Supercritical Fluid Extraction of Surfactant from Si-MCM-41

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Supercritical fluid extraction has been carried out on as-synthesized Si-MCM-41 in a study to evaluate the efficiency of SFE in the recovery of the organic template cetyltrimethylammonium hydroxide (CTMAOH) from the pores of Si-MCM-41. Effects of different extraction parameters on the extraction efficiencies were investigated. The results show that modified CO_2 is required to extract CTMAOH. High extraction efficiencies are obtained at 85°C and at both 100 and 350 bar, while the lowest efficiency is obtained at 150 bar. The extraction efficiency also increases initially on increasing the modifier concentration and reaches a limiting value when the concentration is increased further. Among a series of modifiers studied, methanol and acidic methanol (modified with acetic acid) are effective. The modifiers used in the extraction have a significant impact on the properties of the final material. The compound extracted was characterized and identified as CTMAOH.

Introduction

Inorganic microporous material with pore sizes < 2 nm and mesoporous material with pore sizes between 2 and 10 nm allow molecules below a certain critical size into their extensive internal space. Since the catalytically active sites are within the internal space, these materials can act as shape- and size-selective catalysts (Davis, 1998). The discovery of MCM-41 having a very high surface area (> 1000 m^2/g) and uniform pore sizes (tunable from 2 nm to 10 nm) has changed the outlook of the use of mesoporous material for industrial applications (Kresge et al., 1992; Beck et al., 1992; Vartuli et al., 1994; Kawi et al., 2001; Shen and Kawi, 2001; Xia et al., 2001, 2002), and the opportunities for advancement of nanotechnology in materials design and molecular engineering in catalysis (Ying, 2000; Thomas and Raja, 2001).

The synthesis of MCM-41 is reminiscent of the synthesis of zeolites with a self-assembled surfactant molecular array forming the template. These surfactants are burned off at a later stage of preparation in order to yield the mesoporous MCM-41. However, removal of the surfactant using this method is undesirable, as the cost of the surfactant contributes to a large portion of the cost of synthesis (Whitehurst, 1992). Such combustion may also result in the emission of potentially toxic vapors. Liquid extraction is another method to recover the surfactant from the as-synthesized MCM-41, and it allows the surfactant to be recovered for reuse (Whitehurst, 1992). However, while liquid extraction overcomes some problems associated with calcination, this process also has disadvantages, such as substantial extraction times (hours to days) and large volumes of required solvents.

In two previous communications (Kawi and Lai, 1998a,b), supercritical fluid extraction (SFE) was used to recover the surfactant template from the mesopores of as-synthesized MCM-41. This article shows in more detail that not only is the SFE of surfactant from MCM-41 successful, the final mesoporous material also possesses better characteristics, that is, more uniform pore size and larger pore diameter. Moreover, SFE offers extractions in a shorter time with lower volumes of solvent required, potentially making it more economical to synthesize MCM-41 in a large quantity.

Materials and Methods

Preparation of Si-MCM-41

Two hundred g of cetyltrimethylammonium bromide (CTMABr; Merck) was dissolved in 1500 mL of water and the solution was passed through an ion-exchange column

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filled with IRA-400 resin to obtain the surfactant cetyltrimethylammonium hydroxide (CTMAOH). Five L of water were flushed through the ion-exchange column to recover CTMAOH. The resulting solution was stirred and heated to concentrate the CTMAOH solution to 20.8% by weight.

Purely siliceous MCM-41 (designated here as Si-MCM-41) was prepared according to the literature (Kresge et al., 1992), that is, 17.21 g of Aerosil and 393.56 g of CTMAOH solution were mixed together and stirred at room temperature for 6 h to form a gel having a molar composition of 1 SiO_2:0.96 CTMAOH:60.2 H_2O. The gels were loaded into polypropylene bottles and heated without stirring for crystallization at 96°C for 48 h. The resulting solid was recovered by filtration, washed with water, and dried at 50°C, forming the as-synthesized Si-MCM-41.

For characterization, some as-synthesized Si-MCM-41 was calcined to remove the organic template. Water was removed by heating the sample in air at 100°C for 1 h. The temperature was subsequently raised to 550°C at a heating rate of 1°C/min and maintained at 550°C for 20 h to completely oxidize the organic template.

Supercritical fluid extraction

As-synthesized Si-MCM-41 was used for SFE. High-purity CO_2 (SOXAL) was used as the supercritical fluid (SF). The modifiers used were HPLC-grade methanol (Merck), ethanol (Hayman), 2-propanol (Fisher), distilled water, and 0.1 M acetic acid (Baker) in methanol (Merck).

All experiments were performed using a Jasco SFE system (Figure 1), which consists of a tank of high-purity CO_2, a CO_2 pump (Jasco PU-980 pump), a modifier pump (Isco 100DM syringe pump), a chiller, a 10-mL extractor (Jasco), an oven, and a pressure restrictor [Jasco 880-81 Back Pressure Regulator (BPR)]. Approximately 0.5 g of as-synthesized Si-MCM-41 was used for each SFE experiment. By setting the chiller at -5°C, CO_2 was sufficiently chilled to a liquid form to prevent cavitation in the CO_2 pump operating at the desired flow rate (≈ 1.00 mL/min). The desired extraction temperature and pressure were set on the oven and BPR, respectively. Upon achieving the desired pressure, the modifier pump was turned on and SFE was performed at the desired conditions. The extracted compound (analyte) together with the modifier was collected in a vial at the BPR outlet. The pressure investigated spanned from 60 bar to 350 bar and the temperature from 35°C to 125°C.

Thermogravimetric analysis (TGA) was used to determine the extraction efficiency on both as-synthesized samples and the samples after SFE by comparing their weight loss. This allowed the determination of the amount of organic template remaining in the samples after SFE, and the amount of organic template removed can be expressed as a percentage of the original amount of organic template present.

Characterization of calcined and SF extracted MCM-41 and extracted compound

N_2 adsorption/desorption analyses were done on Quantachrome Autosorb-1 (AS-1) using N_2 at 77.4 K as the adsorbate. X-Ray diffraction (XRD) was performed on the as-synthesized and calcined materials and materials after SFE using a Shimadzu XRD-6000 Spectrometer with Cu Kα radi-

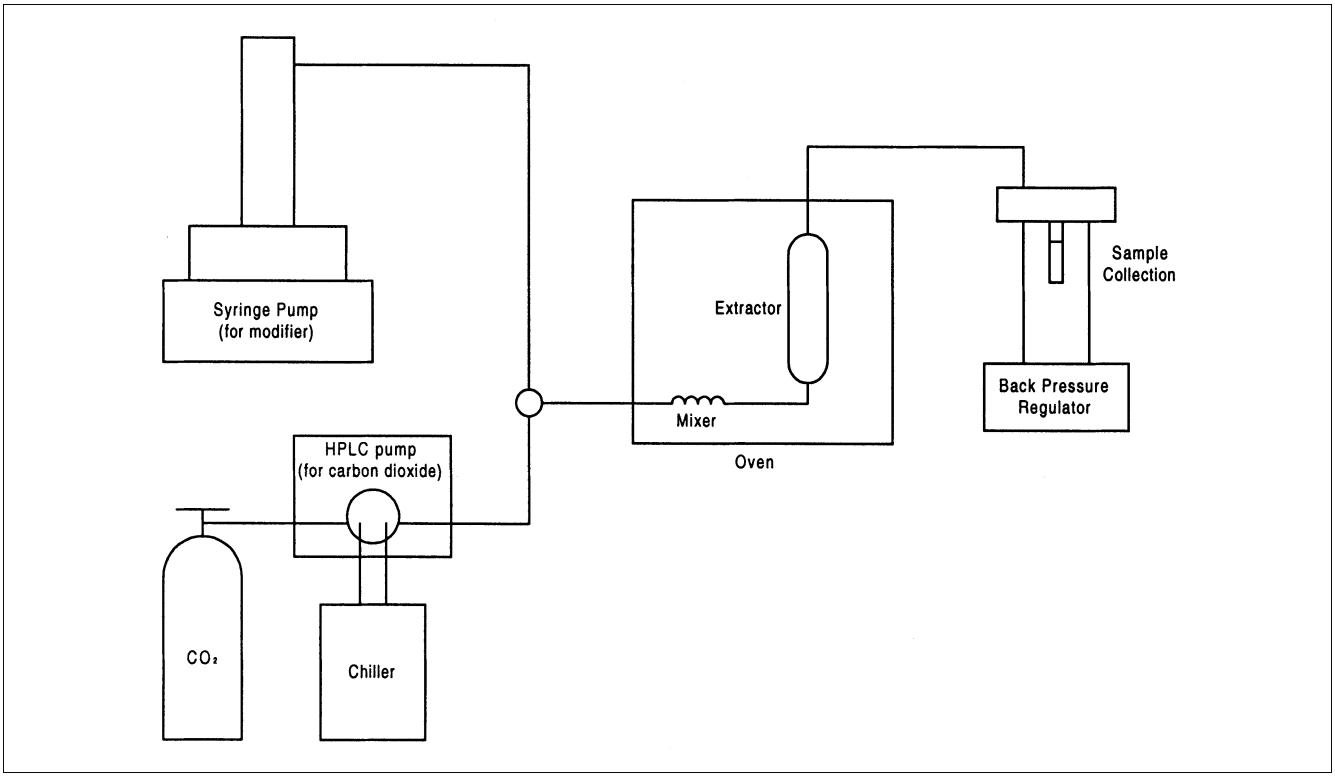

Figure 1. Experimental setup of the SFE equipment.

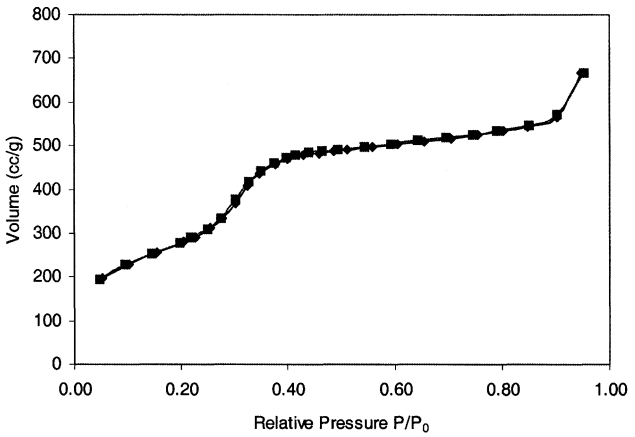

Figure 2. Adsorption / desorption isotherms for Si-MCM-41.

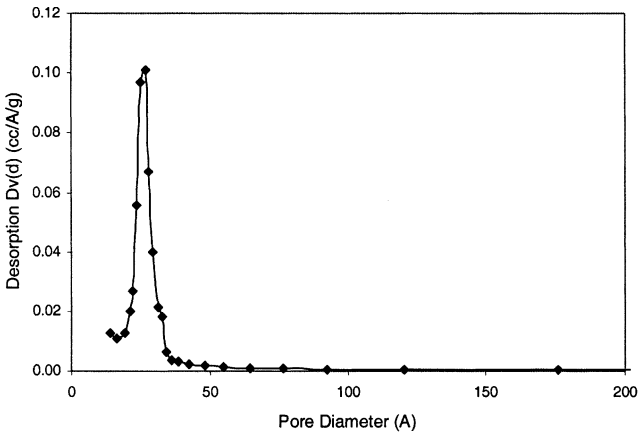

Figure 3. Pore-size distribution for Si-MCM-41.

ation. Thermal gravimetric–differential thermal analysis (TGA/DTA) was performed using a Shimadzu DTG-50 analyzer on the as-synthesized samples and the samples after SFE. The samples were heated to 700°C at a heating rate of 20°C/min and the reference material used for DTA was α-alumina.

Methanol was removed from the analyte using a vacuum pump, and the solid remaining was mixed with KBr powder and pelletized. Fourier transform infrared spectroscopy (FTIR) was performed on the pellet using a Shimadzu DR-8001 infrared spectrophotometer. A standard was prepared by grinding KBr powder with solid CTMAOH in a weight ratio of 100:1.

Results and Discussion

Characterization of calcined Si-MCM-41

The calcined Si-MCM-41 exhibits a surface area of 1,030.8 m^2/g, pore volume of 0.949 cm^3/g, and an average pore diameter of 2.64 nm. The N_2 adsorption/desorption isotherms for Si-MCM-41 (shown in Figure 2) displays a typical reversible type IV isotherm with no hysteresis, which is consistent with the literature (Schmidt et al., 1995; Branton et al., 1994). Figure 3 shows the pore-size distribution (PSD) for Si-MCM-41. The mesopore parameters and cumulative pore volume are obtained from PSD curves. The reversible type IV isotherm and the uniformity of PSD prove the structural uniformity of synthesized Si-MCM-41.

In our previous communication (Kawi and Lai, 1998a), the XRD pattern for calcined Si-MCM-41 was shown to be similar to the literature results (Beck et al., 1992; Chen et al., 1993a; Schmidt et al., 1994, 1995). The calcined Si-MCM-41 exhibits a strong peak at $2\theta = 2.46°$, corresponding to the (100) plane for a hexagonal unit cell. Using Bragg's law and assuming first-order diffraction, the hexagonal unit-cell dimension (a_0) is calculated to be 41.5 Å. The XRD pattern of as-synthesized Si-MCM-41 (not shown) has $a_0 = 44.7$ Å. This reduction in a_0 of calcined MCM-41 is consistent with the literature (Chen et al., 1993a), proving that there is pore contraction after calcination.

The weight loss for as-synthesized Si-MCM-41 is characterized by TGA/DTA (not shown). The weight loss before 150°C is mostly attributed to water physically absorbed in Si-MCM-41 pores, and that between 150 and 400°C is due to the removal of the organic template associated with Si-O in Si-MCM-41. Between 150 and 250°C, removal of the organic template takes place via base-catalyzed Hofmann elimination and subsequent trimethylamine desorption. From 250°C to 400°C, hexadecene and its decomposition products are desorbed and oxidized. The DTA of the as-synthesized Si-MCM-41 shows a broad endothermic signal for the desorption of trimethylamine followed by a very intense exothermic signal at 350°C for the oxidation of hexadecene. The gradual drop in weight after 400°C is mostly due to the condensation of silanol groups to form siloxane bonds (Chen et al., 1993a). The template content was calculated from the weight loss between 150 and 400°C. For as-synthesized Si-MCM-41, the template content was determined to be 45.7 wt. %, which is consistent with the literature (Chen et al., 1993a; Kresge et al., 1992).

Analysis of SFE results

Using only pure CO_2, no extraction of the organic template from Si-MCM-41 was observed for all pressures and temperatures investigated. Similarly, CO_2 without modifiers was also unable to extract pure CTMAOH (solid form) placed in the extractor. Hence, pure SF CO_2 appears to have insufficient solvating power to dissolve even pure CTMAOH, not to mention CTMAOH from the pores of MCM-41. This is not surprising, as the different formation mechanisms of Si-MCM-41 (Kresge et al., 1992; Monnier et al., 1993; Chen et al., 1993b) suggest that there are interactions of the cationic CTMA template with silicate anions that are preferred over small Cl^- or OH^- anions. The template remains in the void volume of the silicate framework after synthesis, with its positive charge either compensated by framework siloxy groups, or ionic–dipolar interactions with the siloxy groups. In order to remove the template, siloxy groups must either be protonated or there must be additions of other charge-compensating cations. So, there is no extraction by pure CO_2 that cannot displace the template–siloxy interaction.

Hence, modifiers are used to extract CTMAOH from MCM-41, as they may interact with the analyte/matrix com-

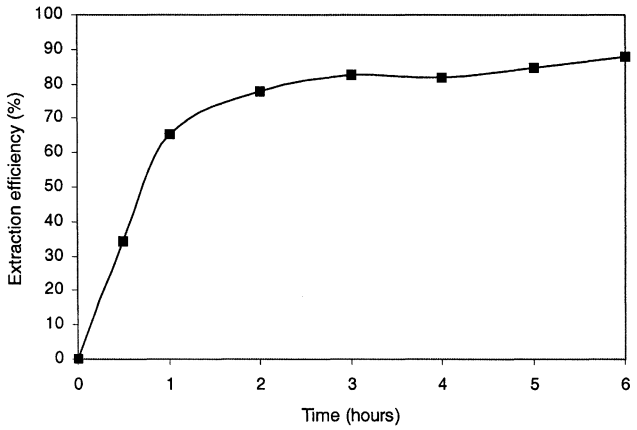

Figure 4. Extraction efficiency vs. extraction time.

CO_2 flow rate—1.0 mL/min; methanol (modifier) flow rate —0.1 mL/min; extraction pressure—350 bar; extraction temperature—85°C.

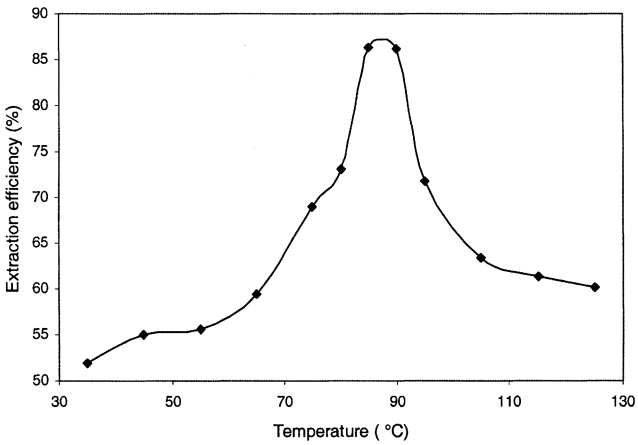

Figure 5. Extraction efficiency vs. extraction temperature.

CO_2 flow rate—1.0 mL/min; methanol (modifier) flow rate —0.1 mL/min; extraction pressure—350 bar; extraction time—3 h.

plex to promote the removal of CTMAOH from the MCM-41 surface, and increase the solvating power of CO_2 to dissolve the displaced CTMAOH and transport it out of MCM-41 pores. It should be noted here that, due to unavailable data in the literature describing the phase behavior of CO_2 in the presence of CTMAOH, all of the phase behavior for CO_2 or modified CO_2 in the presence of CTMAOH is assumed to be the same as those in the absence of CTMAOH, as the concentration of CTMAOH in our study is presumably small.

Methanol, a common SFE modifier, is used to determine the extraction time. Keeping all other parameters constant, SFE was carried out on as-synthesized MCM-41 for different times, and extraction efficiencies were calculated. Figure 4 shows the extraction efficiencies as a function of time. Obviously methanol-modified CO_2 can extract CTMAOH from MCM-41 pores, with a substantial extraction (65.2%) in just one hour of extraction. The extraction curve in the first hour is a steep straight line, corresponding to a constant extraction rate. After one hour, the extraction rate decreases and the extraction curve reaches a limiting value. These results show that methanol is able to displace $CTMA^+$ groups from siloxy groups. A substantial number of silanol groups interact with the template ions by ionic–dipolar interactions, and these template ions are believed to be those removed by methanol within the first hour of extraction. The remaining unextracted template interacts with siloxy species via charge compensation, and is harder to displace even after 3 h of extraction. Upon displacement of the $CTMA^+$ groups from MCM-41 internal surfaces, the $CTMA^+$ groups are believed to be dissolved in the SF and transported out of the mesopores and collected at the BPR outlet.

Figure 5 shows the extraction efficiencies between 35 and 125°C at maximum BPR pressure 350 bar. The optimal temperature for the extraction of CTMAOH from MCM-41 pores is 85°C, suggesting two possible driving forces at work in the SFE of CTMAOH from Si-MCM-41. Between 35 and 85°C, the increase in extraction efficiencies with temperatures is believed to be due to the increase in desorption kinetics of the $CTMA^+$ groups. There may be an energy barrier of desorption that needs to be overcome before methanol can effectively displace the $CTMA^+$ groups that are attached to the siloxy groups via ionic–dipolar interactions or charge compensation. Desorption, thus, became the rate-limiting parameter at lower temperatures. Yet, beyond 85°C, higher temperatures result in lower extraction efficiencies. The mechanism causing the lower extraction efficiencies is not really clear at this point. It is believed that at elevated temperatures where desorption of the $CTMA^+$ groups is enhanced, the SF density decreases, causing the solubility of the $CTMA^+$ groups in the SF to become the rate-limiting parameter. Another possible explanation is that higher temperatures in SFE result in higher volumetric flow rates through the extractor, thereby reducing the contact time between methanol and $CTMA^+$ groups.

Figure 6 shows the extraction efficiency vs. methanol concentration (mole fraction) from 5 to 23 mol % methanol-modified CO_2 at 85°C and 350 bar. These extraction condi-

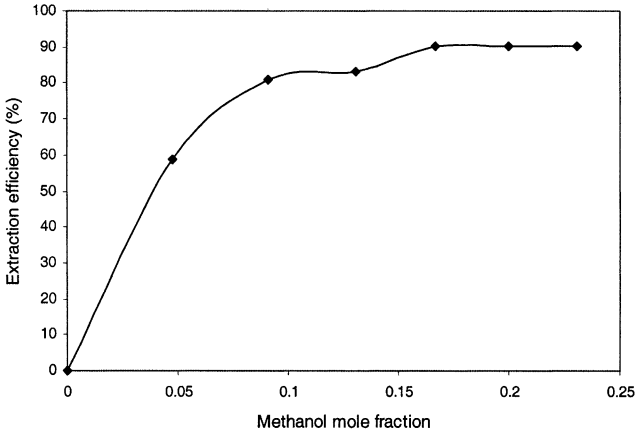

Figure 6. Extraction efficiency vs. methanol concentration.

CO_2 flow rate—1.0 mL/min; extraction temperature—85°C; extraction pressure—350 bar; extraction time—3 h.

tions are supercritical since, using the phase equilibrium of binary mixtures of CO_2 and methanol (Reighard et al., 1996), pressures > 165 bar produce one-phase mixtures over a 0–100 mol % methanol composition at temperatures up to 100°C. From Figure 6, by increasing the methanol concentration from 4.8 mol % to 16.7 mol %, the recoveries of CTMAOH increase significantly. However, increasing the methanol concentration from 16.7 mol % to 23.1 mol % does not increase extraction efficiency very much.

The functions of modifiers have been briefly discussed earlier. Several hypotheses to explain the effects of modifiers have also been proposed in various earlier literature. The addition of organic modifiers such as methanol to SF CO_2 has been shown to increase the bulk solubility and extraction efficiency of many compounds (Ashraf-Khorassani et al., 1995; Langenfeld et al., 1994; Breen et al., 1996; Lou et al., 1996; Yang et al., 1995). This enhanced bulk solubility can shift the matrix/fluid distribution of the analyte, resulting in favorable partitioning to the SF. Alternatively, the modifier could cover the active sites and prevent readsorption or partitioning of the analyte back onto the matrix active sites (Langenfeld et al., 1994). The modifier can also alter the sample matrix to allow the modified SF to access remote sites in the matrix and allow the transport of the analyte to the bulk fluid (Fahmy et al., 1993). Furthermore, modifiers can selectively interact with the analyte/matrix complex, lowering the activation energy barrier of desorption, which is significant for strongly adsorbed species (Alexandrou et al., 1992).

The increased extraction efficiencies of CTMAOH from MCM-41 with modifiers are believed to be due to a combination of two factors: interaction with $CTMA^+$ groups and an increase in bulk solubility of methanol-modified CO_2. The effects of either just high temperatures or the addition of modifiers are not sufficient for this substantial extraction. The combined effects of high temperatures and modifiers are required to overcome the energy barrier of desorption, allowing methanol to effectively displace those $CTMA^+$ groups attached to the silanol groups via ionic-dipolar forces. Upon displacement of $CTMA^+$ groups, the modifier then acts to increase the bulk solubility in modified CO_2, transporting $CTMA^+$ groups out of the sample matrix.

To study the effects of various modifiers at 350 bar, five different modifiers were used: methanol, ethanol, 2-propanol, water, and 0.1 M acetic acid in methanol. Since the modifier concentration has been used as volume percentage (Nemoto et al., 1997; Ashraf-Khorassani et al., 1995; Oostdyk et al., 1993; Langenfeld et al., 1994; Fernandez et al., 1996), the modifier concentration used in this study is calculated to be 9.09% (v/v). The extraction efficiencies that were obtained are tabulated in Table 1.

The results for the methanol-modified extraction were discussed earlier. Using 0.1 M acetic acid in methanol as the modifier, the extraction efficiencies obtained have similar trends to that obtained using methanol alone as the modifier, since the concentration of acetic acid is quite low. However, the presence of acetic acid in the extraction fluid causes significant modifications to the material after extraction. This will be discussed later.

The effectiveness of these modifiers could be correlated with the polarity of the modifiers. Of all the modifiers investigated, water has the highest polarity, followed by methanol, ethanol, and 2-propanol. This follows closely with the extraction efficiencies that were obtained. The polarity of a modifier is believed to be important in its effectiveness, since the main function of the modifier in this system is to compensate the charge on $CTMA^+$ groups, thereby allowing $CTMA^+$ groups to be desorbed from the sample matrix. Although there seems to be a correlation of the polarity of the modifiers with the extraction efficiency, this explanation is rather preliminary and subsequent work is needed to confirm this correlation.

Table 1. Extraction Efficiency vs. Modifier Identity for Si-MCM-41

Sample Matrix	Pres. (bar)	Extraction Efficiency* (%)				
		MeOH**	EtOH†	iPOH††	Water	HOAc/MeOH‡
Si-MCM-41	350	86.3	40.6	25.7	93.6	82.8

*Extraction at 85°C at CO_2 flow rate – 0.1 mL/min, modifier flow rate – 0.1 mL/min, extraction time – 3 h.
**Methanol.
†Ethanol.
††Isopropanol or 2-propanol.
‡0.1 M Acetic acid in methanol.

The high extraction efficiency obtained using water as the modifier would be extremely useful in recycling CTMAOH. Using an organic solvent as the modifier involves the additional step of removing the solvent and recovering CTMAOH after extraction. However, using water as the modifier, CTMAOH would be obtained in an aqueous solution after extraction and all that is required is to concentrate the solution to the desired concentration (~ 20 wt. %). However, water is only slightly soluble in CO_2 (< 0.3% v/v), and any attempts to create higher water concentrations in SF CO_2 produce two phases (Taylor, 1996). CO_2/water exhibits Type IV phase behavior, and, hence, at 85°C and 350 bar, the extracting fluid exists as two phases, liquid water and SF CO_2 (Takishima et al., 1986).

Characterization of Si-MCM-41 after SFE

Figure 7 shows the PSDs of the various samples of MCM-41 after SFE but before calcination. The extraction efficiencies of the samples are tabulated with the measured surface areas, pore volumes, and pore diameters in Table 2. After extraction but before calcination, MCM-41 extracted using CO_2 modified with 0.1 M acetic acid in methanol shows the sharpest PSD with the largest uniform pore diameter obtained (3.0 nm). This indicates that the material after extraction with this modified fluid exhibits highly uniform pores, and compared with the calcined MCM-41, the calcined sample exhibits a broader PSD and a smaller pore size (2.64 nm). The smaller pore size indicates that pore contraction may have occurred during the calcination of the sample. Hence, using SFE to remove the organic template produces a more structured material compared to that prepared using calcination. Apart from the pore size, the surface area and pore volume of the extracted sample using acetic-acid-modified methanol are also larger than the calcined sample. This is so because SFE may be able to remove the blockages in MCM-41 channels that even calcination was unable to remove. Besides

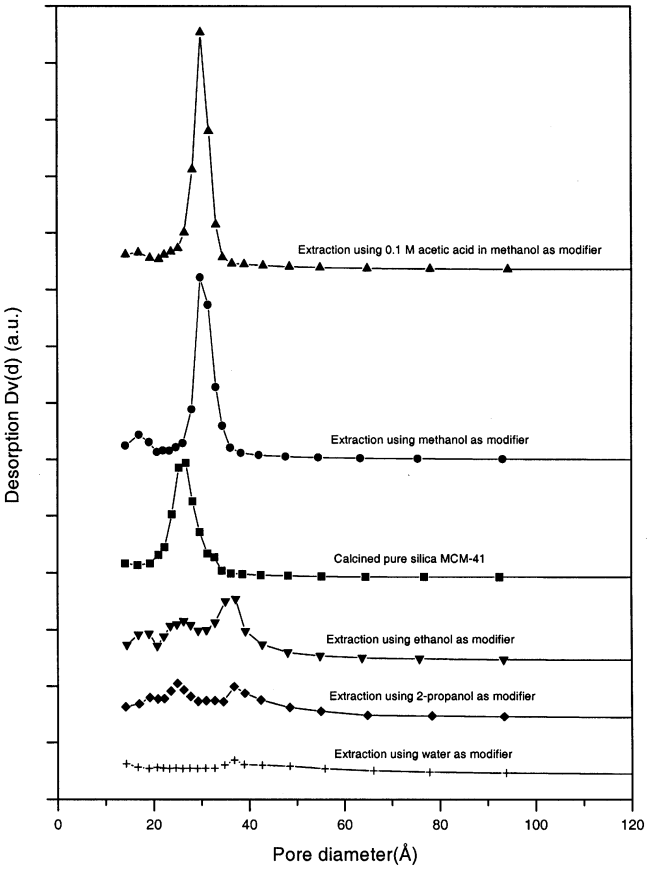

Figure 7. Pore-size distributions of the calcined and extracted Si-MCM-41.

this, the surface area and cumulative pore volume of this sample after extraction are also the highest compared with other samples extracted using CO_2 modified with other solvents, showing that 0.1 M acetic acid in methanol is a good modifier for extracting CTMAOH from MCM-41 pores.

Furthermore, methanol is also a suitable SFE modifier, since the sample extracted using methanol-modified CO_2 has a narrower PSD, larger pore size, and a larger pore volume than the calcined samples. For extraction using both ethanol and 2-propanol-modified CO_2, no discernible pore sizes are observed from PSD. The reason lies with the low extraction efficiencies obtained using these two modifiers, indicating that the organic template was not completely extracted from the MCM-41 pores. The presence of this unextracted organic template interfered with the determination of the surface areas, pore volumes, and pore sizes during N_2 adsorption analysis, resulting in no significant pore size after extraction. However, upon calcination, determination of these properties becomes possible.

Using water-modified CO_2 yields high extraction efficiency. However, from the PSD shown in Figure 7, the structure of the sample seems to have completely collapsed. A possible explanation lies with the poor hydrothermal stability of Si-MCM-41 (Chen et al., 1993a; Shen and Kawi, 1999; Kawi and Shen 2000a,b,c). Under the extraction conditions, silicate hydrolysis may have occurred, resulting in structural degradation of MCM-41. Hence, although water as the modifier yields high extraction efficiencies and is cheap, the modification to the material renders it unsuitable as a modifier.

To remove any residual template and to ensure that the material after extraction possesses good structural stability under thermal treatment, the same samples, including the directly calcined sample, were calcined again at 550°C in flowing air for 10 h. The results of N_2 adsorption analysis are shown in Table 2, with the PSD of the samples shown in Figure 8. The PSDs for the directly calcined Si-MCM-41 after one and two cycles of calcination are also included for comparison.

Using Figure 8 and Table 2, the calcined sample that was previously extracted using CO_2 modified with 0.1 M acetic acid in methanol shows a slight increase in the surface area and pore volume after calcination, due to the removal of any residual template in the material after SFE. Other effects of calcination include a slight broadening of the PSD and a slight

Table 2. Nitrogen Adsorption/Desorption Results of Various Si-MCM-41 Materials

Sample*	Extr. Eff. (%)	Specific Surface Area (m^2/g)	Cumulative Pore Vol. (cm^3/g)	Pore Size (nm)
Calcined	—	1,031	0.949	26.4
After recalcination	—	897	0.725	23.6
Methanol	86.3	1,007	1.080	29.5
After calcination	—	1,135	1.106	30.0
HOAc/Methanol**	82.8	1,132	1.212	30.0
After calcination	—	1,267	1.212	28.2
Ethanol	40.6	695	0.744	None†
After calcination	—	1,071	0.884	24.5
2-Propanol	25.7	493	0.505	None†
After calcination	—	1,197	0.976	25.0
Water	93.6	431	0.623	None†
After calcination	—	509	0.613	None†

*All samples used are Si-MCM-41. Solvent name represents the modifier used in the extraction.
**0.1 M acetic acid in methanol.
†No uniform pore sizes detected.

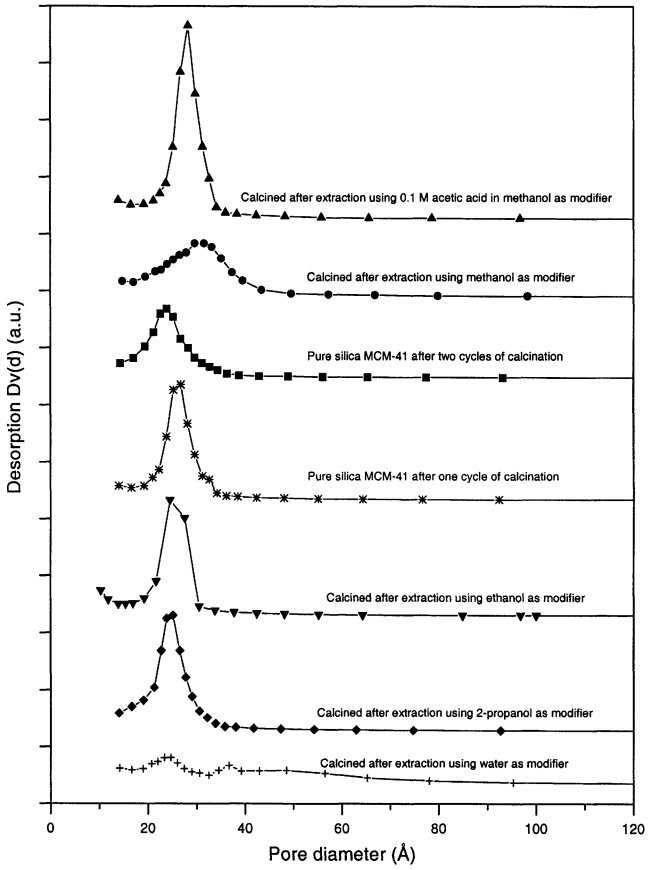

Figure 8. Pore-size distributions of extracted Si-MCM-41 upon calcination vs. calcined Si-MCM-41 after one and two cycles of calcination.

decrease in the pore diameter (0.18 nm) from that before calcination (3.00 to 2.82 nm). However, even with the slight decrease in pore diameter, the overall properties of this sample after calcination are still better than the directly calcined sample where its PSD deteriorated with repeated calcination (Figure 8). From Table 2, the surface area and pore volume of the directly calcined sample are also reduced after calcination, whereas the values for this sample remain unchanged after extraction and calcination.

Even though the use of methanol-modified CO_2 results in Si-MCM-41 with uniform and narrow PSD, subsequent calcination causes deterioration in its structure, as the sample extracted by methanol-modified CO_2 shows an extremely broad PSD. Even though the sample has a high surface area, high pore volume, and a pore size that remains almost unchanged with calcination (2.95 to 3.00 nm), the broad PSD indicates that this sample does not have a uniform PSD after calcination. Hence, the much better stability of the sample extracted using acidic methanol (0.1 M acetic acid) as the modifier indicates that the acid has a significant impact on the stability of the final material.

Looking at the PSD of samples calcined after extraction with ethanol or 2-propanol-modified CO_2, the stability of these materials is not apparent. Although high surface areas and pore volumes are obtained after calcination, these values are only comparable to the directly calcined (one-cycle) sample. Comparison of these values should be made with the directly calcined sample after one cycle of calcination, since these extracted samples are only subjected to one cycle of calcination. The lower pore diameters, and broader and lower PSDs of these extracted samples also indicate that these samples may not be different from the directly calcined sample. Since the extraction efficiencies obtained for these samples before calcination are low, the removal of the organic template is more by calcination than by extraction. Thus, for these samples, the ion-exchange mechanism for the removal of the template during the extraction is not significant, and these extracted samples, upon calcination, have properties similar to the directly calcined sample. For the sample extracted using water-modified CO_2, uniform pores are not observed, indicating that the pore structure has collapsed.

In a previous article (Kawi and Lai, 1998a), Si-MCM-41 after SFE has $d_{100} = 3.87$ nm and $a_0 = 4.47$ nm, which are similar to those results obtained for as-synthesized Si-MCM-41. Hence, the material after SFE has a larger unit cell size, indicating larger pore diameters. Table 2 shows that the sample after SFE with methanol-modified CO_2 does possess a larger pore diameter (2.95 nm) than the calcined sample (2.64 nm). Hence, for Si-MCM-41, the SFE process retains the pore diameter of the material that otherwise would be reduced by calcination. In other words, SFE is able to remove the organic template from Si-MCM-41 pores without significant pore contraction. Furthermore, the XRD pattern for the sample after SFE has a narrower peak, indicating that it may possess better crystallinity than the calcined Si-MCM-41. Hence, the XRD results show that SFE does not modify the structure of MCM-41 and that the material still possesses its uniform mesopores after SFE. In fact, the crystallinity of the material after SFE is even better than the calcined one. XRD and N_2 adsorption results sufficiently prove that the material after SFE is still MCM-41.

Figure 9 shows FTIR spectra characterizing the organic template extracted from Si-MCM-41 and the reference CTMAOH. The excellent agreement between these two spectra (in 400–4,000 cm^{-1}) confirms their structural consistency. The FTIR result also confirms the GC-MS result (Kawi and Lai, 1998a), which shows similar mass spectra for the reference CTMAOH solution and the compound extracted from SFE. The close similarity between the two FTIR and GC-MS spectra indicates that CTMAOH extracted from Si-MCM-41 by SFE has no changes in its chemical structure and can be reused for future synthesis of MCM-41, hence, minimizing its production cost.

Conclusions

SFE is effective in extracting the organic template from the pores of as-synthesized MCM-41 using methanol or acidic methanol-modified supercritical CO_2 at 85°C and 350 bar. Depending on extraction conditions, MCM-41 materials after SFE can retain their uniform pore-size distribution and high surface areas and have a larger pore size than the calcined MCM-41. The extracted template is also unmodified and may be reused in future synthesis. SFE also allows much faster extraction as compared to conventional liquid extraction. However, the SFE conditions used so far may not be opti-

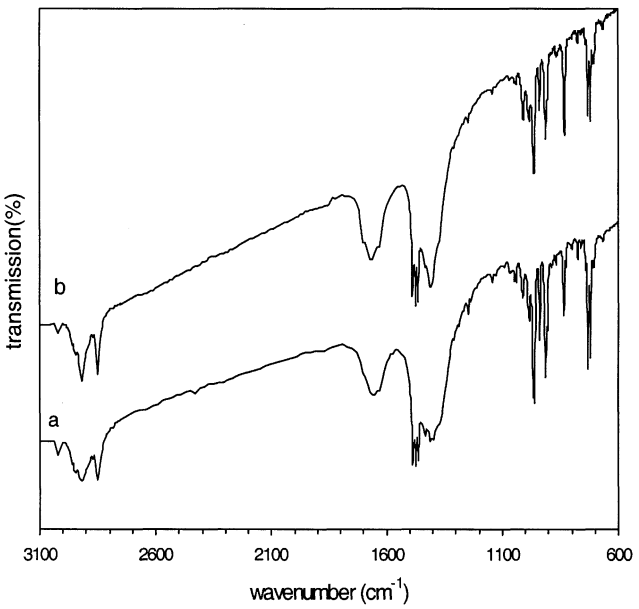

Figure 9. FTIR results of (a) KBr mixed solid sample of extracted CTMAOH, (b) KBr mixed solid sample of reference CTMAOH.

mum, and more work will be required to further optimize the SFE conditions and to explain the results observed so far.

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