spectroscopy.

²⁹Si MAS (Magic Angle Spinning) and ¹H–²⁹Si CPMAS (Cross polarisation) NMR spectra were recorded at room temperature on a Bruker Advance II 300 MHz spectrometer, with a double-channel 7 mm Bruker MAS probe. The recording conditions are given in Table 1.

Table 1: Recording conditions of the ²⁹Si MAS and ¹H–²⁹Si CPMAS NMR spectra.

²⁹ Si	
MAS	CP MAS

Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	1.87	4
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	/	1
Recycle time (s)	80	8 ^b
Spinning rate (kHz)	4	4
Scans number	2500	2500

^a TMS : TetraMethylSilane

^b The relaxation time T₁ was optimized

RESULTS AND DISCUSSION

PMO synthesis

The ethane PMO was synthesized by condensing the precursor (1,2-bis(triethoxysilyl)ethane) around a soft template (Brij 76) under acidic conditions. This synthesis resulted in a material with an ordered pore **arrangement** and narrow pore size distribution. The pore **arrangement** of this PMO is similar to that of ordered mesoporous silicas, such as MCM-41. However, the PMO material contains a high concentration of ethane units within the silica framework. This property makes the PMO more hydrophobic than pure silica. Even so, the PMO material still contains silanol groups. Thus, in order to render the PMO even more hydrophobic, the surface silanol groups were capped by grafting of a trimethylsilyl group. A schematic representation of the hydrophobized ethane PMO is shown in Scheme 1. A detailed characterization of the ethane PMO will be discussed in the following sections.

Intrusion-extrusion study

The intrusion-extrusion experiments with water and LiCl aqueous solutions were performed on PMO 76 Ethane sample. The corresponding curves (**first intrusion-extrusion cycle and second intrusion**

curve) are shown in Figure 1. As shown in previous works, the volume variation observed at low pressure (< 5 MPa) corresponds to the compressibility of the particle bed and filling of its interparticular porosity [20,46]. The intrusion of water occurs at a quite low pressure (below 5 MPa). Therefore, from these low pressures and taken into account what is mentioned above, it is difficult to determine the behavior of this HLS system. However, according to the TG analysis (see below), all the liquid was expelled from the solid at atmospheric pressure. Therefore, the intrusion process seems to be reversible and occurs at very low pressures (< 3 MPa). Such a system seems to show a spring or better a shock-absorber behavior, but with very low energetic performances. For the others HLS (with 5, 10 and 20 M LiCl aqueous solutions) the intrusion steps are clearly observed at high pressures on the corresponding P-V diagrams. The inflexions observed on the extrusion curves at low pressure are probably related with the material flexibility, but the intrusion is irreversible and the « PMO 76 Ethane – LiCl aqueous solution » systems display a bumper behavior. Indeed, whatever the electrolyte concentration, the second intrusion curve is superimposable with the extrusion one of the 1st cycle. Such a behavior will be confirmed by TG analysis. Therefore, as previously observed for HLS based on pure-silica zeolites [47,48], a change of the system behavior is observed between water and LiCl aqueous solutions. However, and surprisingly, for the PMO-based systems an evolution of the behavior in an opposite direction is observed: the intrusion becomes not reversible for LiCl aqueous solutions. According to the NMR results (see below), a less hydrophobic surface of the samples intruded with LiCl aqueous solutions might explain such a difference. The intrusion pressure values are close to 13, 18 and 37 MPa for 5, 10 and 20 M LiCl aqueous solution, respectively. The increase of intrusion pressure with electrolyte concentration is a well-known phenomenon [26,28,30]. In HLS the intrusion pressure is generally determined by Laplace-Washburn equation: $P = 2\gamma \cos\theta/r$, where γ – vapor-liquid surface tension, r – pore radius and θ – solid-liquid contact angle. Thus, the pressure rise can be explained by an increase of the surface tension and the contact angle with the LiCl concentration. It can be supposed that the rise of the contact angle is predominant in our case, since the surface tension increases only by 35 % from pure water to 20 M LiCl aqueous solution (72.8

and 98 mN/m, respectively [49]), whereas the pressure rises by 2.8 times from 5 M to 20 M LiCl aqueous solutions. It should be also noticed that this increase of intrusion pressure is the most pronounced among all other reports on high pressure intrusion in mesoporous silicas.

The intrusion volume is about 0.7 mL per gram of PMO and increases with the LiCl concentration (0.63, 0.68 and 0.72 mL/g for 5, 10 and 20 M LiCl, respectively). Due to the high intruded volume, the maximal value of absorbed energy achieves 27 J/g that is close to the best values obtained for the systems based on pure silica zeolites [26,47] and higher than ones of the systems based on hydrophobized silica [33-38].

X-ray diffraction

The characterization of the PMO 76 Ethane sample by X-ray diffraction was performed before and after intrusion-extrusion experiments. The XRD patterns are reported in Figure 2 (only the 0.6- 5° 2 θ range is shown since no peaks are observed for 2 θ > 5°). In all cases, three XRD peaks are clearly evidenced on the XRD patterns and indicate the (100) reflection and the second-order reflections (110) and (200). These well-resolved signals are indicative for a 2-D hexagonal pore ordering. For the intruded-extruded samples, only a very slight shift of the XRD peaks towards high angle values is observed. This indicates that the pore ordering is preserved after the intrusion-extrusion experiments. The mean hexagonal unit cell parameter (a_{hex}) determined from these XRD patterns is ranging from 7.11 nm (nonintruded sample) to 7.01 nm (20 M LiCl intruded sample). Such a shift, in agreement with the N₂ adsorption-desorption analysis, might be due to a slight compacting of the pore walls (0.1nm) after intrusion-extrusion experiments.

Thermogravimetric analysis

The thermogravimetric curves of the PMO 76 Ethane sample before and after intrusion-extrusion with water and 20 M LiCl aqueous solution are given in Figure 3. For the nonintruded sample, two steps of weight loss are observed. The first one at low temperature (30°-150°C) is quite small (0.8-

1.2 wt.%) and attributed to the desorption of physisorbed water molecules. The low value of this weight loss reveals the hydrophobic character of the PMO 76 Ethane material. The second step is more pronounced (weight loss 15.1 wt.%) and starts at 260°C. It corresponds to the decomposition of the PMO material, the oxidation of organic bridges and the dehydroxylation reactions. After only a drying step at room temperature, the TG curve of the water intruded sample is very similar to that of the nonintruded sample. Therefore, it can be concluded that water is completely expelled from the solid at atmospheric pressure revealing thus the reversible character of intrusion of this HLS system, which seems to show a spring or better a shock-absorber behavior. It is not the case of the intruded sample with 20M LiCl aqueous solution after drying at room temperature, without washing. Its TG curve displays three main weight losses. The last one (14 wt.%), observed in the temperature range 550 -780°C, might be attributed to the removal of chloride compounds. Indeed, the XRD pattern of the product after heating at 800°C (not reported) corresponds to a mixture of lithium silicates (Li_2SiO_3 and $\text{Li}_2\text{Si}_2\text{O}_5$) with traces of cristobalite indicating clearly that the silica of the PMO material reacted with LiCl. Therefore, only the two first weight losses are characteristic of the intruded PMO 76 Ethane sample. The first weight loss, below 150°C and close to 45 wt.%, corresponds to the removal of the water molecules arising from the intruded liquid and from those trapped in the interparticular porosity due to the low drying temperature. Such a weight loss, confirms the bumper behavior of the “PMO 76 Ethane– 20M LiCl aqueous solution” system. The second weight loss (8 wt.%) occurring between 220 and 520°C can be assigned to the degradation of the organic network of the PMO material. This weight loss, calculated for 100 % of PMO 76 Ethane solid is similar to the one observed for the nonintruded sample (i.e., 15 wt.%).

N₂ adsorption-desorption measurements

It is worthy to note that for this characterization, the intruded samples were carefully washed with distilled water and dried at 70°C for 24 hours. N₂ adsorption-desorption isotherms of the nonintruded sample and the intruded ones with H₂O and 20 M LiCl aqueous solution are given in Figure 4. The

isotherms are mainly of type IV with a H2(a) hysteresis, which according to IUPAC [50] can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. The isotherms are almost superimposable up to $p/p_0=0.5$, but the samples intruded with water and 20 M LiCl aqueous solution show higher mesopore volume. BET surface area of the samples is close to 420 m²/g and the total pore volume is equal to 0.83 mL/g for the nonintruded sample and 0.90 mL/g for both intruded ones with a mesopore volume of 0.68 and 0.75 mL/g, respectively. The increase of pore volume for the intruded samples can be related with a partial breaking of siloxane bridges (see NMR results) after intrusion-extrusion experiments. It can be also hypothesized that in the nonintruded sample mesopores are partially obstructed by the HMDS molecules less or more strongly grafted on the surface after hydrophobization and these molecules would be eliminated during the intrusion at high pressure. Such a hypothesis seems to be also confirmed by NMR spectroscopy. The pore diameter (BdB) ranges between 4.2 to 5.1 nm with an average value of 4.5 nm. This average value is the same for all the samples. Therefore, the slight decrease of the unit cell parameter observed by XRD (0.1nm) is therefore probably due to a compacting of the pore walls of the PMO material.

NMR spectroscopy

Also here the intruded samples were carefully washed with distilled water and dried at 70°C for 24 hours. The ²⁹Si MAS NMR spectra of PMO 76 Ethane samples before and after intrusion–extrusion experiments with 20 M LiCl aqueous solution are shown in Figure 5. The spectrum of the nonintruded sample exhibits three main resonances at 9, -58 and -65 ppm and a broad one at -46 ppm. The resonances at -46, -58 and -65 ppm can be assigned to Si species covalently bounded to carbon atoms: T₁ [C-Si(OH)₂(OSi)], T₂ [C-Si(OH)(OSi)₂] and T₃[C-Si(OSi)₃] sites, respectively [51-55]. The observation of these T sites in the ²⁹Si MAS NMR spectrum confirms the presence of the -CH₂-CH₂- moieties in the framework. A slight increase of T₁ and T₂ signals confirmed on the ¹H-²⁹Si CP MAS NMR spectra (Figure 6) is observed for the intruded sample. It can be ascribed to the formation of

silanol defects under 20 M LiCl intrusion arising from the breaking of siloxane bridges. Furthermore, the absence of any other signal for the Q^n $[\text{Si}-(\text{OSi})_n(\text{OH})_{4-n}]$ species between -90 and -120 ppm confirms that practically no silicon-carbon bond was cleaved either during the synthesis or after intrusion-extrusion experiments. The resonance at 9 ppm corresponds to silicon from the trimethyl silyl function, which was used to cap the silanol groups. In the intruded sample, on the MAS spectrum the area of this component is slightly lower than the one of the nonintruded sample indicating, in agreement with the N_2 physisorption results, the presence of a slightly lower amount of trimethyl silyl functions in the intruded PMO material. From these NMR data, we can conclude that the PMO material largely stays intact, even after the high pressure treatment with a 20M LiCl solution. This, together with the XRD and nitrogen sorption data, confirms the high structural stability of the ethane PMO.

CONCLUSION

In this work an ethane bridged periodic mesoporous organosilica has been studied for the first time as a porous matrix for heterogeneous lyophobic systems which can be used for absorption and storage of mechanical energy. High pressure intrusion-extrusion experiments with electrolyte solutions have shown that “PMO 76 Ethane –LiCl aqueous solution” systems demonstrate a bumper behavior with an irreversible intrusion. The intrusion pressure increases with the salt concentration from 13 to 37 MPa for 5 and 20 M LiCl aqueous solutions, respectively. This pressure rise of 2.8 times with salt concentration is the highest observed for the HLS based on mesoporous materials and should be mostly related with the increase of solid-liquid contact angle. An increase of intruded volume from 0.63 to 0.72 mL/g for 5 and 20 M LiCl aqueous solutions, respectively, has been also observed. Due to the high intruded volume, the maximal value of absorbed energy achieves 27 J/g, which is close to the best values obtained for the systems based on pure silica zeolites and higher than for ones based on hydrophobized silica. With water, as nonwetting liquid, the intrusion occurs at low pressure but

all the liquid is expelled from the solid at the pressure close to atmospheric one. The corresponding HLS system seems to behave as a spring or better a shock-absorber.

Characterization of the ethane PMO shows that the ordered pore arrangement largely stays intact after the intrusion-extrusion experiments, proving the mechanical stability of the sample. However, the slight increase of the mesopore volume for the intruded samples can be due to the breaking of some siloxane bonds. Another explanation can be the slight decrease of the amount of grafted HMDS molecules in the PMO material after intrusion under high pressure. Consequently, this decrease leads to a less hydrophobic surface which could explain the bumper behavior observed for the “PMO 76 Ethane– LiCl aqueous solution” systems. With the high absorbed energy value, we have shown for the first time that PMO materials are indeed very interesting materials for heterogeneous lyophobic systems.

ACKNOWLEDGEMENTS

JAM acknowledges the Flemish Government for long-term structural funding (Methusalem)

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