Supercritical fluid extraction of surfactant template from MCM-41

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Supercritical fluid extraction was used to extract and recover >90% of the surfactant template from the pores of as-synthesized pure siliceous MCM-41 and the MCM-41 after supercritical fluid extraction shows more uniform pore size distribution than the calcined MCM-41.

Since the discovery of the M41S family of mesoporous materials by Mobil scientists in 1992,[1,2] intensive research has been undertaken by various researchers on the synthesis mechanism and applications of these new materials. Current synthesis involves the use of liquid surfactant as the liquid-crystal templates and these templates are normally removed by calcination to yield the porous materials.

Removal of the template by calcination destroys the template which constitutes *ca.* 50 mass% of the as-synthesized material.[3] Recently, the use of liquid extraction to remove the templates has been reported.[4–6]

The present work describes a new and alternative method of recovering the surfactant templates from as-synthesized materials using supercritical fluid extraction (SFE). This should result in significant savings as the recovered templates can be reused in future synthesis. The MCM-41 materials and the extracted templates were shown to have retained their structures and properties after SFE. In addition, SFE may be used to remove surfactant templates at much lower temperatures from new mesoporous materials, which mesopores could easily collapse under high temperature calcination.

The pure siliceous MCM-41 material were synthesized using cetyltrimethylammonium hydroxide (CTMAOH) and fumed silica. A gel with a molar composition of 1 CTMAOH : 1.04 SiO_2 : 62.50 H_2O was prepared and loaded into polypropylene bottles. The gel was heated at 96 °C for 48 h after which the as-synthesized materials were washed by centrifugation and recovered by filtration. A small part of the as-synthesized sample was calcined in air at 550 °C for 15 h in order to serve as a comparison to samples that underwent SFE. SFE was performed on the remaining samples under different extraction conditions. Supercritical CO_2 modified with MeOH (which was used to increase the solvating power of the supercritical fluid) was used for extraction. The range of pressures and temperatures investigated in this study span from 150 to 350 bar and from 35 to 125 °C, respectively.

The SFE experiments were carried out using a Jasco SFE system consisting of a HPLC pump for carbon dioxide, a syringe pump for the modifier, a chiller for cooling the pump head, an oven for controlling the extraction temperature, an extraction vessel for holding the sample during extraction and a back pressure regulator for controlling the extraction pressure. Powder X-ray diffraction (XRD), which was performed using a Shimadzu XRD-6000 Spectrometer, and N_2 absorption and desorption, which was performed using Quantachrome Autosorb-1 at 77 K, were used to characterize the MCM-41 materials after calcination and after SFE. FTIR (Shimadzu DR-8001) and GC–MS (Hewlett Packard Model 6890) were used to identify the chemical structures and composition of the extracted surfactants. Using TGA (Shimadzu DTG-50), extraction efficiencies of the SFE process were determined by comparing the mass loss between the as-synthesized sample and the samples after SFE.

Table 1 shows the extraction efficiencies under different conditions. The results show that no surfactant template was extracted when pure CO_2 was used as the supercritical fluid since it does not have sufficient solvating strength at the typical working pressures to quantitatively extract surfactants that are quite polar.[7] However, by adding a small amount of methanol into the supercritical CO_2, substantial extraction of the template was achieved. In fact, the highest extraction efficiency (*i.e.* 93.2%) was achieved using a methanol flow rate of 0.2 ml min^{-1}. The addition of methanol as a modifier dramatically increases the bulk solubility of the analytes (extracted surfactants). The enhanced bulk solubility properties of the supercritical fluid cause a shift in the matrix/fluid distribution of the analyte, resulting in favorable partitioning to the supercritical fluid.[8] Using the methanol-modified supercritical CO_2 an increase in the extraction pressure increases the extraction efficiency due to the increase in the solvating power of the supercritical fluid.[9,10]

The results in Table 1 also indicate that there exists an optimum temperature for maximum extraction efficiency since the extraction efficiency achieved at 85 °C is much higher than that at 45 or 125 °C. It has also been shown that, by increasing the extraction temperatures, the energy barrier of desorption can be overcome, resulting in higher extraction efficiencies.[11,12] Hence, the extraction of the surfactant template from MCM-41 is facilitated by the higher temperature at 85 °C. However, at 125 °C, the increase in temperature results in a lower density of the supercritical fluid, thereby lowering the solvating power of the fluid and hence the extraction efficiency.

Fig. 1 shows the powder X-ray diffraction patterns of the calcined MCM-41 and the MCM-41 after SFE (with extraction efficiency of 93.2%). The results show that both the XRD patterns correspond well with those reported for pure siliceous MCM-41. The 2θ position for the MCM-41 after SFE is lower than that of the calcined MCM-41, indicating a larger unit cell size for the MCM-41 after SFE. In fact, the 2θ position for the MCM-41 after SFE is similar to the as-synthesized sample, indicating that pore contraction did not occur during the removal of the surfactant template by SFE. The narrower XRD pattern for the sample after SFE may also indicate that the sample after SFE possesses better crystallinity than the calcined

Table 1 Extraction efficiencies under various conditions for a CO_2 flow rate of 1 ml min^{-1} for 3 h[a]

Extraction temperature/°C	Extraction pressure/bar	Methanol flow rate/ ml min^{-1}	Extraction efficiency (%)
85	350	0.0	0.0
45	350	0.1	55.6
85	350	0.1	81.0
125	350	0.1	61.7
85	250	0.1	57.3
85	150	0.1	41.5
85	350	0.2	93.2

[a] Flow rate of CO_2 measured at the pump head cooled to −5 °C. Using Peng Robinson equation of state, the variation in the density of CO_2 at −5 °C between 150 and 350 bar is only 3%.

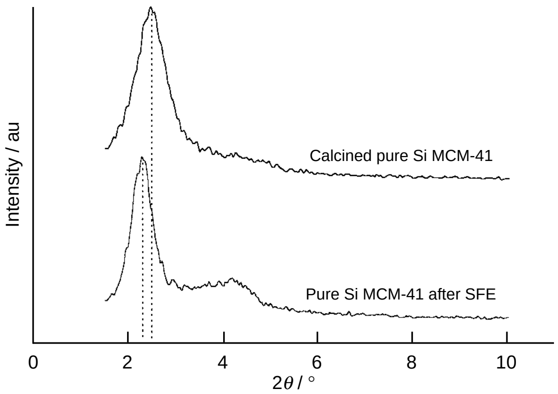

Fig. 1 X-Ray diffraction patterns of the calcined MCM-41 and MCM-41 after SFE

Table 2 Properties of as-synthesized, calcined and SFE samples

Sample	a_o/Å	Pore diameter, d_p/Å	A_{BET}/ $m^2\ g^{-1}$	Pore volume/ $cm^3\ g^{-1}$
As-synthesized	44.7	—	—	—
Calcined	41.5	26.4	1031	0.95
SFE	44.7	29.4	1007	1.08

sample. Assuming hexagonal symmetry, the unit cell sizes of the materials are calculated and tabulated in Table 2.

The N_2 isotherms (not shown) also show no hysteresis in both the calcined and SFE samples. The surface areas were calculated using BET analysis while the pore diameters were calculated from the desorption branch of the isotherms using BJH analysis. The results of these calculations are also collected in Table 2. The surface areas of both the calcined and SFE samples are comparable. In agreement with the XRD results, the pore size of the calcined sample is lower than the SFE sample, indicating again that SFE is able to remove the surfactant template without affecting the pore size and the pore structure of MCM-41. Also, the pore size distribution of the SFE sample is sharper than the calcined sample, indicating that the samples after SFE have slightly more uniform pores than the calcined samples.

GC–MS was performed to identify the constituents of the extracted surfactant and the MS results of the extracted surfactant were compared with the MS results of CTMAOH dissolved in methanol (used as a standard). Fig. 2 shows the MS results obtained and both Fig. 2(*a*) and (*b*) have peaks at the same *m*/*z* values, indicating that the extracted material is CTMAOH.

FTIR (results not shown) was also used to identify the extracted surfactant. The absorbance spectrum of the extracted organic template is similar to that of pure CTMAOH, indicating again that no changes to the structure of the CTMAOH were detected after SFE. The GC–MS and FTIR results show that as the chemical structure and composition of the extracted surfactant remain the same as those of the fresh surfactant, the extracted surfactant could be recycled and reused as a template in the synthesis of MCM-41 materials.

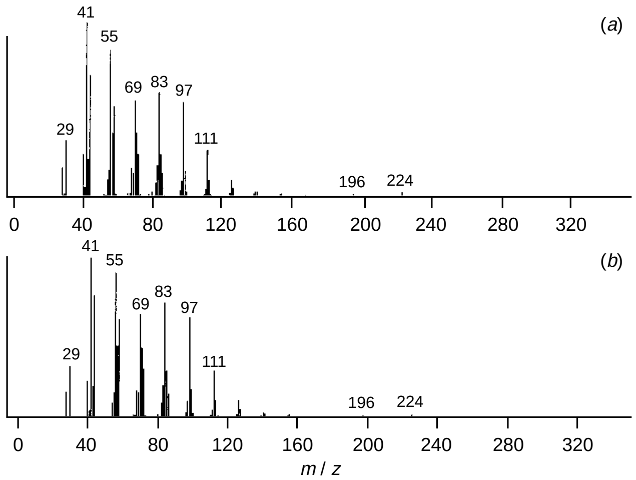

Fig. 2 The mass spectra of (*a*) a standard solution of methanol and CTMAOH and (*b*) extracted surfactant in methanol

In conclusion, supercritical fluid extraction is effective in extracting the organic template from the pores of as-synthesized MCM-41. The MCM-41 materials after SFE retained their uniform pore size distribution and high surface areas and in fact have a larger pore size than the calcined MCM-41. The structure of the surfactant extracted by SFE was also unmodified and may be reused in the future synthesis of MCM-41.

Notes and References

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