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Microwave assisted template removal of siliceous porous materials†

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Organic templates of meso- and macro-porous siliceous materials can be completely removed within minutes by microwave digestion, resulting in highly ordered inorganic frameworks with higher surface areas, larger pore volumes, lower structural shrinkage and richer silanol groups compared with those from conventional template removal methods.

The surface and pore properties of meso- and macro-porous materials are of vital importance for specific utilities such as adsorption, catalysis and separation. The organic (template) and inorganic (framework) separation is a necessary step to achieve porous structures. Until now, calcination (thermally, by ultraviolet light[1] or by microwaves[2]) and extraction (by conventional solvent or by supercritical fluid[3]) are two general methods for removing the organic component. However, the three most important requirements, (1) complete removal of the template, (2) minimum operation time, (3) ideal structural and surface properties of inorganic framework, by any of the methods can not be simultaneously achieved. Here we present a new method to remove organic template by microwave digestion (MWD), which shows many benefits over these other methods such as extreme rapidness, lower structural shrinkage, larger surface areas and pore volumes, and retention of a higher degree of silanol groups.

Mesoporous or macro-mesoporous hybrid siliceous materials were prepared according to previous literature procedures.[4–8] MWD[9] of the samples was performed with a microwave sample preparation system model MK-II within minutes (see Table 1). The system was equipped with Teflon sample vessels which were transparent for microwave energy, operated at approximately 1200 W. The maximum pressure and temperature were 1.3 MPa and 200 °C, respectively. The working frequency was 2450 MHz and the working voltage was 220 V. The sample amount was approximately 0.1–0.2 g with 1.5 ml of 15 M HNO_3 and 1 ml of 9.3 M H_2O_2 as the solvent. Post functionalizations for the mesoporous silica samples were conducted by microwave irradiation.[10] Introduction of Pb^{2+} onto the pore wall surfaces was conducted by soaking 0.2 g of functionalized samples in 20 mL ethanol solution containing 0.379 g of $PbAc_2\cdot 3H_2O$. The adsorption capability of heavy metal ions for the functionalized samples was investigated by measuring the concentration of the remaining Pb^{2+} in the mother-liquor by UV-vis spectra. Samples prepared by thermal calcination or ethanol extraction were also prepared and analysed for comparison (see ESI for details†). The discussions below are focused on mesoporous material SBA-15 prepared using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Aldrich) and tetraethyl orthosilicate (TEOS, 98%, Aldrich) under acid conditions.[4]

Fig. 1 shows the IR transmission spectra of SBA-15 samples: (a) as-synthesized, (b) extracted by ethanol at 78 °C for 24 h, (c) after MWD for 2 min and (d) after thermocalcination at 550 °C. A broad band around 3400 cm^{-1} appears for all samples, which is partially caused by the O–H stretching vibration mode of the adsorbed water molecules, whose bending vibration mode is responsible for the band recorded at 1630 cm^{-1}. Several infrared absorption bands at around 2850–3000 and 1350–1500

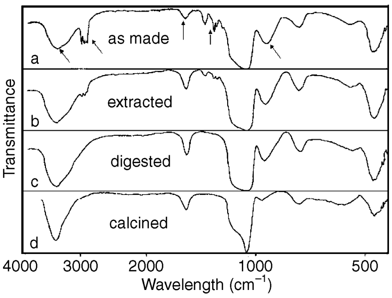

Fig. 1 IR spectra of (a) as-made, (b) ethanol extracted, (c) microwave digested and (d) calcined SBA-15 mesoporous materials .

Table 1 Comparison of the physicochemical properties of porous materials treated by microwave digestion and thermal calcination

			BET surface area/m² g⁻¹		Total pore volume/cm³ g⁻¹		Primary pore size[h]/nm	
Type	Sample	T_{digest}/min	Digested	Calcined	Digested	Calcined	Digested	Calcined
Powder	SBA-15[a]	2	853.5	6 79.2	1.41	1.15	8.8	7.8
	SBA-15[b]	3	619.1	520.1	1.32	0.96	9.9	7.9
	SBA-16	2	668.8	622.5	0.76	0.47	7.5	5.4
	FDU-1	2	795.2	659.3	1.01	0.92	12.3	10.2
	MCM-41	5	1058	1036	0.95	0.92	3.4	3.2
Mesoporous film	MF-1[c]	3	739.2	634.1	1.21	1.05	8.9	7.6
	MF-2[d]	3	671.4	511.8	0.84	0.61	7.9	5.8
Macro-mesoporous membrane	MMM-1[e]	5					230	192
	MMM-2[f]	5					262	206
	MMM-3[g]	5					110	< 100

[a] TEOS, [b] sodium silicate as the silica source. Templated by [c] P123 ($EO_{20}PO_{70}EO_{20}$), [d] F127 ($EO_{106}PO_{70}EO_{106}$). Templated by PS spheres with the radii of [e] 270 nm, [f] 300 nm, [g] 130 nm. [h] Calculated from BET adsorption data using the Barrett–Joyner–Halanda (BJH) model for mesoporous materials and from SEM observations for macro-mesoporous materials.

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† Electronic supplementary information (ESI) available: syntheses, XRD patterns, SEM image, Pb^{2+} extraction images, ^{29}Si MAS NMR and TG curves. See http://www.rsc.org/suppdata/cc/b2/b202180c/

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cm^{-1} shown in spectrum (a) and (b) can be assigned to C–H stretching and bending vibrations of the template P123, respectively, while in spectrum (c) and (d) these absorptions are nearly indiscernible. This suggests the efficient removal of the organic template by thermocalcination and MWD while partial removal by ethanol extraction. More importantly, the relative intensity of Si–OH bending bands at around 960 cm^{-1} is nearly the same for as-made, ethanol extracted and microwave digested samples, but much weaker for the calcined sample, suggesting that both MWD and ethanol extraction methods lead to the retention of a high level of silanol groups on the pore wall surface while thermocalcination will inevitably reduce their number. Elemental analyses show that the carbon contents in both digested and calcined samples are below the detection limit (0.3 wt%), suggesting that the template removal is higher than 99.5% while for the ethanol extracted sample the carbon content is as high as 8.7 wt%. TG curves of the samples indicate that the weight loss is approximately 16% for the digested SBA-15 and 10% for the calcined sample. ^{29}Si NMR data show that the Q_3/Q_4 value for the digested sample is about 49%, slightly lower than for the as-made sample (62%) but much higher than that for the calcined sample (18%), giving further direct evidence of the presence of a high abundance of silanol groups. These results clearly indicate that MWD simultaneously leads to fast, complete template removal and almost intact silanol groups preservation.

Powder X-ray diffraction (PXRD) patterns for all the samples show three distinct Bragg diffraction peaks, which can be indexed to [100], [110] and [200], suggesting the formation of highly ordered 2D hexagonal mesostructures. The d_{100} values are 11.4, 11.1 and 9.7 nm for as-made, microwave digested and calcined samples, respectively. N_2 sorption isotherms indicate that the digested sample features a steep rise in adsorption at higher relative pressure (P/P_o) compared with the calcined sample, suggesting that the former has a larger primary pore size. The BET surface area, total pore volume and primary pore size of the digested SBA-15 sample are 854 $m^2\ g^{-1}$, 1.41 $cm^3\ g^{-1}$ and 8.8 nm, while those of the calcined sample are 679 $m^2\ g^{-1}$, 1.15 $cm^3\ g^{-1}$ and 7.8 nm, respectively. It is obvious that the microwave digested sample has a lower structural shrinkage and better structural quality compared with the calcined sample.

The transmission electron microscopy (TEM) image (Fig. 2) of digested SBA-15 shows well-ordered hexagonal arrays of mesopores (1D channels) in large domains. The morphology is wheat-like and is as same as that of typical as-made SBA-15. These results further suggest that the MWD does not lead to collapse of the structural order of the as-made sample.

As discussed above, MWD leads to fast and complete removal of the template, and the silanol groups on the surface are more abundant than for samples treated by thermocalcination. This feature provides a possibility for a high degree of functionalization of the pore wall surface. This can be reflected by measurements of the UV-vis absorption of Pb^{2+} solutions (Fig. 3) and the corresponding photograph (see ESI†). The absorbance at 270 nm decreases in the order (a) calcined, (b) ethanol extracted and (c) digested SBA-15, suggesting that the loading amount of Pb^{2+} by thiol-functional groups is the highest for the digestion treated sample. This phenomena can be explained by assuming that the digested sample has the largest amount of free silanol groups, while in the extracted sample the silanol groups are partially embedded in the amphiphiles and in the calcined sample the silanol groups are reduced in number by thermal treatment. Thus the digested sample has the highest amount of active sites for post-functionalization and ion adsorption. Elemental analysis provides further direct evidence for a high degree of functionalization. The elemental contents for functionalized mesoporous SBA-15 are (wt%), *via* MWD (C, 8.7; H, 2.2; S, 4.6), extraction (C, 15.2; H, 2.8; S, 4.2) and calcination (C, 5.4; H, 1.2; S, 2.3), respectively. It should be emphasized here that MWD is a complete template removal method that operated at a relatively low temperature and it is based on oxidation reactions. This feature contributes to the higher retention of silanol groups. Rapid calcination by microwave irradiation[2] at about 1000 °C does not lead to this feature.

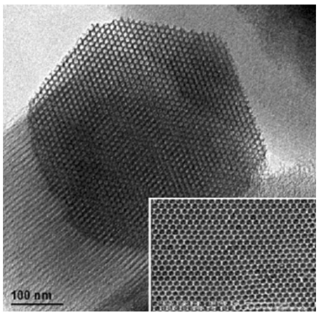

Fig. 2 TEM image of microwave digested SBA-15. Inset, SEM image showing the highly ordered macro-mesoporous material MMM-1.

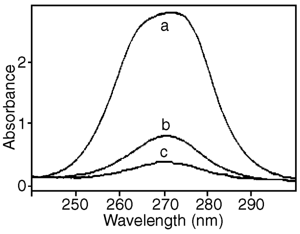

Fig. 3 UV-vis spectra of Pb^{2+} solutions treated with thiol-functionalized mesoporous materials SBA-15 *via* (a) thermocalcination, (b) ethanol extraction and (c) microwave digestion.

The MWD method can also be applied to other siliceous porous materials such as mesoporous powders, mesoporous films and macro-mesoporous membranes (Table 1). The general results are similar to those of SBA-15 powder as mentioned above: (1) very fast and complete removal of the template, either amphiphiles or PS, (2) very low structural shrinkage, *e.g.* for macro-mesoporous materials, the shrinkage ratio is approximately 10–20%, much lower than that of thermocalcined sample (above 30%), therefore the long range order can be retained (see Fig. 2, inset), (3) the surface and pore properties are successfully improved, which is reflected by large surface areas, high total pore volumes, large primary pore sizes (especially for SBA-16 powders) and rich surface silanol groups, thus paving the possibility for high ratio post functionalizations.

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10 0.4 g of digested sample was suspended in 20 mL of 10% v/v solution of (3-thiolpropyl)trimethoxysilane (MPTS) in ethanol within the same preparation system and was microwave irradiated for 5 min.