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Low-Silica [Me]AlMCM-41 (Me = Na, K, Cs, Ca) Mesophases and Corresponding Mesoporous Materials

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An aluminosilicate MCM-41 with a highly ordered mesoscopic structure and Si/Al molar ratio of 1.25 has been synthesized in basic medium in the presence of sodium ions. Standard procedures to exchange Na^+ for other cations in calcined MCM-41 led to a gradual collapse of the structure along with a partial dealumination. Various [Me]AlMCM-41, with Me = K^+, Cs^+, Ca^{2+}, could be obtained by completely exchanging sodium ions prior to calcination, i.e., in the presence of surfactant molecules. These molecules prevent framework dealumination during exchange, while preserving the long-range mesoscopic ordering of the parent [Na]AlMCM-41. The [Me]AlMCM-41 thus obtained possessed all the properties of materials that would have been obtained directly in the presence of the corresponding cations. Moreover, structural and textural properties of the calcined products are very similar to those of the directly calcined [Na]AlMCM-41, suggesting that the nature of the charge compensating cation has little influence on the thermal stability.

Introduction

One of the most interesting properties of zeolites is their ability to reversibly exchange cations.[1,2] The composition of a zeolite can thus be varied by simply contacting the solid with an aqueous solution of the corresponding metal. For example, a large amount of alkali cations such as Cs^+ have been introduced in zeolites' cavities without alteration of the crystallinity.[3,4] Upon activation, these cations aggregate to form small oxide clusters, exhibiting a relatively strong basic character.[3,5] CsX and CsY zeolites have thus been used as catalysts in reactions such as Knoevenagel condensations, which require the presence of a strong base.[3] However, the applications of modified zeolites are limited by their pore openings, into which bulky molecules cannot penetrate. It would be of particular interest to synthesize materials that combine properties similar to those of zeolites with a wider pore dimension. In principle, MCM-41 mesoporous materials[6] may fulfill these conditions, provided that they contain sufficiently high aluminum contents. Indeed, aluminum tetrahedra generate charge defects in the silicate framework of MCM-41 which are compensated by cations. In as-made compounds, these cations are either the ammonium headgroups of surfactant molecules or sodium ions introduced in the synthesis gel.[7] Upon calcination, the thermal degradation of organic molecules produces proton species that can act as Brønsted or Lewis acid sites.[8−11] Moreover, Na^+ cations become theoretically accessible and exchangeable, as they are in many zeolite frameworks. Unfortunately, it has been reported that incorporation of Cs cations in calcined MCM-41 by ion exchange could significantly destroy the structure.[12] Moreover, previous studies have established that the ion-exchange capacity of MCM-41 is limited, with some cations being embedded in the walls and, consequently, hardly accessible.[13] For these reasons, the preparation of highly ordered [Me]AlMCM-41 (Me = K, Cs, Ca) with high Me contents is difficult. One possibility would be to synthesize mesostructured aluminosilicates with high Al contents directly in the presence of the alkali cations. Previous attempts to synthesize AlMCM-41 with low Si/Al ratios were more or less successful. Decreasing the Si/Al molar ratio below 10 generally leads to a significant reduction of the mesoscopic organization.[14−17] In certain cases, X-ray powder patterns of MCM-41 with

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Si/Al $<$ 2 show only a unique broad reflection characteristic of disordered materials and the corresponding calcined compounds possess a wide distribution of pore sizes.[15,16] Moreover, calcined Al-rich solids often show a signal characteristic of octahedrally coordinated species in the ^{27}Al NMR spectrum, resulting from a partial dealumination of the walls.[7,18−21]

However, the preparation of mesoporous aluminosilicates with Si/Al close to 1 containing exclusively tetrahedral Al species and that remain highly ordered upon calcination at high temperature has been reported.[22−24] These solids are prepared from gels containing Na^+ cations and attempts to obtain similar compounds in the presence of other alkali cations were unsuccessful. Actually, there are only a couple of papers that report the preparation of MCM-41 in the presence of Ca^{2+} or Cs^+ cations.[12,25,26] Nevertheless, both the alkali cation and aluminum concentrations are low (Si/Al $>$ 25) and a reliable procedure to prepare Al-rich MCM-41 from gels containing these cations has not yet been published.

The aim of the present article is to show that as-made [Na]AlMCM-41 with Si/Al close to 1 can be easily converted to [Me]MCM-41 (Me = K, Cs, Ca). The transformation is performed in the presence of surfactant molecules and does not alter the long-range organization of the mesopores. The properties of the various [Me]MCM-41before and after calcination are compared with those of the parent [Na]MCM-41.

Experimental Section

Synthesis. A mesoporous aluminosilicate was synthesized following a recipe adapted from the literature.[24] Typically, 8.511 g $Al(O^iPr)_3$ was dissolved in a solution containing 7.252 g of NaOH in 90 mL of H_2O. Water (941 mL) was then 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 completely dissolve the surfactant. Tetraethyl orthosilicate (TEOS, 8.685 g) was then added and the gel (with the composition $Al(O^iPr)_3/SiO_2/NaOH/CTMABr/H_2O$, 1:1:4.32:2.13:1250) 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. The synthesis gel was then covered and stirring was maintained for 12 h at room temperature. The solid, further denoted [Na]AlMCM-41, was then recovered by filtration, washed with distilled water, and air-dried at room temperature. After drying, a portion of the material was calcined to remove the organics and to estimate the thermal stability. The compound was slowly heated to 800 K in air and the temperature was maintained for ca. 16 h.

Exchange Procedure. A 100-mL portion of an aqueous solution of metal chloride (CsCl, KCl, or $CaCl_2{\cdot}2H_2O$, all purchased from Aldrich) was heated at 50 °C. Then 1 g of as-made [Na]AlMCM-41 was dispersed in the liquid and the suspension was stirred vigorously for 30 min. For treatments with Cs and K the concentration of the solution was 5×10^{-2} M, whereas for $CaCl_2{\cdot}2H_2O$ it was 2.5×10^{-2} M. This corresponds to a Me/Na molar ratio of about 3 for Cs and K and Ca/Na = 1.5. After 30 min, the solid was recovered by centrifugation and washed with distilled water. The above procedure could be repeated up to 6 times. After the complete treatment, the mesoporous solid was air-dried at room temperature and calcined in air at 800 K.

Characterization. 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 Micromeretics ASAP 2010 apparatus. Before the measurement, approximately 50 mg of the sample was dehydrated under vacuum at 573 K overnight.

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.

The aluminum and alkali cation contents in the various materials were determined by ICP after the solids had been dissolved in HF/HCl solutions.

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 chemical shifts were referenced to tetramethylsilane (TMS). Signals of aqueous solutions (1 N) of $Al(NO_3)_3$ and NaCl were used to reference ^{27}Al and ^{23}Na chemical shifts, respectively. All spectra were recorded using a "one pulse" sequence with pulse lengths of 2 μs (30°), 1 μs (20°), and 2 μs (45°) for ^{29}Si, ^{27}Al, and ^{23}Na nuclei, respectively. Short recycle delays (typically 250 ms) were used for ^{27}Al and ^{23}Na nuclei. By contrast, ^{29}Si spectra were recorded with a recycle delay of 100 s to ensure complete relaxation of all silicon species.

TEM pictures were taken on a JEOL 2010 microscope with an accelerating voltage of 200 kV. Samples were embedded in an epoxy resin and sectioned on an ultramicrotome.

Results and Discussion

The chemical formula of as-made [Na]AlMCM-41, deduced from chemical analysis and thermogravimetry, is $(Na_{0.32}CTMA_{0.12})Si_{0.56}Al_{0.44}O_2$. This corresponds to a molar ratio Si/Al = 1.25, which is not very different from that of the precursor gel. Approximately 30% of the defect charge associated with tetrahedral aluminum is compensated by ammonium cations, with the rest being neutralized by sodium ions.

The well-defined X-ray powder pattern of the solid (Figure 1) is typical of a highly ordered material with a hexagonal array of mesopores.[6] The pattern is of excellent quality as compared to those usually reported in the literature for MCM-41 materials with such high aluminum content. The regularity of the mesopore system was confirmed by TEM. Nonporous dense phases or disorganized parts were never detected, with all particles showing a perfectly ordered mesoporous network (Figure 2a).

The ^{27}Al MAS NMR spectrum of [Na]AlMCM-41 shows a major signal at ca. 50 ppm along with a weak line at 5 ppm (Figure 3). The major signal can be unambiguously assigned to tetrahedral aluminum species. The weak contribution around 5 ppm indicates the presence of species with a higher coordination, most

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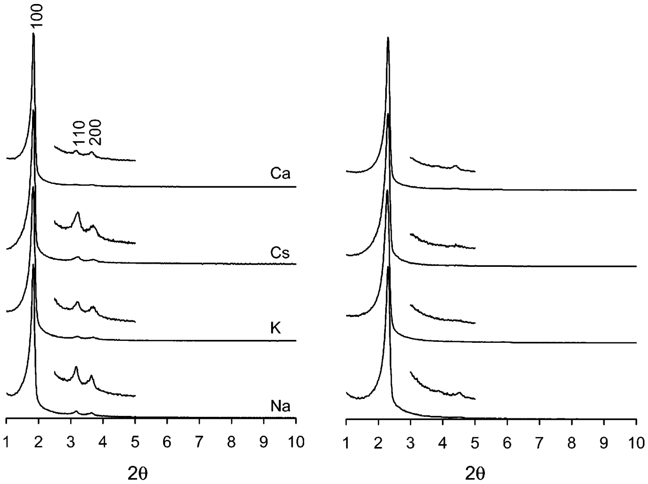

Figure 1. X-ray powder diffraction patterns of as-made (left) and calcined (right) solids. Portions of the spectra have been amplified by a factor of 5 to better show d_{110} and d_{200} reflections.

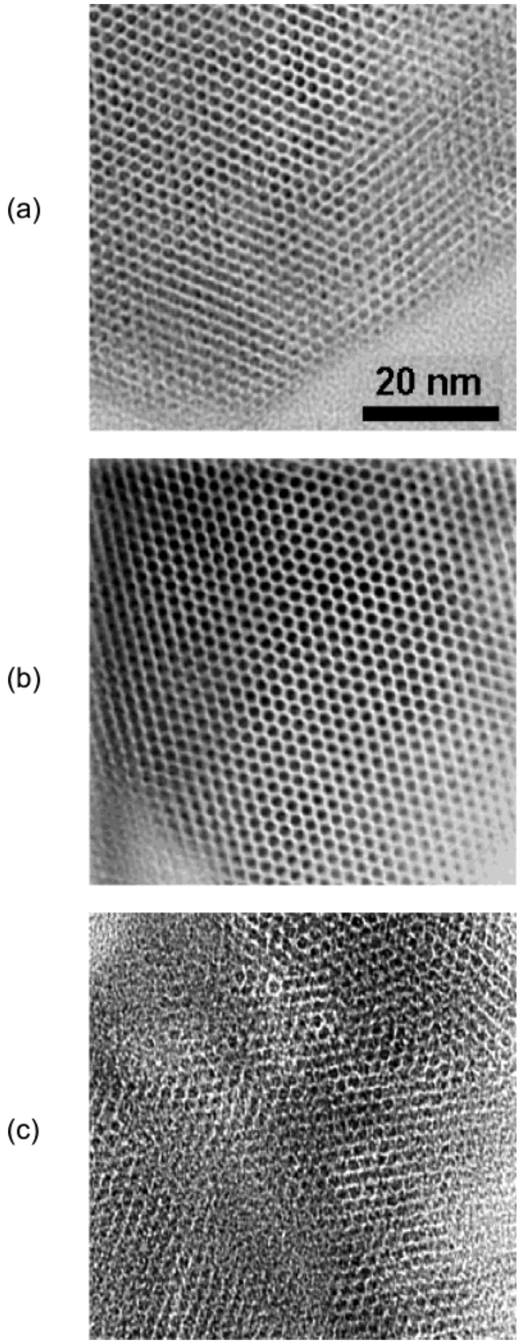

Figure 2. TEM pictures of as-made [Na]AlMCM-41 (a), and [Cs]AlMCM-41 before (b) and after (c) calcination.

likely 6-coordinate species. However, their contribution to the total amount of aluminum does not exceed 5%. The ^{29}Si NMR spectrum of [Na]AlMCM-41 contains a single signal at −82 ppm, along with a shoulder at −87 ppm (not shown). On the basis of ^{29}Si NMR chemical shifts in aluminosilicates and zeolites, the spectrum of [Na]AlMCM-41 corresponds to essentially $Si(OAl)_4$ (Q^4) species.[27] The shoulder around −87 ppm indicates that a small fraction of silicon species possess one aluminum atom in their coordination sphere (Q^3 species). However, the absence of signals assigned to Q^2, Q^1, and Q^0 species between −90 and −110 ppm confirms that the Si/Al ratio is close to 1.

The array of regular mesopores is preserved upon calcination at high temperature, as evidenced by X-ray diffraction (Figure 1). Nevertheless, the relative diminution of the intensity of the (110) and (200) reflections with respect to the (100) reflection in the XRD pattern suggests that calcination slightly modifies the long-range ordering of the pores. This may arise from the contraction of the structure upon calcination, manifested by the shift of the basal reflection toward high angle values (Figure 1 and Table 1). Despite this, all aluminum atoms remain tetrahedrally coordinated after the thermal treatment. The ^{27}Al NMR line centered on 50 ppm is quite broad due to a modification of the local geometry around Al atoms upon calcination (Figure 3). This change in geometry increases the second-order quadrupolar coupling constant value (C_Q), which broadens the NMR signal. Previous studies have shown that calcination of mesoporous aluminosilicates with Si/Al < 4 was accompanied by a partial dealumination, though otherwise signals did not appear in the region characteristic of octahedrally coordinated Al species in the NMR spectrum.[24] This was attributed to the formation of "NMR invisible" aluminum species in highly distorted asymmetric environments.[28] For a [Na]MCM-41 with Si/Al = 1.25, we have previously reported that the decrease of the NMR signal at 55 ppm corresponded to about 30% dealumination upon calcination.[29] The BET surface area of calcined [Na]AlMCM-41 is 549 m^2/g (Table 1), in good agreement with data already reported for similar materials.[24] The mean pore size diameter is around 19 Å, i.e., at the border between micro- and mesoporosity.

[Na]AlMCM-41 was first exchanged following a conventional procedure. The mesostructured solid was calcined at 800 K and then subjected to a series of treatments with aqueous solutions of potassium chloride at room temperature. Conditions were strictly similar to those described in the Experimental Section for exchanges on as-made [Na]AlMCM-41. Chemical analysis and ^{23}Na NMR spectra of the treated materials

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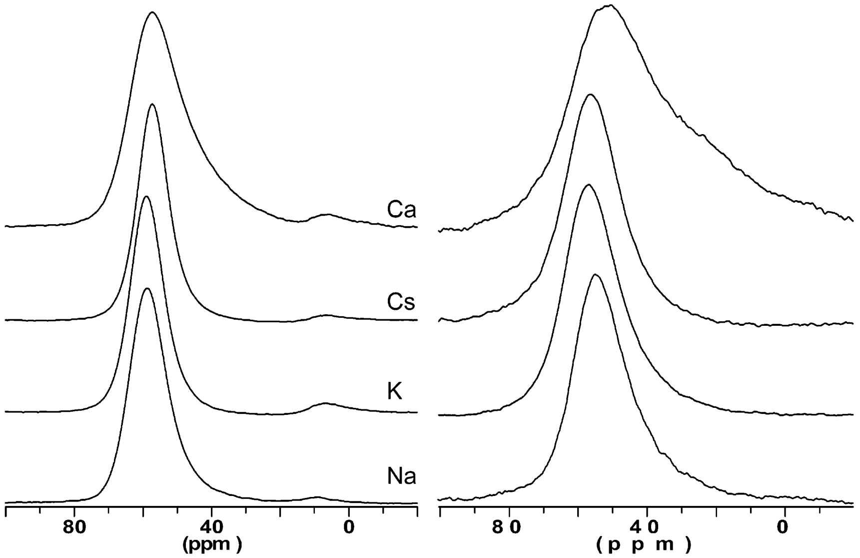

Figure 3. ^{27}Al MAS NMR spectra of as-made (left) and calcined (right) solids.

Table 1. Textural and Structural Properties of the Different [Me]AlMCM-41 Products

	d_{100} (Å)		S_{BET}	$Ø_p$	V_p	WT
Me	as-made	calcined	(m^2/g)	(Å)[a]	(cm^3/g)[b]	(Å)[c]
Na	47.2	39.2	549	19	0.30	21.9
K	48.0	40.2	522	20	0.28	21.5
Cs	46.9	40.4	372(567)[d]	20	0.29	20.6
Ca	47.5	39.9	553	19	0.32	22.1

[a] Calculated on the adsorption branch using the BJH model. [b] Measured at $P/P_0 = 0.5$. [c] Estimated by WT = $a_0 - Ø_p$, where a_0 is the unit cell: $a_0 = \sqrt{3}/2d_{100}$. [d] The BET surface area in parentheses was calculated using the density of the parent [Na]AlMCM-41 (see text).

Table 2. Structural and Textural Properties of Calcined [Na]AlMCM-41 upon Exchange with an Aqueous Solution of Potassium Chloride

no. of exchanges	Id_{100} (%)[a]	S_{BET} (m^2/g)	V_p (cm^3/g)[b]
0	100	549	0.30
1	55	463	0.28
2	33	402	0.24
4	20	384	0.23
6	15	355	0.17

[a] Relative intensity of the d_{100} reflection peak in the XRD pattern. [b] See footnote *b* of Table 1.

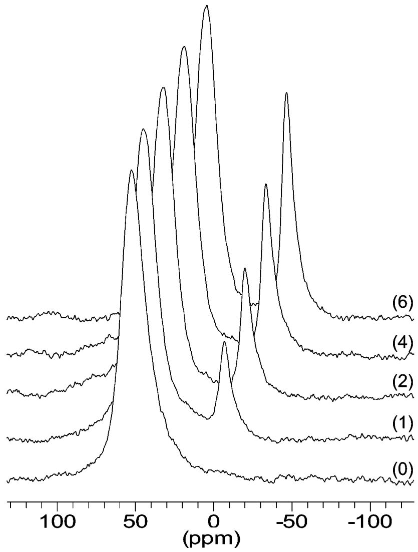

Figure 4. Evolution of the ^{27}Al NMR spectrum of calcined [Na]AlMCM-41 upon exchanges with an aqueous solution of potassium chloride. For a better comparison, spectra have been normalized with respect to the signal at ca. 55 ppm. The number of exchanges is given in parentheses.

indicate that an exchange between Na$^+$ and K$^+$ cations effectively occurs. The Na concentration decreases rapidly during the first exchange, then more slowly during the others. After six treatments, more than 25% of sodium ions originally present in [Na]AlMCM-41 remain in the solid. This supports the idea that only a fraction of Na$^+$ ions are located at the surface of the mesopores and are thus easily accessible to other cations. However, the intensity of the X-ray diffraction pattern, as well as the BET surface area, continuously decreases with the number of exchanges, suggesting that the structure gradually collapses in the presence of water (Table 2). The degradation of the structure generates the formation of octahedrally coordinated aluminum species, as evidenced by ^{27}Al NMR (Figure 4). As can be seen in the figure, the relative intensity of the NMR line characteristic of 6-coordinated species increases proportionally to the number of exchanges. The above results tend to show that calcined AlMCM-41 materials are not stable in the presence of water, even at low temperature, and that conventional exchange procedures cannot be applied to mesoporous aluminosilicates with high aluminum contents.

Similar experiments have been performed on as-made [Na]AlMCM-41, with the expectation that the presence of surfactant molecules in the pores prevents the gradual destruction of the structure in the presence of water. The chemical composition of the as-made compound is modified upon treatment with an aqueous solution of metal chloride, as illustrated in Figure 5 in the particular case of cesium chloride. The Na content decreases monotonically while the Cs concentration increases with the number of treatments. The (Na + Cs)/Al ratio remains constant, suggesting that Cs cations progressively replace sodium ions. Moreover, thermogravimetric analysis of the treated samples shows that the amount of organics is unchanged (Figure 5), which clearly demonstrates that ion exchange occurs exclusively between inorganic cations. After six treat-

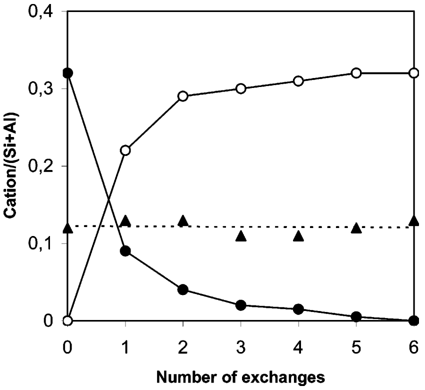

Figure 5. Evolution of the fraction of Na^+ (●), Cs^+ (○), and $CTMA^+$ (▲) in the mesostructured compound with the number of exchanges. Fractions are given with respect to the chemical formula of the starting solid: $Na_{0.32}CTMA_{0.12})Si_{0.56}Al_{0.44}O_2$. The dotted line represents the average $CTMA^+$ value.

ments the exchange is complete and further treatments no longer modify the composition of the solid. Very similar conclusions have been obtained with the other cations K^+ and Ca^{2+}. In particular, the nature of the cation has very little influence on the evolution of the Na concentration with the number of treatments.

The long-range hexagonal ordering of the [Na]AlMCM-41 precursor is preserved after six treatments, as evidenced by X-ray diffraction (Figure 1) and TEM (Figure 2). By contrast to calcination, ion exchange is not accompanied by a contraction of the structure, and the position of the d_{100}, d_{110}, and d_{200} peaks is unchanged (Table 1). TEM pictures of the [Cs]AlMCM-41 mesophase are characteristic of the perfectly ordered array of mesopores observed on all exchanged products. Dense phases or less regular regions that could result from a partial degradation of the mesoscopic ordering were not detected. Moreover, the interplanar distance and pore diameter measured directly on the pictures are the same as those of [Na]AlMCM-41, thus supporting the XRD data. Additionally, the environment of aluminum atoms is preserved during ion exchange (Figure 3). For Cs- and K-exchanged compounds, the ^{27}Al NMR spectra are exactly the same as that of the parent [Na]AlMCM-41. By contrast, treatments with aqueous solution of calcium chloride slightly broaden the NMR line at 55 ppm. The location of cations in MCM-41 is not well documented, but in the case of aluminum-rich materials with Si/Al ratios close to 1, Na^+ cations are expected to be in the vicinity of Al tetrahedra. When Na^+ ions are exchanged for monovalent cations such as Cs or K, the cation concentration is unchanged and it is reasonable to assume that the charge density around Al atoms is not greatly perturbed. Under such conditions, the nature of the cation has little influence on the position and width of the ^{27}Al NMR line. Upon treatments with Ca^{2+}, each calcium replaces two sodium ions, which necessarily changes the repartition of charges within the aluminosilicate framework. As the positive charge of the cation is delocalized over two aluminum tetrahedra, the local electric field gradient is modified, which affects the shape of the NMR line. Despite this, the intensity of the signal characteristic of octahedral aluminum does not increase, and ion exchange is not accompanied by a partial dealumination of the aluminosilicate framework.

The combination of X-ray diffraction, thermal analysis, and NMR data clearly establish that ion exchange essentially modifies the nature of the cation. The long-range mesoscopic ordering, the organic content, and the Si/Al ratio remain similar to those of as-synthesized [Na]AlMCM-41. The solids, denoted [K]AlMCM-41, [Cs]-AlMCM-41, and [Ca]AlMCM-41, can be considered as K-, Cs-, and Ca-analogues of the parent [Na]AlMCM-41, respectively, and they possess all the characteristics of materials that would have been prepared directly in the presence of the corresponding cations.

In addition to the possibility to prepare organic/inorganic hybrid materials with unusual compositions, the postsynthesis treatment presented in this paper shows that inorganic cations in MCM-41 can easily diffuse into the pores, even in the presence of surfactant molecules. These molecules possess long alkyl chains, exhibiting a hydrophobic character, and relatively hydrophilic cationic headgroups. Hydrated cations such as Na^+, K^+, Cs^+, or Ca^{2+} can hardly penetrate the hydrophobic core of the micelles and they most probably diffuse through the region at the organic/inorganic interface. Despite diffusion limitations due to the presence of surfactant micelles in the mesopores, the exchange is relatively fast, as evidenced by the rapid variation of the Na^+ concentration in Figure 5. The average BET pore size and the d_{100} distance obtained from the XRD pattern of the calcined product provide an estimation of the wall thickness (Table 1). Assuming that the contraction of the wall upon calcination is similar to that of the unit cell, one can estimate the wall thickness to be ca. 25 Å in as-made [Na]AlMCM-41. This result, in conjunction with the homogeneity of the framework deduced from ^{29}Si NMR spectra, suggests that a high proportion of Al atoms are located inside the walls. Despite this, the associated charge-compensating Na+ cations are readily mobile and accessible to other inorganic cations, which was not the case for calcined [Na]AlMCM-41.

All solids have been calcined in air at 800 K to establish whether the nature of the charge-compensating cation has an influence on the thermal stability. As shown in Figure 1, XRD patterns of calcined materials still show the characteristics of mesoporous materials. As for [Na]AlMCM-41, the diminution of the intensity of the d_{110} and d_{200} reflections with respect to the intensity of the d_{100} peak indicates a significant reduction of the mesoscopic order. Despite this, neither the position nor the intensity of the d_{100} reflection has changed, suggesting that the nature of the cation does not influence the contraction and the stability of the structure upon calcination. The presence of regular mesopores in calcined materials was confirmed by TEM (Figure 2c). The picture of calcined [Cs]AlMCM-41 illustrates the modification of the long range mesoscopic ordering observed on all exchanged materials upon calcination. Mesopores are still locally ordered but their arrangement tends to be more chaotic at moderately long distance, which is not the case before calcination.

^{27}Al NMR spectra of all the samples show essentially a broad reflection around 50 ppm, characteristic of tetrahedrally coordinated Al species (Figure 3). Minor contributions due to 6-coordinate Al species, which were visible around 0 ppm in the spectra of as-made materials, have disappeared. This suggests that the corresponding species have been transformed into either 4-coordinate Al atoms or “NMR invisible” species. However, integration of the spectra shows that the intensity does not significantly differ from that of calcined [Na]AlMCM-41, suggesting that the amount of “NMR invisible” aluminum and, consequently, the extent of dealumination do not strongly depend on the charge-compensating cation. The spectrum of calcined [Ca]AlMCM-41 is broader than the others. The assignment of signals present between 20 and −20 ppm is not trivial and cannot be made using standard NMR techniques. Indeed, the NMR line may result from highly distorted 4-coordinate species with strong second-order quadrupolar coupling constants or from the superposition of signals arising from Al species with different coordinations. Further developments are in progress to tend to distinguish between theses two possibilities. Sorption analyses of the calcined exchanged compounds support observation that the nature of the cation does not influence the stability of the structure upon calcination (Table 1). K- and Ca-modified solids possess a BET surface area and an average pore size very close to those of the parent [Na]AlMCM-41. For the Cs-exchanged MCM-41, the BET surface area is reduced by about 25%, but the calculation does not take into account the variation of the composition of the solid. Following the modification of the molecular weight of [Na]AlMCM-41 upon exchange with Cs^+ cations (the molecular weight varies from ca. 67 to 102 g), the density of the compound is increased by approximately 35%. To evaluate correctly the evolution of the sorption properties of the mesoporous product upon exchange with Cs^+ cations, all calculations have been performed using the density of the parent [Na]AlMCM-41. Under such conditions, the BET surface area of [Cs]AlMCM-41 is 567 m^2/g (Table 1). Together with a mean pore diameter of 20 Å, this value confirms that [Cs]AlMCM-41 is not less structurally ordered than the other compounds.

Conclusion

A method has been developed to prepare MCM-41 materials with high concentrations of framework aluminum and alkali cations. Starting from as-made [Na]-AlMCM-41, an ion exchange is performed in the presence of the micelles of surfactant molecules. XRD, solid-state NMR, and thermal analysis data provide evidence that exchange occurs exclusively between inorganic cations, without dealumination and reduction of the long-range mesoscopic order. Sorption capacities of calcined materials show that the nature of the cation has little or no influence on the thermal stability of exchanged products. The present postsynthesis method constitutes an elegant way to prepare MCM-41 materials with unusual compositions, which are impossible to obtain by direct synthesis methods. The method can be generalized to other cations and to MCM-41 with higher Si/Al ratios, with the obtained solids being potentially attractive as catalysts or adsorbents.

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