

Influence of the extraction methods to remove organic templates from Al-MCM-41 molecular sieves

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Received 15 November 2003; accepted 28 February 2005

Abstract

The influence of template extraction methods on the structure and physico-chemical properties of Al-MCM-41 molecular sieves has been investigated. Up to 78% of template in Al-MCM-41 could be removed either by extraction with ordinary solvents or methanol-modified supercritical CO₂. Complete template removal was achieved by calcination. Both, solvent and supercritical fluid extraction media influenced the structure, texture and acid properties of the resulting Al-MCM-41 materials and, consequently, their catalytic activity for the Friedel–Crafts acylation of 2-methoxynaphthalene.

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Keywords: Al-MCM-41; Template; Extraction; Supercritical fluid extraction

1. Introduction

In the last decade, mesoporous molecular sieves have attracted much attention as catalytic materials because they offer not only tuneable acid strength and well-defined pore diameters but also more accessible active sites than microporous zeolites. For instance, MCM-41 molecular sieves containing aluminium in their framework provide acid sites that allow bulky fine chemicals processing [1–3].

Current syntheses of MCM-41 involve the use of organic templates which constitute nearly 50 mass% of the as-synthesised material. These templates are conventionally removed by calcination but the mesopore structure could collapse under the long duration, high temperature conditions.

In order to avoid the adverse effects associated to template removal, liquid solvent extraction have been successfully used to remove part of the template from the silicate framework before the calcination step. Such processes are nevertheless limited by consumption of large amounts of organic solvents and energy requirements [4].

An alternative method of removing and recovering the templates from as-synthesised materials using supercritical

fluid extraction (SCFE) has been also described for pure siliceous MCM-41 [5,6]. Supercritical fluids (SCF) are an acceptable alternative to ordinary liquid solvents for the rapid extraction due to their physical–chemical properties, such as low viscosity, high diffusivity and density. Thus, the diffusion coefficients of solutes in SCFs are higher than those in ordinary liquids and mass transfer is usually more favourable. Supercritical CO₂ is commonly the preferred fluid on account of its critical properties ($T_C = 31.1\text{ }^\circ\text{C}$, $P_C = 72\text{ bar}$), suitable for most extraction applications, low toxicity and cost. The addition of small amounts of methanol into supercritical CO₂ improves the bulk solubility properties of pure CO₂ due to polarity effects. As a consequence, a more favourable partitioning to the supercritical fluid should allow the removal of organic templates at much lower temperatures, avoiding the collapse of the mesopore structure.

The effects of solvent and supercritical fluid extraction methods were investigated in the present study with respect to the structural and physical–chemical properties of the Al-MCM-41 mesoporous materials. Their catalytic activity was further compared for the Friedel–Crafts acylation of 2-methoxynaphthalene.

The acylation of aromatic compounds is an important step in synthesis of various pharmaceuticals and the acylation of

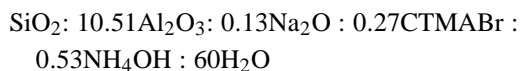
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2-methoxynaphthalene is of particular interest because of the commercial production of anti-inflammatory drugs [7].

2. Experimental

2.1. Preparation of the parent material

Al-MCM-41 with a Si/Al ratio of 30 was prepared according to standard procedures [8]. The synthesis gel of molar composition:



was prepared using reactions mixtures composed of sodium silicate (63% SiO₂, 18% NaOH, Riedel-Haen); aluminium sulphate and silica (Aerosil 200); cetyltrimethylbromide (CTMABr); 30% aqueous ammonia; ethanol and deionized water. The obtained solids were thoroughly washed with distilled water and dried in air at 90 °C. This sample is identified as PM.

2.2. Template removal

The template was removed from the parent Al-MCM-41 sample according to the following methods:

- Calcination (CAL): 3 g of the dry sample was heated for 1 h, under a N₂ flow of 100 cm³ min⁻¹ and heating rate (β) of 1 °C min⁻¹, followed by calcination under a dry air flow of 100 cm³ min⁻¹, at 550 °C, for 12 h.
- Solvent extraction (SE1): 3 g of the dry sample was used for soxhlet extraction in a 0.15 M HCl/1:1 ethanol:heptane solution, for 40 h, followed by filtration, washings with deionized water and room temperature drying.
- Solvent extraction (SE2): 3 g of the dry sample was stirred in a 0.05 M H₂SO₄/ethanol solution, for 1 h, at 78 °C, followed by filtration and washing. This procedure was further repeated twice [4].
- Supercritical fluid extraction (SCFE): the experiments were carried out at 100 bar, 85 °C, for 15 min, using an Autoclave Engineers #08U, 0650FS batch system. Supercritical CO₂ modified with 20% MeOH was used for extraction. This procedure was further repeated three times.

Samples named as SE1, SE2 and SCFE were further heated in a dry N₂ flow of 100 cm³ min⁻¹ and heating rate (β) of 1 °C min⁻¹, at 550 °C for 1 h, followed by calcination in air for 6 h, in order to remove residual template. In order to assure the complete exchange of Na ions and to obtain the acidic H-Al-MCM-1 form (CAL-H; SE1-H; SE2-H and SCFE-H), the calcined samples were treated prior to acid sites characterisation and catalytic testing [1]. Thus, the calcined samples were ion exchanged in a 1 M NH₄NO₃ aqueous solution, at 60 °C, for 12 h. After washing with deionized water, the air-dried NH₄-Al-MCM-41 samples were calcined at 550 °C for 4 h.

2.3. Characterisation

Bulk chemical compositions were determined using atomic absorption spectrometry. Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu XRX-6000 diffractometer, using Ni-filtered Cu K α radiation. Surface areas and isotherms were obtained using an ASAP 2010 apparatus.

Adsorbed pyridine FT-IR spectra were collected on a Bomem MB100 spectrometer, using self-supported wafers of 10 mg treated in a vacuum cell at 400 °C and 10⁻³ Torr, for 2 h. Prior to pyridine adsorption, reference spectra were collected at 150 °C. Pyridine was then admitted and, after saturation, the cell was evacuated and the spectra collected at 150 °C [9]. Quantitative acidity analyses were carried out by temperature-programmed desorption of *n*-butylamine.

Extraction efficiencies (*E*, %) were determined using differential thermogravimetric analyses (Shimadzu H-50), by comparing the weight losses [5] from the parent Al-MCM-41 (PM) and samples CAL, SE1, SE2 and SCFE, according to:

$$E(\%) = \frac{ML_S}{ML_P} \times 100, \quad (1)$$

where ML_S and ML_P are, respectively, the weight losses of the sample and of the parent Al-MCM-41, after heating up to 700 °C, at heating rate (β) of 10 °C min⁻¹, under a 50 cm³ min⁻¹ N₂ flow.

2.4. Reaction

The acylation of 2-methoxynaphthalene experiments were carried out at 132 °C, in a stirred batch reactor equipped with a reflux condenser, using 0.5 mmol 2-methoxynaphthalene; 5 mmol acetic anhydride; 10 cm³ chlorobenzene and 50 mg of calcined Al-MCM-41 [4,7]. The reaction products were analysed by GC-MS (QP5050 Shimadzu) and a DB-5 column. The identification of reaction products was further carried out using ¹H NMR (Varian GEMINI 300) and 1-acyl-2-methoxynaphthalene was characterised on the basis of radio-frequency absorption at δ 2.66.

3. Results and discussion

3.1. Template removal

A typical DTG profile for template removal from the parent material is shown in Fig. 1d. Two main weight losses are considered [4,9,10]. A first loss, between 25 and 130 °C, is assigned to adsorbed water and solvent molecules. The template loss starts at nearly 150 °C and occurs in several steps, which may be related to different interactions between the organic template with the siloxy groups (130–300 °C) or Al species (300–600 °C).

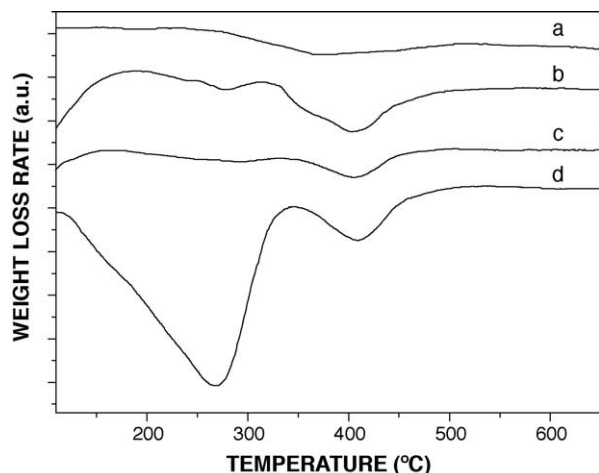


Fig. 1. DTG plots: (a) SE2, (b) SE1, (c) SCFE and (d) PM.

Fig. 1a–c shows the DTG profiles for samples SE2, SE1 and SFSE. The interactions of the organic template with the Al species are considered to be stronger than with the siloxy groups [4,9–11]. This thus suggests that the template associated to siloxy groups may be mostly removed either by solvent or SCF extraction. In addition, the amount of template associated to framework Al species may be related to the framework Al content and acid strength.

After three successive supercritical fluid extractions (SCFE) for template removal from the parent Al-MCM-41 material, DTG plots were obtained as shown in Fig. 2. It may be assessed that up to 78% of HTMA⁺, corresponding to 92% of the template associated to siloxy groups could be removed during the supercritical fluid extraction procedure. After the third extraction step, the area under peak II remained constant, suggesting that, even in a supercritical fluid extraction media, the template molecules strongly associated to framework Al species could not be removed. Similar behaviour was found for sample SE1 (Fig. 1b) but

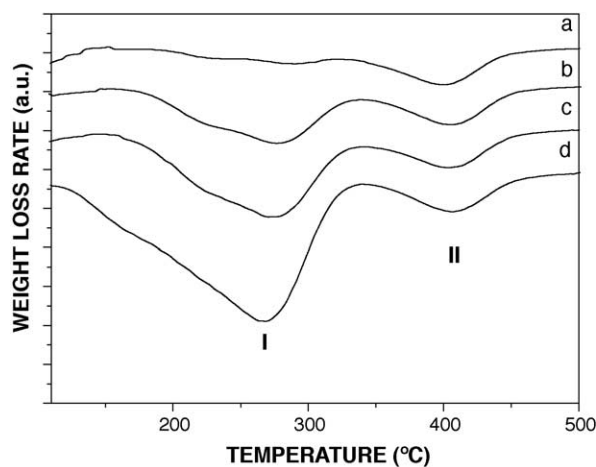


Fig. 2. DTG plots for Al-MCM-41 materials after supercritical fluid extractions for template removal: (a) third extraction step, (b) second extraction step, (c) first extraction step and (d) parent material (PM).

Table 1
Efficiency of template removal

Sample	Efficiency (%)
SE1	74
SE2	86
1st step	38
SCFE	
2nd step	56
3rd step	78
CAL	100

for sample SE2 (Fig. 1a) treated with H₂SO₄, the removal of these species was apparently accompanied by dealumination. Conversely, supercritical fluid extraction from pure siliceous MCM-41 material may attain 100% efficiency in a single extraction step [12]. The efficiency values for template removal from the parent Al-MCM-41 material (PM), according to the investigated procedures are collected in Table 1.

3.2. Structural and textural characterisation

The main textural properties of the parent and post extraction Al-MCM-41 materials are collected in Table 2.

Powder X-ray diffraction patterns of the acid form of the parent (PM), and calcined materials (CAL, SE1, SE2 and SCFE) are shown in Fig. 3. The parent material exhibited

Table 2
Structural and textural properties of the materials after template extraction and/or calcinations

Sample	a_0 (Å)	d_{100} (Å)	A_{BET} (m ² /g)	V_p (cm ³ /g)	D_{PM} (Å)
PM	55.3	47.9	–	–	–
CAL-H	44.0	38.1	782	0.89	37.9
SE1-H	46.1	39.9	834	0.99	38.8
SE2-H	45.5	39.4	764	0.86	37.2
SCFE-H	51.8	44.9	688	0.79	39.9

a_0 : hexagonal unit cell parameter, d_{100} : interplanar distance, A_{BET} : surface area, V_p : pore volume and D_{PM} : average pore diameter.

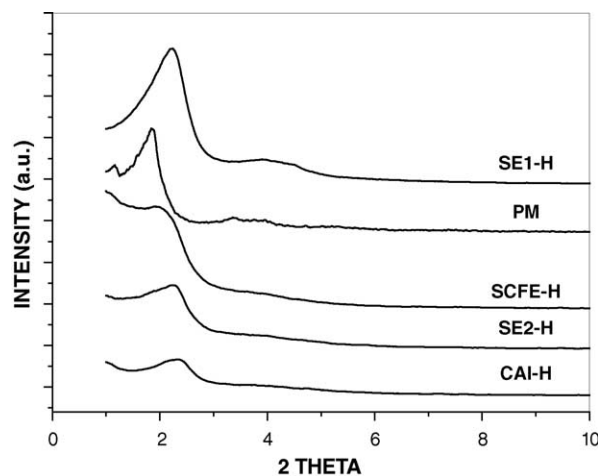


Fig. 3. Powder X-ray diffraction patterns of acid and parent Al-MCM-41 materials.

three diffraction peaks in the low angle range between 2° and $10^\circ 2\theta$, corresponding to reflections at [100], [110] and [200], respectively, at 47.0, 26.3 and 22.7 Å. These reflections are indexed on a hexagonal lattice and the presence of higher order reflections such as (110), (200) and (210) indicates a highly ordered material [4,9–11]. In spite of this, previous papers [10,12] reported that poorly ordered Al-MCM-41 materials should be expected from preparation methods using aluminium sulphate as reagent.

The calcined materials showed lattice contraction caused by the removal of template and condensation of siloxy groups [9,12]. The diffraction peaks corresponding to reflections at [110] and [200] were no longer found for the directly calcined (CAL) material or for that after extraction in H_2SO_4 media (SE2). In addition, the broader and less intense main peak indicates distortion of the long range mesopore structure and poorer hexagonal arrays of the calcined materials (CAL, SE2 and SCFE) with respect to the parent Al-MCM-41.

The pore size distribution and pore volumes were determined using the BJH method [13] and the nitrogen adsorption isotherms are shown in Fig. 4 for the calcined materials. According to the isotherm classification by IUPAC, they correspond to typical hysteresis-free, type IV isotherm. The sharp inflection is assigned to capillary condensation within uniform mesopores and its P/P_0 position is related to the diameter of the mesopores. On the other hand, the sharpness of this inflection is related to the uniformity of pore size in the material [4,9–11].

Corroborating with the findings from X-ray diffraction analyses, the SCFE material showed a smooth inflection while the HCl/ethanol/heptane-treated material (SE1) showed the sharper inflection. These results suggest that highly uniform pores and ordered lattice were conserved for sample SE1, even after extraction and calcination.

The pore size distributions of the calcined materials are shown in Fig. 5. A broader pore size distribution was determined for the sample after three supercritical

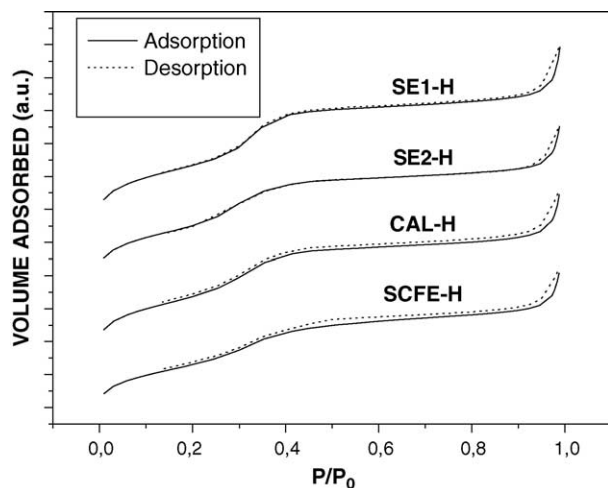


Fig. 4. Adsorption-desorption isotherms of nitrogen.

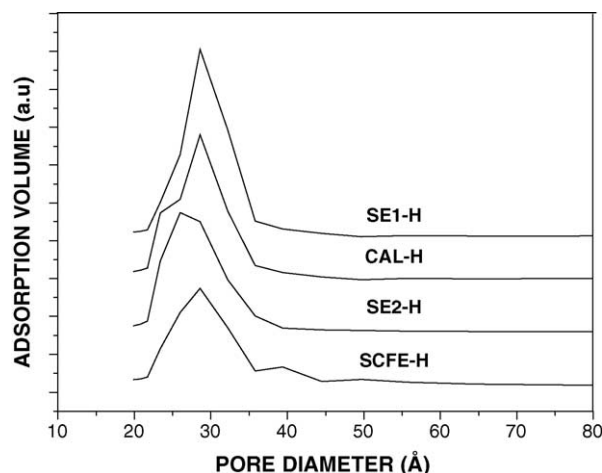


Fig. 5. Pore size distributions.

fluid extractions (SCFE). The average pore diameter of 25–35 Å was found for the samples but the SCFE material showed another peak, centered in 40 Å. These figures also suggest that the porous structure of Al-MCM-41 might be increasingly damaged after successive extraction steps in methanol-modified supercritical CO_2 [12].

An additional inflection at $P/P_0 \approx 0.9$ in the adsorption-desorption isotherms of the calcined materials was assigned to nitrogen condensation in macropores or between small MCM-41 particles [4,13].

3.3. Acidity and catalytic testing

Four main bands were found in the region of 1580–1400 cm^{-1} of the spectra shown in Fig. 6. A band at 1550 cm^{-1} was assigned to adsorbed pyridinium ion, which is related to Brønsted acid sites. The bands at 1460 and 1445 cm^{-1} were, respectively, assigned to chemisorbed pyridine on strong and weak Lewis acid sites while the band at 1490 cm^{-1} was assigned to the overlapping of bands of adsorbed pyridine on both Lewis and Brønsted sites [9].

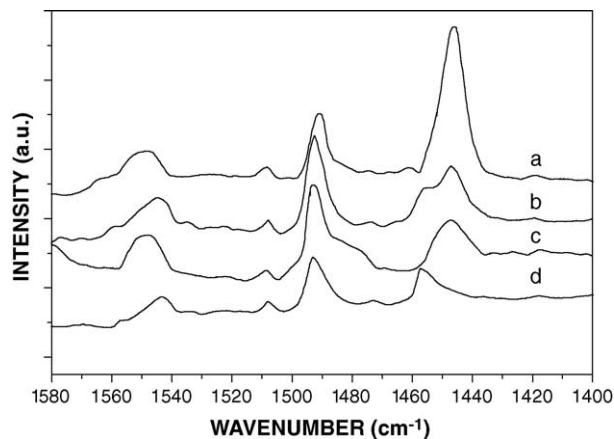
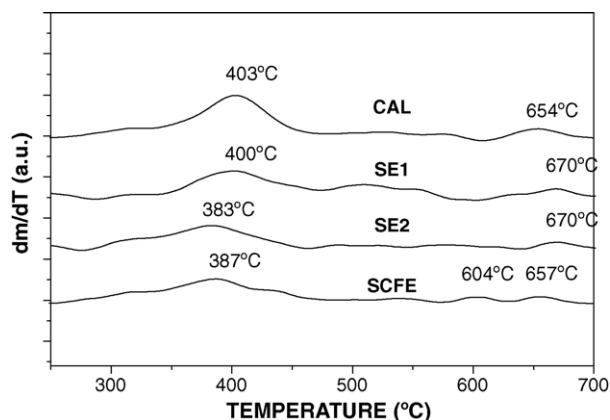


Fig. 6. FT-IR spectra of adsorbed pyridine: (a) SE2-H, (b) SCFE-H, (c) CAL-H and (d) SE1-H.

Fig. 7. TPD of *n*-butylamine.

At least three bands were found for each of the investigated materials. An intense band at 1445 cm^{-1} , indicating the adsorption of pyridine on weak Lewis acid sites suggested that a dealumination process occurred during the template extraction from the Al-MCM-41 material treated in sulphuric acid, SE2-H. These assumptions were also in accordance with those results previously found using X-ray diffractometry.

In opposition, the band assigned to pyridine adsorbed on weak Lewis acid sites was not found in the spectra obtained for sample SE1-H, which had been treated with HCl/heptane azeotropic mixture.

The four bands were clearly defined in the spectra collected for sample SCFEH but the band assigned to Brönsted acid sites was better resolved in the spectra for sample CALH.

The quantitative analyses of the acid sites have been derived from the *n*-butylamine–TPD profiles shown in Fig. 7 and are collected in Table 3, where the results of catalytic testing are also presented.

The combined analyses of the nature and the number of surface acid sites, as characterised by FT-IR and by the amount of *n*-butylamine desorbed from the Al-MCM-41 materials, confirmed previous results. As expected, the extraction in HCl/ethanol/heptane solution produced an Al-MCM-41 material with more Brönsted acid sites (SE1) due to cation exchange of sodium ions in the acidic media. On the other hand, extraction in H_2SO_4 /ethanol solution produced a material with more Lewis acid sites, probably due to dealumination. Mild Brönsted acids have been reported as more favourable catalysts than Lewis acids for the Friedel–Crafts

acylation of 2-methoxynaphthalene [7]. These features are also in accordance with the results of catalytic testing.

The conversion of 2-methoxynaphthalene increased with the total amount of acid sites on the catalysts but no straight correlation could be drawn for the turnover numbers. The material treated in the supercritical fluid (SCF) showed only a moderate conversion of 2-methoxynaphthalene and, instead, the turnover number over it was higher than for the calcined and solvent-treated materials. These findings have been then interpreted as a consequence of the textural properties of the materials treated according to different template removal procedures.

The reaction selectivity toward the kinetic isomer, 1-acyl-2-methoxynaphthalene, attained 100% over the Al-MCM-41 catalysts and the conversion values nearly corresponded to those previously reported [4,7] for the Friedel–Crafts acylation of 2-methoxynaphthalene under similar experimental conditions.

4. Conclusion

The extraction in acidic solution provides a simultaneous template removal and cation exchange procedure. However, Lewis instead of Brönsted acid sites may be produced, due to dealumination of the parent material, during the long contact with the extraction media.

Alternative template extraction in methanol-modified supercritical CO_2 may be achieved in much less time but the fine tuning of experimental conditions is a major requirement in order to avoid significant damage of the porous system of the Al-MCM-41 molecular sieve.

In both cases, the complete removal of template may be successfully attained after an additional calcination step.

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Table 3
Acidic and catalytic properties

Sample	Acid sites ($\mu\text{mol/g}$)	Selectivity (%)			X (%)	TON
		1-Ac- 2MN	6-Ac- 2MN	8-Ac- 2MN		
CAL-H	310	100	0	0	11.0	3.5
SE1-H	250	100	0	0	7.1	2.8
SCFE-H	230	100	0	0	5.2	4.0
SE2-H	130	100	0	0	3.6	1.5

X: conversion and TON: turnover number.