Synthesis of stable and directly usable hexagonal mesoporous silica by efficient amine extraction in acidified water

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The amine template of hexagonal mesoporous silica (HMS) can be efficiently recovered and re-used by a new extraction procedure in acidified water rendering a directly usable high quality mesoporous support.

Following the earliest reports on M41S materials,[1] Pinnavaia and coworkers[2,3] introduced an alternative route to synthesize mesoporous materials based on a hydrogen bonding interaction between a neutral amine and a non-ionic silica precursor. These materials were denoted hexagonal mesoporous silicas (HMS). An important advantage in the synthesis of these materials is the cost reduction by employing a less expensive and non-toxic surfactant and the mild reaction conditions. HMS materials are claimed to have larger pores, to be more stable and to have thicker pore walls than their MCM-41 counterparts.[4] Owing to the weak hydrogen bonding interactions, more than 90% of the neutral template can be recovered by a simple extraction procedure using ethanol as extracting solvent. A few other attempts to extract the surfactants of mesoporous templated materials have been described in the literature (MCM-41,[5,6] Al-MCM-41,[7] Al-HMS,[8] mesoporous alumino- and galloalumino-phosphate[9]). In all cases, a huge amount of organic solvent is required and, mostly, the extraction needs to be followed by a calcination step to remove the remaining surfactant or the surface ethoxy groups produced during extraction.

We report on an optimized HMS synthesis including the complete extraction of the template with acidified water. This procedure yields not only a directly usable high quality support that does not require a further calcination step, but also allows re-use of the recovered template several times. Obviously, a water extraction procedure fits very well in the striving to green or sustainable chemistry.

HMS was prepared at room temperature using dodecylamine (DDA) as structure directing agent and tetraethylorthosilicate (TEOS) as silica source, according to the procedure reported elsewhere.[4] In a typical template removal, 1 g of as-synthesized material was added to 100 ml solvent and refluxed for 1 h. The residual solid was then filtered off and washed with a second 100 ml portion of solvent and dried at room temperature. Several extracted samples were prepared: HMS-E and HMS-W(HCl/DDA), where E and W indicate extraction in ethanol and water, respectively. HCl/DDA indicates the molar ratio of HCl in the solution and DDA in the as-synthesized HMS. Furthermore, portions of the as-synthesized HMS materials that were calcined in air at 550 °C for 16 h were designated as HMS-C.

The amount of template in the extracted samples (see later, Table 1) is calculated from thermogravimetric analysis. The DTG curve for as-synthesized HMS shows weight losses at 225 and 290 °C, attributed to the thermal decomposition of DDA. A notable difference in the shape of the DTG curve can be observed for the ethanol extracted HMS-E (weight loss at 270 and 400 °C). Information on the origin of these weight losses was obtained by refluxing 1 g of calcined HMS in pure ethanol for 1 h, denoted as HMS-RE. This final material shows weight losses at the same temperature as HMS-E, attributed to the esterification of the surface with ethoxy groups. This can also be inferred from IR spectroscopy (Fig. 1) where HMS-E and HMS-RE show the same bands (2905, 2936 and 2982 cm^{-1}) in the C–H vibration region. Although the extraction of surfactant molecules in ethanol is very efficient (no decomposition of DDA in the DTG curve and complete absence of DDA-bands in the IR spectrum), it yields a surface that is completely unreactive toward subsequent activation owing to the presence of chemically bonded ethoxy groups, and a subsequent calcination at 450 °C is required for further possible application of the support.

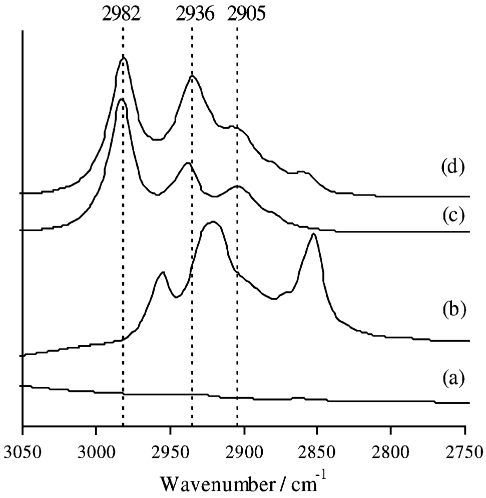

Fig. 1 Diffuse reflectance IR spectra of samples: (a) HMS-W(1), (b) dodecylamine, (c) HMS-RE and (d) HMS-E. The spectra were measured at 200 °C under an oxygen flow.

For the water-extracted HMS-W(0) 69% of the template was present, whereas for the acidified water-extracted HMS-W(1) and HMS-W(2) no weight losses were observed in the DTG curves (Table 1). The absence of template is further evidenced by the IR spectrum of HMS-W(1), where no C–H vibrations are observed. This significant difference in the degree of extraction

Table 1 Amount of template after extraction and physical properties of HMS samples

Sample	Amount of template (%)	BET surface area/ m^2 g^{-1}	$V_{\text{prim.pores}}$^{a}/ cm^3 g^{-1}	d_{100}^{b}/nm	KJS pore diameter/ nm
HMS-C	—	1015	0.71	3.70	3.55
HMS-E	0	932	0.78	3.79	3.70
HMS-W(0)	69	—	—	—	—
HMS-W(1)	0	1051	0.83	3.84	3.70
HMS-W(2)	0	791	0.54	3.63	—^{c}
HMS-RC	—	908	0.67	3.78	3.30

^{a} Primary pore volume measured after the capillary condensation step (P/P_0 ≈ 0.45) in the N_2 isotherm. ^{b} Basal spacing. ^{c} The pore size distribution was too broad and irregular to determine the peak diameter.

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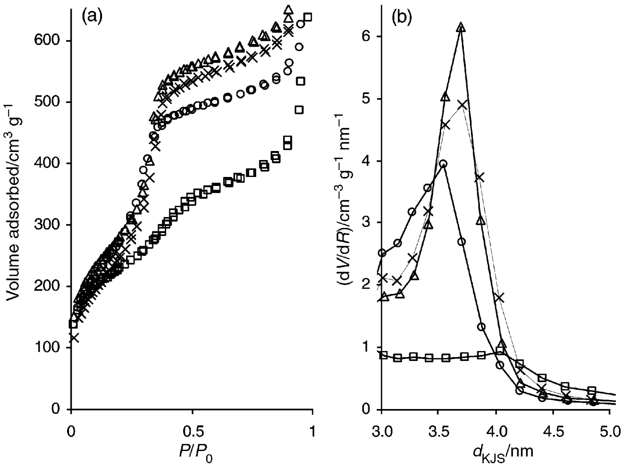

Fig. 2 N_2 sorption isotherms (a) and KJS pore size distributions (b): (□) HMS-W(2), (○) HMS-C, (×) HMS-E and (△) HMS-W(1). The textural mesopore filling of the samples (between P/P_0 = 0.9 and 1) is not shown.

can be attributed to the very low solubility of DDA in pure water, even at elevated temperature. Addition of HCl converts DDA into soluble dodecylammonium chloride (DDAHCl), which facilitates the extraction.

The effect of solvent extraction is shown in Fig. 2(a) and the physical properties of the HMS samples are also listed in Table 1. Compared to the calcined and ethanol-extracted sample, N_2-sorption results show that the template removal in acidified water [HMS-W(1)] also maintained the uniform hexagonal mesoporous structure. To calculate the pore size distribution (PSD), it is generally agreed that the BJH method underestimates the size of pores[10,11] and therefore, the KJS procedure[12] [Fig. 2(b)] is used, which is based on a corrected Kelvin equation for hexagonal materials. It is remarkable that HMS-W(1) has a more narrow PSD, a higher BET-surface area, higher primary pore volume and higher d_{100} value than the calcined and the ethanol-extracted samples. Furthermore, the amount of HCl seems to be a critical parameter in the acidified water extraction procedure. An excess of HCl [HMS-W(2)] results in a poorly ordered structure.

As to its potential use, an important step besides efficient water extraction is the re-usability of the template. To achieve this goal, the recovered DDAHCl was converted to DDA by the addition of NaOH to the extraction solvent. The precipitated DDA was dried and re-used in a fresh synthesis (HMS-RC). As can be seen in Table 1, HMS-RC has very similar characteristics as the calcined HMS-C, indicating that no degradation of the surfactant has occurred.

In summary, the results reported here clearly reveal that the amine template can be recovered easily and efficiently from hexagonal mesoporous silica in acidified water, resulting in a high quality and directly usable molecular sieve. Our synthetic approach therefore provides new opportunities in the synthesis of mesoporous supports while avoiding high-temperature treatment and organic solvents, while the template can also be re-used.

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