Chem. Mater. **2004,** *16,* 1961−1966

A Fast and Efficient Ion-Exchange Procedure To Remove Surfactant Molecules from MCM-41 Materials

Natacha Lang and Alain Tuel*

Institut de Recherches sur la Catalyse, CNRS, 2, avenue Albert Einstein,
69626 Villeurbanne Cedex, France

Received October 28, 2003. Revised Manuscript Received January 20, 2004

A pure silica MCM-41 and two aluminosilicates with Si/Al = 1.25 and 30 have been synthesized hydrothermally under basic conditions in the presence of cationic surfactants. Organic molecules could be completely extracted from the mesopores by treating as-made compounds with an ethanolic solution of ammonium nitrate at 333 K. The procedure is particularly efficient for the low-silica compound: all surfactant molecules are removed within less than 15 min. After treatment, NH_4^+ cations, which balance the charge of aluminum atoms in aluminosilicates, can be removed by heating extracted Al-MCM-41 at moderate temperature. In the pure-silica material, the in-situ decomposition of NH_4^+ cations directly forms silanol groups on the surface of the mesopores. Extracted materials possess highly ordered structures with properties similar to those of directly calcined materials. The procedure reported here is fast, cheap, and efficient to remove completely surfactant molecules from the pores of MCM-41 materials with various compositions.

Introduction

The discovery of MCM-41 type materials opened new perspectives in the fields of catalysis, separation, and molecular sieving. These materials can now be prepared within a broad composition range, typically from pure silica MCM-41 to aluminosilicates with Si/Al ≈ 1. They were originally prepared using the S^+I^- pathway, involving electrostatic interactions between rodlike micelles of quaternary ammonium surfactants (S^+) and anionic silicate species (I^-).[1] Later, the so-called counterion-mediated $S^+X^-I^+$ pathway was developed to assemble positively charged silica species (I^+) under strong acidic conditions.[2] Because of the low pH value, incorporation of aluminum is not possible, and this route is used to prepare exclusively pure silica MCM-41. Similar materials, denoted HMS, have also been prepared by a neutral S^0I^0 assembly pathway between primary amines and neutral silicate precursors.[3] The removal of surfactant molecules is commonly carried out by thermal decomposition at high temperature. This generates a high amount of organic residues, typically 45−55-wt % of the as-made MCM-41. Moreover, thermal decomposition is not cost-effective and cannot be reasonably used on an industrial scale. Attempts to remove surfactant molecules by plasma, supercritical fluid extraction,[4] and ozone treatment[5] have been reported. These methods may constitute an alternative to thermal treatment, but they have the disadvantage of not being cost-effective and of destroying surfactant molecules. Organic molecules can also be removed from the pores by a solvent extraction. The method was successfully employed to remove structure-directing agents from microporous crystalline materials with the BEA and MWW topologies.[6−11] The efficiency of the extraction depends in particular on the strength of the interaction between organic molecules and the framework. For MCM-41 materials prepared using the $S^+X^-I^+$ and S^0I^0 pathways, the weak interactions between organic and inorganic phases make that surfactant molecules that can be removed from the mesopores by a simple ethanol extraction.[2,12] In contrast, this method cannot be applied to MCM-41 materials prepared in basic media, in which strong electrostatic interactions between surfactant micelles and the inorganic network exist.

Partial extraction of the template by contacting MCM-41 with a polar solvent containing cation donors was originally reported at Mobil Oil Corp.[13] Following this method, approximately 75% of the template could be removed from an Al-MCM-41 after three treatments in ethanol/heptane/HCl solutions. However, the intensity of the XRD pattern decreased by a factor of ca. 10 upon treatment, suggesting severe damage of the structure. Moreover, structural data like the BET surface area or

---

* Corresponding author: Tel.: +33-4-72 44 53 95. Fax: +33-4-72 44 53 99. E-mail: tuel@catalyse.cnrs.fr.

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(3) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(4) Kawi, S.; Lai, M. W. *Chem. Commun.* **1998**, 1047.

(5) Keene, M. T. J.; Denoyel, R.; Llewellyn, P. L. *Chem. Commun.* **1998**, 2203.

(6) Lami, E. B.; Fajula, F.; Anglerot, D.; Des Courières, T. *Microporous Mater.* **1993**, *1*, 237.

(7) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52.

(8) Takewaki, T.; Beck, L. W.; Davis, M. E. *J. Phys. Chem. B* **1999**, *103*, 2674.

(9) Takewaki, T.; Beck, L. W.; Davis, M. E. *Top. Catal.* **1999**, *9*, 35.

(10) Jones, C. W.; Tsuji, K.; Takewaki, T.; Beck, L. W.; Davis, M. E. *Microporous Mesoporous Mater.* **2001**, *48*, 57.

(11) Zones, S. I.; Hwang, S. J.; Davis, M. E. *Chemistry* **2001**, *7* (9), 1990.

(12) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068.

(13) Whitehurst, D. D. US Patent 5 143 879, 1992.

10.1021/cm030633n CCC: $27.50

the ^{27}Al MAS NMR spectrum of the extracted solid were not reported. Different authors then used the method more or less successfully.[14–16] Results indicate that acids or cationic proton donors in ethanol efficiently remove surfactant molecules from pure silica materials. Chen et al. could remove completely organic molecules from a purely siliceous MCM-41 by treating the solid with a 1 M HCl/EtOH solution at 70 °C for 30 h.[14] This ion-exchange procedure is long, and it may be detrimental to aluminosilicates with low Si/Al ratios. For Al-MCM-41 materials with low Al contents, treatments with alcoholic solutions of K^+, Na^+, or NH_4^+ cations have been shown to partially extract template molecules.[16] According to the authors, the template associated with SiO^- groups would be easily removed while the more strongly bonded molecules associated with aluminum tetrahedra would remain in the solid. The most efficient cations were Na^+ and NH_4^+, but treatments sometimes led to a significant loss of structural order, as evidenced by X-ray diffraction. However, exchanges were performed on materials containing a high proportion of octahedrally coordinated aluminum species, which may influence the template extraction and the stability of the solid as well.

We report here a very fast, cheap, and efficient ion-exchange procedure to remove surfactant molecules from MCM-41 aluminosilicates with various aluminum contents.

Experimental Section

Synthesis. *(1) Pure-Silica MCM-41 (MCM-1).* Pure-silica Si-MCM-41 was synthesized using sodium silicate (26% SiO_2, 8% Na_2O, Prolabo), silica (A200, Degussa), tetramethylammonium hydroxide (TMAOH, 25 wt %, Aldrich), CTMABr, and water. The preparation, adapted from a method of Reddy and Song, was the following:[17]

To a solution containing 1.604 g of TMAOH in 16.3 mL of H_2O, 2.34 g of silica was added under stirring. After 10 min, 2.15 g of sodium silicate was added and stirring was maintained for 1 h (solution I).

A second solution (solution II) was prepared by dissolving 5.65 g of CTMABr in 38.1 mL of H_2O at a temperature of ca. 300 K.

Solution I was then added dropwise to solution II. The obtained gel, with the composition

$$SiO_2\ (1){:}Na_2O\ (0.086){:}TMAOH\ (0.044){:}\ CTMABr\ (0.31){:}H_2O\ (63.3)$$

was stirred at room temperature for about 1 h and then heated at 403 K for 3 days under static conditions. The solid, further denoted MCM-1, was recovered by filtration, washed with distilled water, and air-dried at room temperature.

(2) Al-MCM-41 with Si/Al = 30 (MCM-2). This material was synthesized following the same procedure as that used for the purely siliceous MCM-41, except that 0.326 g of aluminum isopropoxide was added to solution I following the addition of sodium silicate. The obtained MCM-41 is further denoted MCM-2.

(3) Low-Silica MCM-41 (MCM-3). Low-silica MCM-41 material was synthesized following a method adapted from Janicke et al.[18] In a typical preparation, 8.511 g of $Al(O^iPr)_3$ was dissolved in a solution containing 7.252 g of NaOH in 90 mL of H_2O, 941 mL of water was added, and the resulting mixture was stirred for about 30 min. Then, 32.345 g of CTMABr was added and the temperature was increased to ca. 298 K to dissolve completely the surfactant. tetraethyl orthosilicate (TEOS) (8.685 g) was then added, and the gel, with the composition

$$Al(O^iPr)_3\ (1){:}SiO_2\ (1){:}NaOH\ (4.32){:}\ CTMABr\ (2.13){:}H_2O\ (1250)$$

was stirred for 2 h. Concentrated HCl (37 wt %) was then added dropwise to decrease the pH value to 12. After 4 h more, additional HCl was added to decrease the pH to 11. Stirring was then maintained for 12 h at room temperature. The solid, denoted MCM-3, was recovered by filtration, washed with distilled water, and air-dried at room temperature.

After drying, a portion of each mesoporous solid was calcined to remove the organics. The compound was slowly heated to 800 K in air and the temperature was maintained for ca. 16 h.

Characterization. The exchange of surfactant molecules was carried out using alcoholic solutions of ammonium nitrate. Typically, 1 g of MCM-41 was dispersed in 150 mL of ethanol (95%) containing 0.3 g of NH_4NO_3, and the mixture was stirred at 333 K for 15 min. The amount of NH_4NO_3 corresponded to a $NH_4^+/CTMA^+$ molar ratio of 2. Solids were recovered by filtration and washed with cold ethanol, and the above treatment could be repeated twice.

For comparison, the same treatments were performed using 1 M HCL solutions in ethanol (Johnson Mattey).

X-ray diffraction powder patterns were recorded between 1° and 10° (2θ) on a Bruker (Siemens) D 5005 diffractometer using Cu $K\alpha_2$ radiation with steps of 0.02° and 10 s per step.

N_2 adsorption/desorption isotherms for BET surface area and pore size distribution measurements were collected at 77 K using a Catasorb Analyzer. Before the measurement, approximately 50 mg of the sample was dehydrated under vacuum at 573 K overnight.

The evolution of the amount of surfactant in the solids during exchange experiments was evaluated by measuring the intensity of typical vibrations of surfactant molecules in the IR spectra. Spectra were collected on a Bruker Vector 22 spectrometer using KBr wafers. Quantitative measurements were made after normalization of the spectra with respect to the band around 1000 cm^{-1}.

Thermal analysis data were collected on a SETERAM TGDSC 111 apparatus connected to a mass spectrometer. As-made compounds were heated in air from 298 to 1023 K at a heating rate of 5 K/min.

Temperature-programmed desorption (TPD) of ammonia was performed in the 353−853 K temperature range. Exchanged MCM-3 (0.3 g, NH_4^+ form) was purged at 333 K for several hours in flowing helium. The temperature was then increased from 333 to 653 K at a heating rate of 5 K/min. Quantitative measurements of desorbed ammonia were made using a gas chromatograph equipped with a Delsi GC 121 MB catharometer.

Solid-state NMR spectra were collected on a Bruker DSX-400 spectrometer. Magic angle spinning (MAS) experiments were conducted using a double-bearing probe head with 4 mm zirconia rotors. ^{29}Si NMR spectra were referenced to tetramethylsilane (TMS). The signals of an aqueous solution (1 N) of $Al(NO_3)_3$ was used to reference ^{27}Al chemical shifts. All spectra were recorded using a “one pulse” sequence with pulse lengths of 2 μs (30°) and 1 μs (20°) for ^{29}Si and ^{27}Al nuclei, respectively. Short recycle delays (typically 250 ms) were used for ^{27}Al

---

(14) Chen, C. Y., Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

(15) Schmidt, R.; Akporiaye, D.; Stöcker, M.; Ellestad, O. H. In *Zeolites and Related Microporous Materials: State of the Art 1994*; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, W., Eds.; Stud. Surf. Sci. Catal.; Elsevier: Amsterdam, 1994; Vol. 84, p 61.

(16) Hitz, S.; Prins, R. *J. Catal.* **1997**, *168*, 194.

(17) Reddy, K. M.; Song, C. *Catal. Lett.* **1996**, *36*, 103.

(18) Janicke, M. T.; Landry, C. C.; Christiansen, S. C.; Birtalan, S.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **1999**, *11*, 1342.

Table 1. Chemical Composition of MCM-41 Materials

	Si/Al		Na/ (Si+Al)	CTMA+/ (Si+Al)	empirical formula
	gel	solid			
MCM-1				0.18	$CTMA_{0.18}SiO_2$
MCM-2	30	30	0.05	0.18	$Na_{0.05}CTMA_{0.18}Si_{0.968}Al_{0.032}O_2$
MCM-3	1	1.25	0.32	0.12	$Na_{0.32}CTMA_{0.12}Si_{0.56}Al_{0.44}O_2$

Table 2. Structural Parameters of Calcined and Ion-Exchange-Extracted MCM-41 Materials

	S_{BET} (m²/g)	pore diameter (Å)	pore volume (cm³/g)	d_{100}
MCM-1	976	32	0.9	43
	(1085)[a]	(32)	(1.0)	(45)
MCM-2	861	31	0.82	42
	(870)	(29)	(0.81)	(43)
MCM-3	520	19	0.28	39
	(490)	(20)	(0.27)	(46)

[a] Values between parentheses refer to extracted materials.

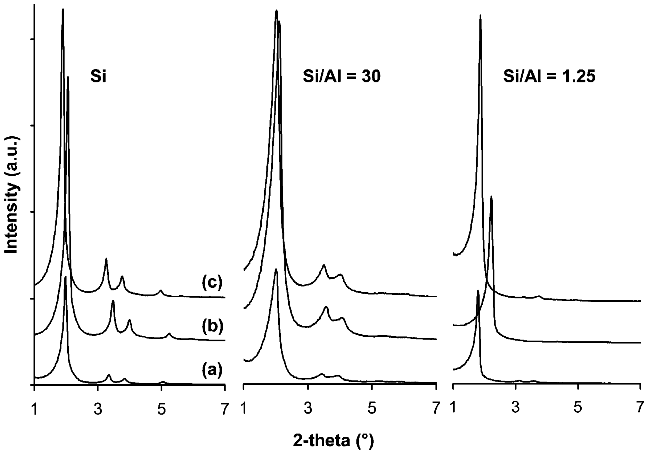


Figure 1. Powder X-ray diffraction patterns of as-made (a), calcined (b), and ion-exchange-extracted (c) MCM-41 materials.

nuclei. By contrast, ^{29}Si spectra were recorded with a recycle delay of 100 s, to ensure complete relaxation of all silicon species.

The aluminum content in the various materials was obtained by ICP after solubilization of the solids in HF:HCl solutions.

Results and Discussion

Parent Materials. The chemical composition and structural and textural properties of the three parent materials are reported in Tables 1 and 2. Chemical data show that the Si/Al ratio in the solid phase is always close to that introduced in the corresponding gel. All as-made mesoporous compounds show well-defined X-ray powder diffraction patterns characteristic of highly ordered hexagonal structures (Figure 1). This is particularly true for the purely siliceous material MCM-1, for which up to five reflections are clearly visible in the diffractogram. The pattern of MCM-3 is also of excellent quality as compared to those usually reported in the literature for materials with such low Si/Al ratios. The quality of XRD patterns of calcined materials indicates that all solids are thermally stable and that the ordered hexagonal structure is retained upon calcination. We can note that MCM-3 significantly contracts upon calcination (the unit cell parameter decreases by about 15%, Table 2). The contraction of the structure probably results from the high aluminum content and from the low synthesis temperature. Indeed, solids obtained at higher temperature possess a higher degree of framework cross-linking and are thus less affected by a thermal treatment.

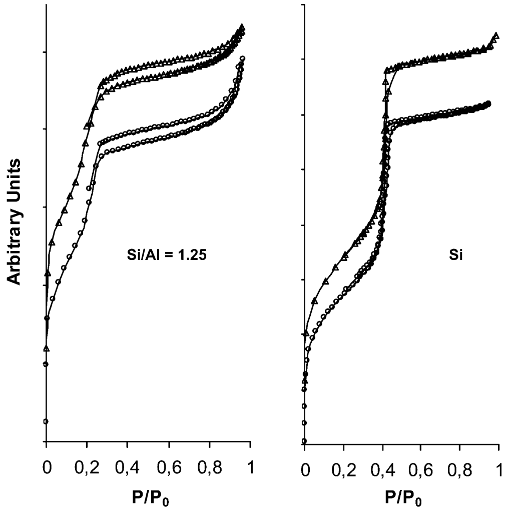


Figure 2. N_2 adsorption/desorption isotherms of directly calcined (r) and NH_4^+-extracted (○) MCM-41 materials.

Figure 2 shows the N_2 adsorption−desorption isotherms for calcined materials. The presence of a sharp sorption step in the p/p_0 region from 0.1 to 0.5 indicates that all solids possess a well-defined array of regular mesopores. The smaller p/p_0 value for MCM-3 is a direct consequence of the decrease of the pore size, due to the high aluminum concentration in the network. The BET surface area, pore diameter, and pore volume are in good agreement with the values reported in the literature for similar materials (Table 2).[17,18]

In the as-made form, MCM-3 contains only tetrahedrally coordinated aluminum species, as evidence by the absence of signal around 0 ppm in the ^{27}Al MAS NMR spectrum (Figure 3a). For MCM-2, the spectrum is similar, but the low aluminum content decreases the signal-to-noise ratio. The ^{29}Si MAS NMR spectrum of MCM-3 (not shown) is composed of a unique line at ca. −82 ppm, characteristic of $Si(OAl)_4$ (Q^0) species, which confirms that the Si/Al ratio is close to unity.[19] Upon calcination, aluminum species remain tetrahedrally coordinated (Figure 3b). The NMR line broadens, but no significant contribution is observed around 0 ppm, in the region characteristic of 6-coordinate aluminum species. Broadening of ^{27}Al NMR signals has been commonly observed during activation of zeolites.[20−22] It results from a distortion of the geometry around Al sites upon dehydration, leading to large second-order quadrupolar coupling constants (C_Q).

---

(19) Klinowski, J. *Prog. NMR Spectrosc.* **1984**, *16*, 237.

(20) Ernst, H.; Freude, D.; Wolf, I. *Chem. Phys. Lett.* **1993**, *212*, 588.

(21) Grey, C. P.; Vega, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8232.

(22) Vega, A.; Luz, Z. *J. Phys. Chem.* **1987**, *91*, 365. Luz, Z.; Vega, A. *J. Phys. Chem.* **1987**, *91*, 374.

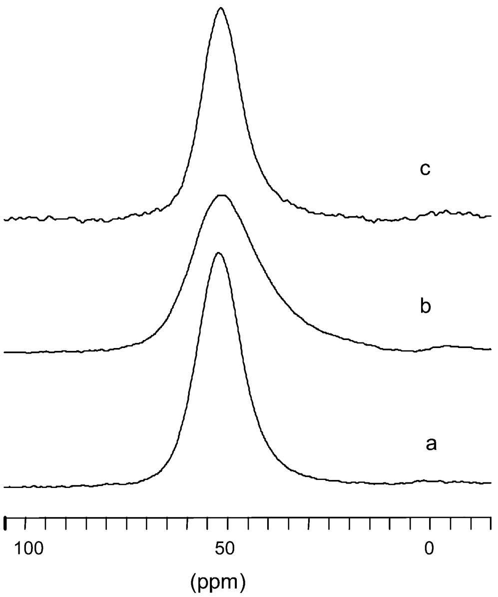


Figure 3. ^{27}Al MAS NMR spectra of as-made (a), calcined (b), and ion-exchange-extracted (c) MCM-3.

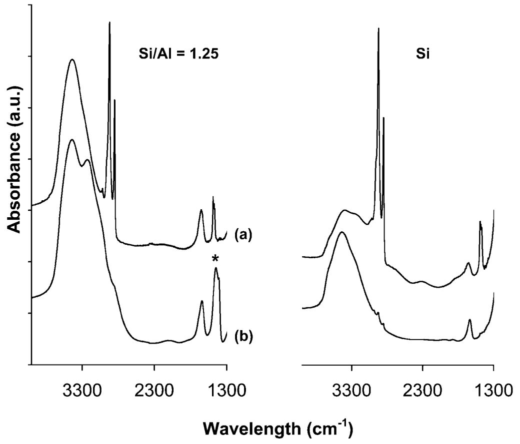


Figure 4. Framework IR spectra of as-made (a) and extracted (b) MCM-41 materials. NH_4^+ ions are identified by an asterisk.

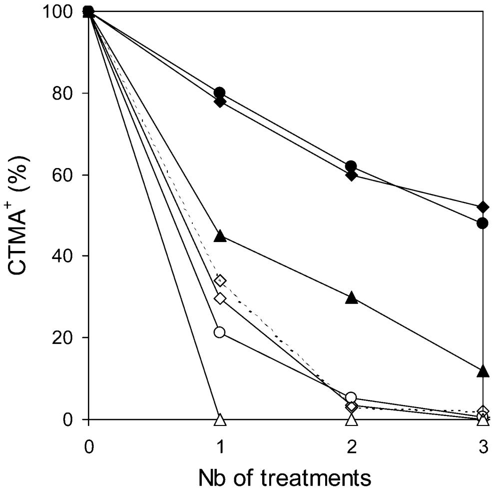


Figure 5. Evolution of IR bands characteristic of CTMA$^+$ cations in MCM-1 (◆, ◇), MCM-2 (●, ○), and MCM-3 (▲, △) with the number of treatments using NH_4NO_3/EtOH (open symbols) and HCl/EtOH (filled symbols) solutions. The amount of CTMA$^+$ cations in MCM-1 treated with NH_4NO_3 was also measured by TGA (dashed line).

Treated Solids. The three as-made compounds have been treated by ethanolic solutions of ammonium nitrate at 333 K (three treatments of 15 min each). X-ray powder patterns of treated MCM-41 materials show highly intense and well-resolved reflections (Figure 1). The intensity of the patterns increased by a factor of ca. 2 after treatment and reached that of calcined compounds, suggesting that surfactant molecules have been removed, at least partially, from the mesopores. Moreover, the d_{100} reflection in the XRD patterns does not shift, which indicates that the treatments do not modify the unit cell. The complete disappearance of bands characteristic of the template in the IR spectra of the treated MCM-41 materials confirmed that surfactant molecules were totally extracted from the pores after three exchanges (Figure 4). The amount of surfactant molecules that remained in the pores after the various treatments was also estimated from TG analysis. Figure 5 shows the excellent agreement between the amounts of CTMA$^+$ cations determined by the two methods in the case of the pure-siliceous compound MCM-1. Nonetheless, organic contents were preferentially measured by IR spectroscopy. This technique is fast compared to thermal analysis and data do not depend on the presence of extra molecules such as water and ethanol inside the pores. By contrast, thermal analysis data can be biased by the presence of such molecules, particularly when the amount of surfactant that remains in the solid is low. When the treatment was performed in pure ethanol, surfactant molecules were not extracted and the intensity of IR bands remained unchanged. Tanev et al.[4] previously reported that pure ethanol could not extract the template from siliceous MCM-41 prepared at 373 K by the electrostatic S^+I^- pathway. However, these authors observed that the structure partially collapsed upon treatment in ethanol, and this was attributed to the low degree of framework cross-linking in electrostatically assembled mesostructures. Our results suggest that long-chain ammonium cations have been exchanged for ammonium ions NH_4^+. The evolution of the IR bands characteristic of surfactant molecules with the number of treatments shows that exchange occurs very rapidly on MCM-3 while it is slower on MCM-1 and MCM-2 (Figure 5). This suggests that the template associated with SiO^- groups is more difficult to exchange than that associated with aluminum tetrahedra. This observation is of prime importance, not only from a fundamental point of view but also for practical applications. Indeed, it was generally accepted that template molecules balancing the charge of AlO_4 tetrahedra could not be extracted from the pores of MCM-41 by ion exchange.[15,16] Experiments performed on MCM-3, in which all CTMA$^+$ cations are associated with aluminum tetrahedra, clearly show that it is not true.

Chemical analysis did not reveal any change in the Si/Al ratios after treatment, indicating that the exchange procedure does not extract aluminum from the network. Moreover, the chemical environment of Al atoms is not modified, as evidenced by ^{27}Al solid-state NMR spectroscopy. The spectrum of exchanged MCM-3 is strictly identical to that of the parent material (Figure 3) and does not show any broadening of the signal, as is the case after calcination. A contraction of the unit cell is observed when exchanged compounds are further calcined at high temperature. The corresponding X-ray powder patterns then match exactly those of the directly calcined solids (Figure 1). Removal of the template by NH_4/EtOH solutions does not alter the size and uniformity of the mesopores (Figure 2). Extracted materials possess specific surface areas, pore diameters, and pore size distributions very similar to those of directly calcined MCM-41 (Table 2). Since extracted materials were not calcined but only evacuated at 573 K before adsorption of nitrogen, this constitutes additional evidence for the complete removal of surfactant molecules from the pores. Attempts to exchange surfactant molecules for other inorganic cations such as Na^+ or K^+ were less successful, particularly for silica-rich materials. More than 50% of the template remained in the mesopores of pure silica MCM-41 when the latter was treated three times with NaCl or KCl solutions. This confirms previous results from Hitz and Prins[16] on the removal of surfactant molecules from the pores of MCM-41 materials. However, these authors never reported a complete removal of the organics, even with NH_4^+/EtOH solutions. The ability of a series of cations to extract template molecules from MCM-41 materials with various aluminum contents and the thermal stability of the corresponding solids will be reported in a forthcoming paper. The higher performance of NH_4^+ ions can be most likely attributed to its chemical and geometrical similarity with heads groups of surfactant molecules.

To compare the above procedure to previously published extraction methods, samples have been treated with HCl/EtOH solutions. It was reported that such a treatment was effective to remove, at least partially, surfactant molecules from the pores of MCM-41 materials.[13−16] The evolution of the amount of surfactant molecules that remains in the solids with the number of treatments (Figure 5) shows that HCl is less efficient than NH_4NO_3 at extracting organic molecules. This is particularly true for the pure silica compound MCM-1, for which less than 60% of the template was extracted after three exchanges of 15 min. The structure of MCM-1 was not affected by a partial extraction, as evidenced by X-ray diffraction and nitrogen adsorption. For MCM-3, about 90% of the template could be extracted. However, chemical analysis of the extracted material gave Si/Al = 1.95 and showed that more than 35% of aluminum species was removed from the solid in the presence of HCl. Moreover, the d_{100} reflection in the X-ray powder pattern of the calcined solid was approximately 2 times less intense than that of directly calcined MCM-3, suggesting a loss in long-range ordering, due to a partial dealumination. As previously reported, hydrogen chloride can effectively be used to extract organic molecules from pure-silica MCM-41, but the treatment is long, due to a relatively slow exchange between $CTMA^+$ cations and protons. By contrast, HCl solutions cannot be reasonably applied to Al-rich materials.

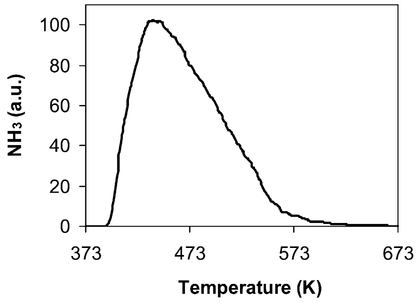
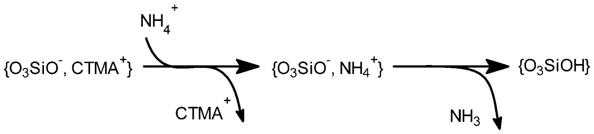


Figure 6. Ammonia TPD curve of NH_4^+-extracted MCM-3.

The IR spectrum of NH_4^+-exchanged pure silica MCM-41 does not show any signal characteristic of NH_4^+ ions, in particular, absorption bands between 1400 and 1450 cm^{-1} (Figure 4). TPD of the sample from 353 to 653 K effectively confirmed the absence of ammonia. The weak interaction between NH_4^+ ions and SiO^- groups at the surface of the mesopores makes that the former probably decompose in situ at low temperature following the reaction leading directly to silanol groups. By contrast, aluminosilicates show signals characteristic of NH_4^+ ions in IR spectra, with intensity proportional to the Al content (Figure 3). In the particular case of MCM-3, the chemical composition $Na_{0.32}CTMA_{0.12}Si_{0.56}Al_{0.44}O_2$ indicates that all surfactant molecules neutralize the negative charge of AlO_4 tetrahedra. After exchange, NH_4^+ ions are stabilized, due to their strong interaction with AlO_4^- sites. A TPD of exchanged MCM-3 shows that the degradation of NH_4^+ cations occurs in the 353−600 K range, with a maximum around 443 K (Figure 6). TPD profiles of $[NH_4^+]$Al-MCM-41 materials usually exhibit three maxima at ca. 490, 673, and 873 K.[23] The peak at 490 K is commonly assigned to Lewis and/or Bronsted sites of weak acidic strength. The other signals at 673 and 873 K are assigned to strong Bronsted sites and strong Lewis sites, respectively. Experiments performed on a series of MCM-41 materials with various aluminum contents have shown that the amount of strong acid sites can be correlated with the fraction of octahedral aluminum in NMR spectra.[23] Octahedral aluminum usually results from the dealumination of MCM-41 upon calcination. The low degradation temperature of NH_4^+ cations in our solids is a direct consequence of the absence of octahedral aluminum. The fact that all ammonium cations (NH_4^+) balance the charge of AlO_4 tetrahedra and the high sodium concentration in extracted MCM-3 makes that the resulting acidity is very weak.



Chemical analysis of extracted materials shows that the amount of Na^+ cations in MCM-3 is unchanged after one treatment. Thus, the above procedure exchanges preferentially surfactant molecules. However, when the treatment is prolonged on surfactant-free materials, the Na content decreases. For MCM-2, the low sodium content in the as-made solid makes that Na^+ cations are exchanged together with surfactant molecules. After complete removal of the organics, Na^+ ions have been totally exchanged for ammonium cations. Thus, calcination of the extracted solid directly leads to the H-form of Al-MCM-41

---

(23) Kosslick, H.; Lischke, G.; Parlitz, B.; Storek, W.; Fricke, R. *Appl. Catal. A: Gen.* **1999**, *184*, 49.

Conclusion

Alcoholic solutions of ammonium nitrate efficiently remove surfactant molecules from MCM-41 materials. The method can be applied not only to siliceous compounds but also to aluminosilicates with various aluminum contents, which is not the case of EtOH/HCl solutions. In particular, a low-silica compound with Si/Al = 1.25 can be extracted within less than 15 min at 60 °C. The above procedure offers many advantages compared to previously reported methods:

(1) It can be carried out without using specific equipment.

(2) The ion exchange preserves the structure, in particular the coordination, of the aluminum species.

(3) The template is intact and can be recovered.

(4) In the case of pure-silica MCM-41, extracted materials contain only silanol groups and can thus be used immediately, without further calcination.

Acknowledgment. We thank the French Ministry of Industry for funding within the ZEOMAT project.

CM030633N