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Dissipative water intrusion in hydrophobic MCM-41 type materials

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Texture-related features of water intrusion in hydrophobised MCM-41 silicas render these materials especially suitable for energy dissipation in mechanical dampers.

The MCM-41-type ordered mesoporous adsorbents disclosed by Mobil[1] in 1992 have opened up novel applications in various fields such as catalysis[2] or chromatography.[3] They differ from commonly used silica gels by their narrow pore size distribution, which makes them excellent model materials for adsorption experiments.[4,5] Conventional functionalised silica gels have been recently proposed as porous matrices for water intrusion-based mechanical devices.[6] Depending on the texture and surface properties of the matrix, the system could be applied for either energy storage or dissipation (damping).[7,8] By forcing water (non-wetting liquid) to invade a hydrophobic porous solid, by means of an external pressure, mechanical energy can be converted into interfacial energy. The capillary pressure P_{CAP} needed for pore intrusion can be written as follows from the Laplace–Washburn relation[9,10] for cylindrical pores.

$$P_{\mathrm{CAP}} = -2\sigma\cos\theta/r \qquad (1)$$

where σ is the surface tension, r the pore radius, and θ the contact angle between the liquid and the solid. The possibility to dissipate mechanical energy depends on the presence of hysteresis in the intrusion–extrusion cycles. MCM-41 presents a narrow pore size distribution easily tailored by varying the conditions of synthesis. These properties suggest that a better control of water intrusion cycles can be attained on these materials.

This work adresses how MCM-41 silicas can be efficiently grafted with alkyl chains and provide a more competitive material than plain functionalised silica gels for this application.

MCM-41 was synthesized from an alkaline silicate solution in the presence of hexadecyltrimethylammonium bromide.[4] Functionalisation was performed with chlorodimethyloctyl silane by a pyridine-assisted reaction. The grafting agent has been shown to provide a good surface coverage thanks to the effect of the side methyl groups.[11] The MCM-41 was compared with a silica gel (Fluka) of similar pore volume functionalised following the same procedure.

The MCM-41 exhibits a much narrower pore size distribution than plain silica gel, as indicated by the sharper step in the adsorption–desorption isotherm on the parent material. On grafted MCM-41, the pore size is too close to microporosity to exhibit a sharp step (Fig. 1). In terms of surface coverage, the chain loading on MCM-41, *ca.* 1.4 grafted chain nm^{-2} is lower than the value of 1.9 grafted chains nm^{-2} obtained on silica gel. Nevertheless, due to the lower initial silanol density of MCM-41,[12] about 75% of the silanols are grafted for the MCM-41 material (1.4 out of 1.5–2 silanols nm^{-2}) *cf.* less than 50% on silica gel (1.9 out of 5 silanols nm^{-2}). This provides evidence of high surface homogeneity for the MCM-41 type material. Besides, despite chain loading differences, similar surface coverage and comparable hydrophobicity are expected on the two materials as further water intrusion experiments confirm.

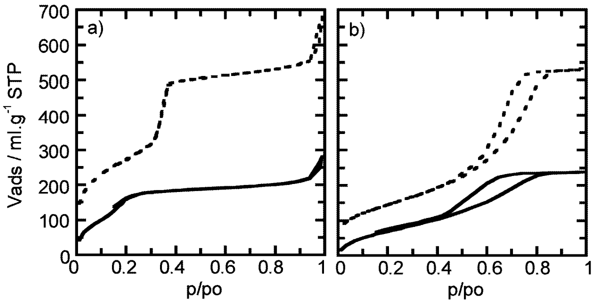

Fig. 1 Nitrogen isotherms at 77 K of grafted materials (—) and parent materials (---) for (a) the MCM-41 material and (b) silica gel.

Table 1 Chain loading n_g, porous volume V_p, specific surface area S_{BET}, pore diameter D_{BdB}[a] of grafted materials (MCM41 and silica gel)) and intrusion/extrusion characteristics (intrusion pressure P_{INT}, extrusion pressure P_{EXT} and dissipated energy E_d)

Grafted materials	Silica gel	MCM-41
V_p/ml g^{-1} (STP)	0.36	0.27
S_{BET}/m^2 g^{-1}	300	450[b]
D_{BdB}/nm	5.7	2.4
n_g/nm^{-2}	1.92	1.36
P_{INT}/MPa	15–45	40–65
P_{EXT}/MPa	0.1–10	15–45
E_d/J g^{-1}	5.1	4.5

[a] BdB: calculated from Broekhoff–De Boer theory.[b] No acceptable correlation coefficient could be attained from BET surface calculations. An indication value is given by geometrical calculation.[4]

Compressibility measurements were performed according to a procedure described elsewhere.[13] A method has been developed to assess pressure and volume values corrected from compressibilities and line deformation. Experiments on both samples were performed at room temperature. The time needed for an intrusion/extrusion run was about 3 min. The results are given in Fig. 2. Pressure is expressed in MPa and volume variation in mm^3 per gram of product taken in standard conditions. For every sample, pressure *vs.* volume curves, denoted *P*/*V* curves, correspond to stable cycles upon several repetitions of the intrusion–extrusion experiments. Moreover, the cycles were reproducible after storage of several weeks in water. Both samples present a recovery of initial (*P*/*V*) state after a compression cycle, with hysteresis on the pressure parameter. When submitting these systems (water + porous solid) to a rising pressure, the liquid has to reach a critical pressure value, the capillary pressure P_{CAP}, to penetrate the porosity. Then, it invades the available porous volume within a defined pressure range up to saturation of the media. Any further pressure rise results in the compression of both liquid and solid. When the pressure is decreased, extrusion of the liquid occurs for a pressure value lower than the intrusion one. This hysteresis is the cause of energy dissipation.

In the case of the grafted silica gel, the intrusion occurs around 30 MPa and the extrusion occurs at low pressure. For

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MCM-41, both phenomena occur at higher pressure, the intrusion taking place around 50 MPa and the extrusion being complete above 15 MPa. Results are gathered in Table 1.

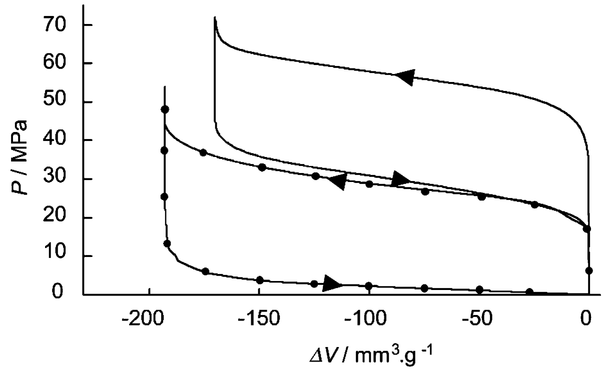

Fig. 2 Water intrusion and extrusion curves for grafted MCM-41 material (—) and grafted silica gel (–●–).

The higher pressure values measured on MCM-41 seem consistent with the lower pore size of this material. The question then arises as to whether pore size alone accounts for the observed results? The classical description of the intrusion and extrusion pressures as a function of pore size is the calculation of advancing and receding contact angles (θ_a and θ_r) by the Laplace–Washburn relation. For the advancing contact angle, a higher value is found for silica gel (θ_a = 126°) than for MCM-41 (θ_a = 116°); this agrees with the higher chain loading on silica gel which provides a more hydrophobic surface. By contrast, the receding contact angle exhibits an inverse trend: θ_r = 96° on silica gel and 104° on MCM-41.

This trend in contact angles corresponds to the relative width of the two hysteresis cycles: the ratio of intrusion to extrusion pressure (P_{INT}/P_{EXT}) is nearly 6 for silica gel and < 2 for MCM-41. It appears that MCM-41 exhibits a smaller hysteresis than silica gel. The presence of hysteresis is usually attributed to a metastable, non-equilibrium state that could be due to surface roughness or chemical heterogeneity.[14] According to this interpretation, the smaller hysteresis cycle for MCM-41 could correspond to a smaller defect density for both pore texture and surface coverage. However, alternative interpretations are possible. If hysteresis in intrusion/extrusion is considered to be similar to hysteresis in adsorption/desorption isotherms, the width of the hysteresis loop can be strongly dependent on the pore size. In the case of adsorption of gases in mesoporous adsorbents, no hysteresis can be observed for pores smaller than a threshold value depending on the capillary critical point of the adsorbate.[15] This model of meniscus instability in small pores seems to apply also to water intrusion/extrusion loops, as suggested by the lack of hysteresis in the case of micropores.[7] In our case, the width of the hysteresis loop for small mesopores would decrease due to the proximity to the capillary critical point, explaining the results observed on MCM-41. Further studies are currently under way to evidence this phenomenon with MCM-41 samples of different pore size as model materials. It is clear that the instability of the meniscus approaching the micropore region can limit the field of validity of the Laplace-Washburn equation.

In terms of mechanical applications, both grafted silica gel and grafted MCM-41 present the desired stability: the intrusion/extrusion results are reproducible upon repeated cycles and storage of the water/adsorbent system for several weeks. However, their different mechanical behaviours have great consequences on the potential use for dissipative devices.

The grafted silica gel behaves like the systems previously studied in the literature:[6,10,13] extrusion typically occurs from 6–10 MPa down to 0.1 MPa. As a consequence, on silica gel, the pressure should be decreased down to atmospheric pressure to lead to water extrusion and to allow a cyclic use. For operational devices, this would impose a constraining step of complete unloading of the system. This is not the case for MCM-41, the behaviour of which is very unusual: whereas high extrusion pressure is commonly observed using mercury or liquid metals[8] as non-wetting liquids, it has never been reported for water in hydrophobic materials featuring a hysteresis loop. MCM-41 appears as an ideal material for dampers operating without complete discharge between successive cycles.

Another advantage of MCM-41 is the easy control of the pore size by changing the surfactant chain length during the synthesis and so the intrusion pressure can be controlled by tailoring the pore diameter. Monodispersity of pore size in MCM-41 also affects the dispersion of the intrusion pressure (the range of intrusion pressure $\Delta P/P$ is 1.0 for silica gel and < 0.5 for MCM-41). Controlling the intrusion pressure and its dispersion at the nanometric level allows the construction of dissipative devices to protect structures from shocks at a fixed and quasi-constant strength.

In addition, the nature and the length of the grafted chains have an influence on the hydrophobicity, the pore radius and, as a consequence, on the intrusion pressure.[13] By combining these synthesis parameters, the chemist can design materials with adjustable properties towards the intrusion phenomenon.

In conclusion, this work demonstrates the potential use of modified MCM-41 materials for a new type of application: dissipation of mechanical energy. One remarkable property is highlighted using these supports namely the shift of the extrusion pressure to higher values. This new property represents a real improvement compared to silica gels and widens the fields of possible applications of dissipation phenomena. Moreover, due to their unique properties, MCM-41 materials are confirmed as useful models for a better understanding of the physical chemistry of surfaces.

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