Synthesis and Characterization of Trivalent Metal Containing Mesoporous Silicas Obtained by a Neutral Templating Route

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A series of trivalent metal cation containing mesoporous silicas have been synthesized using a primary alkylamine, e.g., hexadecylamine as organic templating surfactant. Using this synthesis route, it was possible to prepare materials where trivalent cations were tetrahedrally coordinated, with Si/Me ratios as low as 10 without observing the presence of octahedral species. These materials possessed regular mesopores of about 37 Å diameter and very high surface areas. In contrast to pure silica materials obtained following a similar synthesis route, these solids were not thermally stable, and calcination in air resulted in a partial collapse of the mesopores and in a partial extraction of trivalent cations. However, templating molecules could be easily removed from the mesopores by a solvent extraction. Removal of the template by this way preserved not only the mesopore framework but also the coordination of the cations. Solvent-extracted solids were thermally stable and could be calcined in air at high temperature without observing changes in the nature and coordination of the cations. The present synthesis route seemed thus to be particularly interesting to prepare template-free mesoporous silicas containing relatively high amounts of tetrahedrally coordinated trivalent cations.

Introduction

Researchers at Mobil R & D Corp. have recently described the synthesis of a new family of silicate and aluminosilicate mesoporous molecular sieves designated as M41S.[1−5] These materials have received considerable interest during the past years because of their particularly attractive properties.[6−13] Indeed, M41S materials possess regular mesopores whose diameter can be tailored between about 15 and 100 Å, by using the appropriate alkyltrimethylammonium cation in the synthesis.[14] In addition, these solids exhibit very high surface areas (typically 1000−1200 m^2/g), high hydrocarbon sorption capacities, and thermal stability.

MCM-41, the well-known hexagonal member of this family, is usually prepared with hexadecyltrimethylammonium cations and possesses therefore mesopores whose dimension is in the 35−40 Å range. Patents suggest that MCM-41 and similar materials can be prepared at temperatures of between 50 and 250 °C, with corresponding synthesis times of 14 days and 5 min.[2] M41S have been reported to be formed by a liquid-crystal templating (LCT) mechanism.[14−17] Two different mechanistic pathways have been stipulated for the formation of MCM-41.[14,18] In the first one, liquid-crystal micelles are formed prior to addition of the silica source, while in the second one, silicate species influence the ordering of surfactant molecules. Vartuli et al.[19] recently reported that the first mechanism was very unlikely and that inorganic silicate anions played a prominent role in the formation of MCM-41. That was also the conclusion of Firouzi et al.[20]

Recently, Huo et al.[21] have extended the electrostatic assembly approach and proposed four complementary synthesis routes. In each route, molecular inorganic

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

(2) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C. U.S. Patent 5,102,643, 1992.

(3) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C. U.S. Patent 5,098,684, 1992.

(4) Beck, J. S. U.S. Patent 5,057,296, 1991.

(5) Beck, J. S.; Chu, C. T.-W.; Johnson, I. D.; Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C. U.S. Patent 5,108,725, 1992.

(6) Branton, P. J.; Hall, P. G.; Sing, K. S. W.; Reichert, H.; Schüth, F.; Unger, K. K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2965.

(7) Corma, A.; Navarro, M. T.; Perez-Pariente, J.; Sanchez, F. *Stud. Surf. Sci. Catal.* **1994**, *84*, 69.

(8) Franke, O.; Rathousky, J.; Schulz-Ekloff, G.; Starek, J.; Zukal, A. *Stud. Surf. Sci. Catal.* **1994**, *84*, 77.

(9) Llewellyn, P. L.; Schüth, F.; Grillet, Y.; Rouquerol, F.; Rouquerol, J.; Unger, K. K. *Langmuir* **1995**, *11*, 574.

(10) Rathousky, J.; Zukal, A.; Franke, O.; Schulz-Ekloff, G. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2821.

(11) Corma, A.; Navarro, M. T.; Perez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1994**, 147.

(12) Gontier, S.; Tuel, A. *Zeolites* **1995**, *15*, 601.

(13) Reddy, K. M.; Moudrakowski, I.; Sayari, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1059.

(14) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(15) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Stud. Surf. Sci. Catal.* **1994**, *84*, 53.

(16) Vartuli, J. C.; Kresge, C. T.; Leonowicz, M. E.; Chu, A. S.; McCullen, S. B.; Johnson, I. D.; Sheppard, E. W. *Chem Mater.* **1994**, *6*, 2070.

(17) Beck, J. S.; Vartuli, J. C.; Kennedy, G. J.; Kresge, C. T.; Roth, W. J.; Schramm, S. E. *Chem. Mater.* **1994**, *6*, 1816.

(18) Chen, C. Y.; Burkett, S. L.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 27.

(19) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem Mater.* **1994**, *6*, 2317.

(20) Firouzi, A.; Kumar, D.; Bull, L. M.; Besier, T.; Sieger, P.; Huo, Q.; Walker, S. A.; Zasadzinski, J. A.; Glinka, C.; Nicol, J.; Margolese, D. I.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, *267*, 1138.

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solution species and surfactant molecules assemble at relatively low temperature to form liquid-crystal-like arrays. The four synthesis pathways essentially differ by the electric charge of surfactant micelles and inorganic species. Following this classification, MCM-41 is usually synthesized following pathway I, corresponding to one of the pathways given in ref 21, involving the condensation of a cationic surfactant with anionic inorganic species.

More recently Tanev et al.[22,23] have shown that it was possible to prepare mesoporous molecular sieves using a neutral templating route. Materials are thus formed by a self-assembly of neutral primary amine micelles and neutral inorganic species via hydrogen-bond interactions. The materials thus obtained (HMS = hexagonal mesoporous silicas) differ from conventional M41S materials by larger wall thicknesses, smaller scattering domain sizes, and additional textural mesoporosity. A great advantage of this synthesis route with respect to that developed by Mobil researchers was that the template could be totally removed from the mesopores by solvent extraction. Such a template recovery was not possible for MCM-41 prepared following the original approach because of the strong electrostatic interactions between ionic surfactants and the charged framework. Attempts have been made by Schmidt et al.[24] and Whitehurst,[25] who showed that it was possible to extract partially the template from MCM-41 mesopores by washing the material with a solvent system containing at least one polar solvent and one cation donor. One of the best solvent/cation systems was the azeotropic mixture of heptane and ethanol containing 0.15 M HNO_3 as cation donor. However, the template associated with Al species could be hardly removed, and the procedure resulted in a partial dealumination of the samples. Thus, the total removal of the template could only be achieved by calcination of the solids in air at high temperature.

However, depending on the synthesis conditions MCM-41 may undergo structural modifications and a partial collapse of the mesopore system upon calcination in air. While pure silica materials are not drastically affected, this is not the case for aluminosilicate materials. It has indeed been reported that aluminum could be extracted from tetrahedral lattice positions upon calcination, particularly when the samples are prepared with relatively low Si/Al ratios.[26] Even though no data are reported in the literature on the subject, the removal of trivalent cations from tetrahedral positions is probably more important for Fe^{3+} or B^{3+}, which are known to be less stable in zeolitic framework than Al^{3+}.[27] Therefore, the synthesis of various trivalent metal containing mesoporous silicas by a templating route similar to that of Tanev et al.[23] and the possibility of removing the template by a solvent extraction may be a good alternative for preserving the mesoporosity of the materials and the coordination of incorporated cations.

In the present paper, we report the synthesis of various trivalent cations (Al^{3+}, Ga^{3+}, Fe^{3+}, and B^{3+}) containing mesoporous silicas using a primary amine as templating surfactant. We have examined the influence of the nature of the metallic cation on its incorporation into a mesoporous silica framework. We have also explored, for each cation, the limits within which the incorporation is possible. Template-free materials were obtained either by calcination in air at 650 °C or by a solvent extraction. The influence of both procedures on the preservation of the mesoporosity and on the nature of the trivalent cation site are discussed.

Experimental Section

Materials. The silica source was tetraethyl orthosilicate (TEOS, 98%) obtained from Aldrich. The surfactant molecule, hexadecylamine, was obtained from Aldrich. Isopropyl alcohol (RP, Normapur) and ethanol (RP, Normapur) were purchased from Rhône-Poulenc. Aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$, aluminum isopropoxide $Al(OiPr)_3$, gallium nitrate $Ga(NO_3)_3 \cdot 8H_2O$, iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, tributyl borate $B(OBu)_3$, and boric acid H_3BO_3 were all obtained from Aldrich. All chemicals were used as received and without further purification.

Instrumentation. X-ray powder diffraction patterns were collected on a CGR Theta 60 diffractometer using Cu Kα radiation. A phyllosilicate was used as an internal standard.

N_2 adsorption-desorption isotherms were obtained at 77 K on a CATASORB apparatus. The sample (typically 100 mg) was outgassed at 250 °C for about 10 h prior to adsorption. Pore size distribution curves were calculated using the Horvath−Kawazoe method.

Solid-state NMR spectra were collected on a Bruker MSL 300 FT spectrometer. Samples were placed into zirconia rotors and spun at 4 kHz in a double bearing probe head. ^{27}Al, ^{71}Ga, and ^{11}B NMR chemical shifts were taken with respect to $Al(H_2O)_6{}^{3+}$, $Ga(H_2O)_6{}^{3+}$, and Et_2OBF_3, respectively.

For ^{27}Al NMR measurements, a one-pulse sequence was used with a pulse length of 1 μs (corresponding to a flip of the magnetization of about 15°) and a repetition time of 1 s. Typically, 1000−2000 FIDs were accumulated to obtain a sufficiently good signal-to-noise ratio. The same paramerters were used to record ^{71}Ga spectra. However, due to the usually large ^{71}Ga NMR lines, 20 000−50 000 FIDs were accumulated.

^{11}B NMR spectra were collected with high power proton decoupling (HP/DEC). Because of the relatively short relaxation time of ^{11}B nuclei, the repetition time was only 0.2 s.

^{13}C NMR spectra could be obtained using a high-power proton decoupling sequence with a pulse length of 2 μs (corresponding to about 45°) and 10 s delay between consecutive scans. When necessary, a $^1H-^{13}C$ CP/MAS sequence was used. The $^1H-^{13}C$ contact time was optimized to 2 ms and the repetition time to 5 s.

Finally, ^{29}Si NMR data were collected using a one pulse sequence with a pulse length of 2 μs. Because of the very long relaxation time of silicon species, and particularly the Q^4 species in calcined samples, the delay between two consecutive acquisitions was 300 s. This corresponds approximately to the value used to obtain quantitative information in zeolites. This allowed us to estimate the fraction of ($Q^2 + Q^3$) species for each sample and, thus, the extend of dehydroxylation.

EPR spectra were obtained on a Varian E 9 spectrometer working in the X-band mode, at 295 or 77 K. Before recording the EPR spectrum, calcined samples were outgassed at 500 °C for about 2 h.

Chemical analysis was performed by atomic absorption after solubilization of the samples in HF−HCl solutions. Following this procedure the metal content could be estimated within an experimental error of ±2%.

Synthesis. In a typical synthesis, a first solution was prepared by mixing 1 mol of tetraethyl orthosilicate (TEOS) with 6 mol of ethanol and 1 mol of isopropyl alcohol. In the same time, a second solution was obtained by mixing the

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

(22) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*, 321.

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

(24) Schmidt, R.; Akporiaye, D.; Stöcker, M.; Ellestad, O. H. *Stud. Surf. Sci. Catal.* **1994**, *84*, 61.

(25) Whitehurst, D. D. U.S. Patent 5,143,879, 1992.

(26) Corma, A.; Fornès, V.; Navarro, M. T.; Perez-Pariente, J. *J. Catal.* **1994**, *148*, 569.

(27) De Ruiter, R.; Pamin, K.; Kentgens, A. P. M.; Jansen, J. C.; Van Bekkum, H. *Zeolites* **1993**, *13*, 611.

Table 1. Chemical Composition of the Different Samples

		Si/Me			
no.	sample	gel	product	yield (%)	org (%)
1	Al−HMS(100)	100	88	86	47
2	Al−HMS(100)[a]	100	97	89	55
3	Al−HMS(50)	50	38	85	49
4	Al−HMS(33)	33	27	74	44
5	Al−HMS(20)	20	21	63	31
6	Al−HMS(15)	15	8	50	42
7	Al−HMS(15)[b]	15	11	46	44
8	Al−HMS(15)[a]	15	9	57	54
9	Ga−HMS(100)	100	86	92	52
10	Ga−HMS(50)	50	48	83	46
11	Ga−HMS(33)	33	31	71	40
12	Ga−HMS(20)	20	14	56	32
13	Ga−HMS(15)	15	13	30	24
14	Fe−HMS(100)	100	85	89	55
15	Fe−HMS(50)	50	55	81	50
16	Fe−HMS(33)	33	29	82	50
17	Fe−HMS(20)	20	18	63	35
18	Fe−HMS(15)	15	15	48	29
19	B−HMS(100)	100	150	86	52
20	B−HMS(100)[c]	100	166	88	53
21	B−HMS(50)	50	95	82	51
22	B−HMS(50)[c]	50	94	87	50
23	B−HMS(15)	15	27	97	54
24	B−HMS(3)	3	17	96	52
25	B−HMS(1)	1	7	81	48

[a] The sample was prepared with aluminum ethoxide. [b] The sample was prepared with aluminum isopropoxide. [c] The sample was prepared using boric acid. Org (%) is the percentage of organic matter and water measured by the weight loss between 25 and 1000 °C.

hexadecylamine (0.3 mol) in water (36 mol). Depending on the nature of the trivalent metal precursor, the latter could be introduced in the first solution (for alkoxys such as $B(OBu)_3$) or in the second one. In the special case of aluminium isopropoxide, the precursor was hydrolyzed in water for about 12 h under vigorous stirring prior to addition to the second solution.

The two solutions were then mixed under stirring, and stirring was maintained at room temperature for about 1 h. Then stirring was stopped, and the product obtained aged at 25 °C for 12 h under static conditions. The resulting solid was recovered by centrifugation washed with distilled water and filtered 8−10 times. Finally, the as-synthesized sample was air-dried at room temperature for 24 h.

When the organic templating molecules were removed by a thermal treatment, 2 g of dried solid were placed in a quartz tube and slowly heated (1 °C/min) to 650 °C in an air flow for about 10 h. On the other hand, the template could also be removed by a solvent extraction. In this case, 1 g of dried solid was dispersed in 100 mL of ethanol containing 1 g of sodium chloride, and the mixture refluxed for 1 h. The solid was then separated from the organic solvent by filtration and washed several times with cold ethanol. The procedure was repeated once, and the template-free sample dried at 70 °C for 12 h.

All the samples were prepared following the above described procedure, using the required amount of trivalent metal in the precursor gel. In the following, samples will be denoted Me−HMS(*n*) were Me = Al, B, Fe, or Ga depending on the nature of the metal and *n* is the Si/Me ratio in the precursor gel.

Results and Discussion

Synthesis. The chemical composition of the different samples is listed in Table 1. As a general trend, we observe that the yield of solid is close to 80−90% when the amount of incorporated trivalent element is low (Si/Me > 50). For these samples, the amount of metal incorporated corresponds approximately to that introduced in the gel, except for boron, whose case will be discussed later. For higher metal contents (Si/Me < 50) the yield of product drastically decreases (Table 1). At the same time, the metal content in the solid phase is often higher than in the gel, suggesting a preferential incorporation of the trivalent metal as compared to silicon. This is particularly evident for Al- and Ga-substituted materials. Similar observations were previously reported in the case of zeolites, particularly when they were prepared with high aluminum contents.[28]

The case of boron is interesting as it is the single example were the boron content is significantly lower in the solid phase than in the precursor gel, particularly for samples prepared with high metal contents. In contrast to Al-, Ga-, or Fe-substituted mesoporous silicas, it is possible to obtain samples with low Si/B ratios in the solid phase in relatively high yields (sample B-HMS(1)).

Table 1 also shows that the nature of the trivalent metal precursor does not greatly influence the metal content in the final product (compare for example samples 1 and 2 or samples 19 and 20 in Table 1). However, care has to be taken when analyzing these data because samples with the same content in metal in the gel can have very different amounts of incorporated trivalent cations. Indeed, the synthesis requires the complete solubility of both Si and Me sources in the gel. In the case of metallic precursors with a relatively low solubility in water and alcohols, part of the precursor does not react with silica and surfactant molecules to form the mesoporous material. It is yet recovered by filtration with the solid and taken into account by chemical analysis. This is particularly the case of aluminum alkoxides, whose hydrolysis in water and alcohols is very slow.

In Table 1, the relative weight of organic matter and water in as-synthesized solids is also reported. For samples with a low amount of incorporated metal, it is typically between 45 and 55%. For high metal contents, we observed that the amount of organic matter decreases with incorporation. This is particularly evident on the series of Ga-substituted materials. The case of sample 8 (Al-HMS(15)) prepared with aluminum ethoxide is interesting and clearly demonstrates that the major part of aluminum is probably not incorporated into the silica framework. Indeed, the relative fraction of organics is very high, and corresponds to samples with Si/Al $\approx$ 100. Spectroscopic investigation of the sample will effectively demonstrate that the major part of aluminum is octahedrally coordinated, i.e., at non-framework positions.

The maximum trivalent cation incorporation is approximately the same for Al, Ga, and Fe and corresponds to Si/Me of about 10 in the solid phase. When syntheses are performed with higher metal contents, the yield of solid is very low and spectroscopic investigation of the samples shows the presence of extraframework octahedrally coordinated species. As an example, when a precursor gel is prepared with Si/Al = 5, no solid is obtained even after 24 h of aging at room temperature. This is of course not the case for boron-containing samples that could be prepared with Si/B < 0.5 in the gel. Chen et al.[18] have shown that aluminosilicate MCM-41 could be prepared with Si/Al ratios as low as 29, without observing the presence of octahedral aluminum. Calabro et al.[29] claimed the synthesis of MCM-41 materials with Si/Al ratios below 10, using a di-

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(28) Derouane, E. G.; Detremmerie, S.; Gabelica, Z.; Blom, N. *Appl. Catal.* **1981**, *1*, 201.

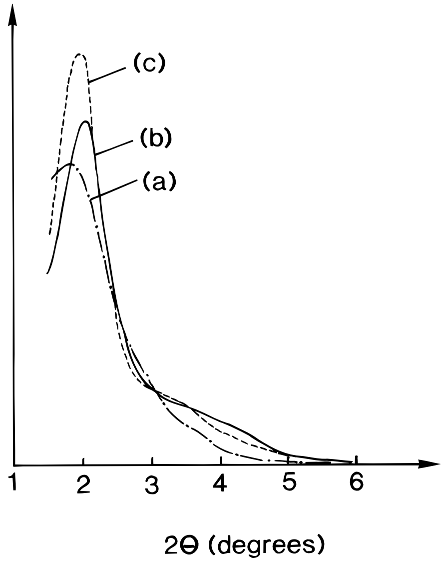

Figure 1. X-ray diffraction patterns of aluminum-containing mesoporous silica (sample 4). As-synthesized form (a), calcined at 650 °C in air (b), and solvent-extracted (c).

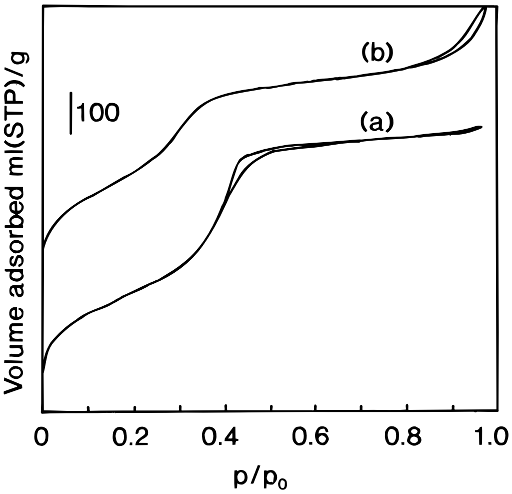

Figure 2. N_2 adsorption−desorption isotherms of aluminum-containing mesoporous silicas. Sample 1 (a) and sample 5 (b) were calcined in air at 650 °C.

Table 2. Characteristics of Various Samples

		Si/Me			
no.	sample	gel	product	S (m^2/g)	Φ_p (Å)[a]
1	Al−MS	100	88	1215 (1166)	30 (36)
4	Al−MS	33	27	1210	25
5	Al−MS	20	21	983 (1079)	32 (37)
6	Al−MS	15	6	1252	22
10	Ga−MS	50	48	929	28
11	Ga−MS	33	31	1125 (1091)	24 (37)
15	Fe−MS	50	55	700 (935)	22 (37)
19	B−MS	100	150	(1056)	(36)
23	B−MS	15	27	1237	32
24	B−MS	3	17	(935)	(38)

[a] Φ_p is the pore diameter obtained from N_2 isotherms. Values in parentheses have been obtained on solvent-extracted samples.

alkoxyaluminotrialkoxysilane as silica−alumina source. More recently, Borade et al.[30] reported the synthesis of Al-rich MCM-41 with Si/Al = 2 in the solid phase. However, the state of Al in calcined samples was not shown, and X-ray diffraction data revealed that the solid did not possess regular mesopores, suggesting that it almost completely collapsed upon thermal treatment.

Characterization of As-Synthesized and Calcined Samples. *X-ray Diffraction.* X-ray powder patterns of most of the as-synthesized samples consist of a single broad peak (reflection (100)) centered around $2\theta = 2°$ and corresponding to a d spacing of about 4.3 nm (Figure 1). This value is of the same order as that reported by Tanev et al. on pure silica materials.[23] Additional reflections (110) and (200) usually observed in ordered MCM-41 materials around $2\theta = 5°$ and characteristic of a hexagonal arrangement of the pores are not observed. This has been attributed to a broadening of X-ray reflections due to relatively small scattering domains arising from the disorder of the materials as compared to MCM-41.[23] However, in some cases, a broad shoulder is observed at about 4−5°, suggesting the presence of a relatively short-range hexagonal order in the sample.

For samples containing low amounts of trivalent cations, calcination in air does not significantly modify the X-ray pattern. The (100) reflection is slightly shifted to higher θ values, indicating a small contraction of the mesopores with respect to as-synthesized samples. On the other hand, when samples were prepared with high metal contents, the mesoporous system partially collapses upon calcination in air, which will be confirmed by N_2 adsorption measurements.

N_2 Adsorption−Desorption Isotherms. The N_2 adsorption−desorption isotherms of two aluminum-containing samples (samples 1 and 5) are depicted in Figure 2. For low aluminum contents, the isotherm is very similar to that usually reported for MCM-41 materials. For higher contents, an hysteresis loop is found at high relative pressures ($p/p_0 > 0.8$). Such a hysteresis has already been observed on both M41S and HMS materials, and it was attributed to a textural or interparticle mesoporisity.[22] This contrasts with data previously published by Tanev et al.,[22] who claimed that a major difference between pure silica MCM-41 and HMS was the presence of additional textural mesoporosity in the latter. However, we have already observed the absence of textural mesoporosity in Ti-containing mesoporous silicas prepared following a recipe similar to that of Tanev et al.[23]

All samples exhibited very high surface areas (typically 900−1200 m^2/g), except solids containing high metal contents (Table 2). We could not find any correlation between the surface area of the samples and the amount of incorporated metal. This was not the case for Ti- or V-containing materials where we observed a continuous decrease in both the surface area and pore volume with the extent of metal incorporation.[12,31]

Horvath−Kawazoe pore size distribution curves show that the pore dimension of the various calcined samples is usually smaller than that of pure silica materials, suggesting that the mesoporous system of most of the samples partially collapses upon calcination in air. This is particularly evident for samples containing relatively high amounts of incorporated trivalent metal (Table 2), which confirms X-ray diffraction observations. This strongly demonstrates that incorporation of trivalent cations in a mesoporous silica reduces its thermal stability. That was not the case for pure silica materials

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(29) Calabro, D. C.; Schmitt, K. D.; Vartuli, J. C. U.S. Patent 5,110,572, 1992.

(30) Borade, R. B.; Clearfield, A. *Catal. Lett.* **1995**, *31*, 267.

(31) Gontier, S.; Tuel, A. *Microporous Mater.*, in press.

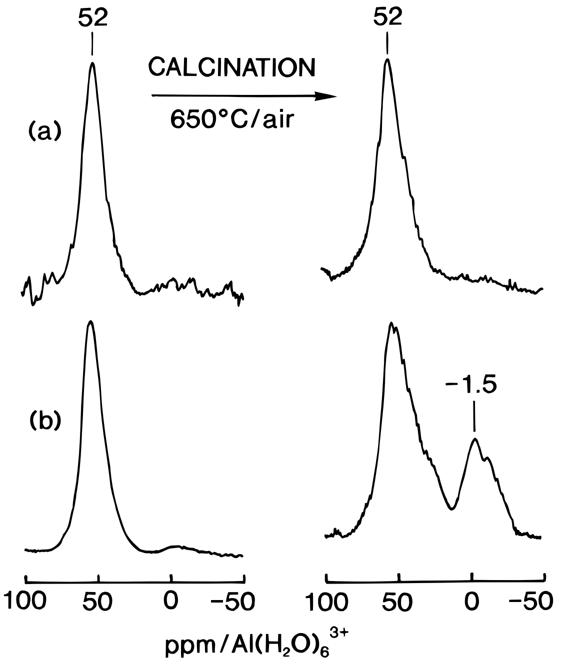

Figure 3. ^{27}Al MAS NMR spectra of sample 1 (a) and 5 (b) before (left) and after (right) calcination in air at 650 °C.

where the mesopores were not drastically affected by calcination. As will be discussed later, the partial degradation of the pores more likely results from stronger electrostatic interactions between the organic micelles and the framework when samples contain trivalent metal cations.

NMR Data. As-synthesized Al−mesoporous silica samples 1−6 show a single and relatively broad peak at about 52 ppm (Figure 3). The line shape and position are very similar to those already reported for MCM-41 for which the peak was attributed to 4-coordinated structural aluminum species.[26] For higher Al contents, the spectrum shows an additional band around 0 ppm, characteristic of octahedrally coordinated aluminum species. This demonstrates that part of the aluminum introduced in the gel was not incorporated in the silica framework during synthesis.

In the same manner, the sample prepared with Al(OC$_2$H$_5$)$_3$ (sample 8) contains more than 75% of its aluminum as nonframework species. As mentioned earlier, the presence of octahedrally coordinated Al species in this sample probably results from the low solubility of the precursor in the synthesis mixture.

After calcination in air, the ^{27}Al MAS NMR spectra of samples 1−3 (Al−HMS(100) and Al−HMS(50)) containing less than 1.5 wt % Al still show a single broad signal around 52 ppm (Figure 3). However, the peak broadens upon calcination, which is the result of modifications of the quadrupolar moment of ^{27}Al nuclei upon dehydration at high temperature. Similar observations have been reported in the past over zeolites.[32] Indeed, a much narrow line and, thus, a higher signal-to-noise ratio could be easily recovered by contacting the calcined samples with water vapor for 24 h prior to acquisition of the NMR spectrum.

For samples with a higher Al content, calcination in air at 650 °C results in a partial removal of framework aluminum (Figure 3). This had already been observed by Corma et al.[26] on Al-containing MCM-41 materials. We observed that the fraction of extracted aluminum increased with the total amount of aluminum in the sample.

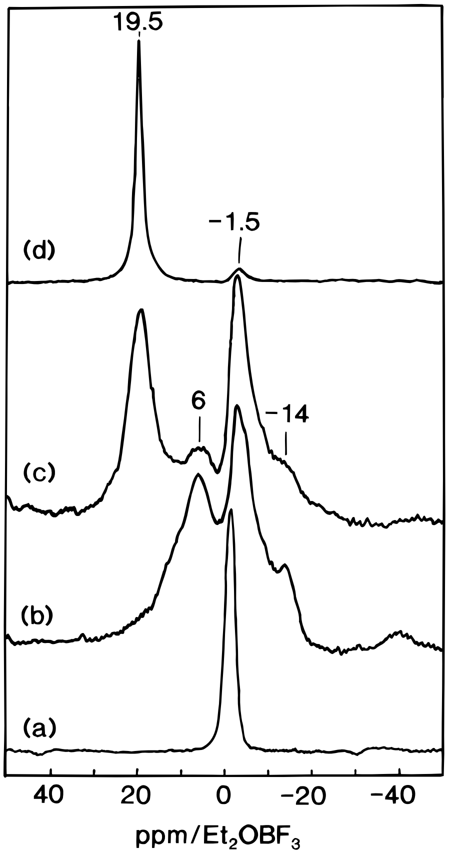

Figure 4. ^{11}B MAS NMR spectra of sample 24. As-synthesized form (a), calcined in air at 650 °C (b), calcined and partially rehydrated with water (c), and totally rehydrated (d).

Very similar observations could be made with boron containing mesoporous silicas. The ^{11}B MAS HP/DEC NMR spectra of as-synthesized materials are composed of a single and relatively narrow line at −1.5 ppm, even for samples containing high boron contents (Figure 4). Such a line has already been reported for boron-containing zeolites and characterizes B^{3+} cations in a tetrahedral environment. Coudurier et al.[33] have published a detailed study of the nature and coordination of boron in boron-substituted zeolites. Their conclusion was that the narrow peak at about −2 ppm observed in as-synthesized or partially hydrated calcined samples could be assigned to B(OSi)$_4$ units.

Upon calcination in air at 650 °C, the ^{11}B NMR spectrum is modified and a second resonance, with a broad characteristic quadrupolar shape is observed (Figure 4). Scholle et al.[34] obtained the same signal upon dehydration of H-boralite and assigned it to BO$_3$ units. They also reported that the narrow line at −3 ppm could be easily recovered upon rehydration of the sample. In the case of B-containing mesoporous silicas, it is interesting to note that lines broaden upon calcination in air (particularly that at −1.5 ppm), which was already observed for aluminum spectra. When the calcined samples are contacted with water vapor at room temperature for 24 h, both peaks at −1.5 ppm and

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(32) Kentgens, A. P. M.; Scholle, K. F. M. G. J.; Veeman, W. S. *J. Phys. Chem.* **1983**, *87*, 4357.

(33) Coudurier, G.; Auroux, A.; Vedrine, J. C.; Farlee, R. D.; Abrams, L.; Shannon, R. D. *J. Catal.* **1987**, *108*, 1.

(34) Scholle, K. F. M. G. J.; Veeman, W. S. *Zeolites* **1985**, *5*, 118.

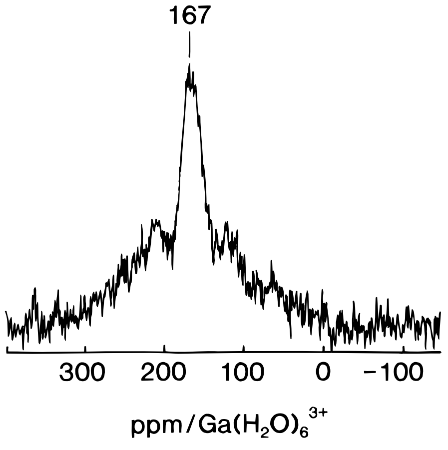

Figure 5. ^{71}Ga MAS NMR spectrum of as-synthesized sample 11.

that attributed to BO$_3$ units decrease. Simultaneously, a new and narrow line is observed at about 20 ppm, whose attribution will be discussed elsewhere (Figure 4). However, the situation is totally reversible and the initial spectrum can be restored upon dehydration of the samples at 500 °C for 10 h.

Figure 5 shows the ^{71}Ga MAS NMR spectrum of a Ga-substituted mesoporous silica (sample 11, as-synthesized). The line is very broad, and consequently the signal-to-noise ratio is low. However, the ^{71}Ga nuclei have a spin $^3/_2$ and a natural abundance of only 40%, as compared to ≈100% for ^{27}Al and ^{11}B. The important line width is probably due, as for aluminum- and boron-substituted materials, to distortions of the tetrahedral Ga(OSi)$_4$ units resulting from the absence of crystallinity of the materials. However, even though the spectrum is not very well resolved, the ^{71}Ga NMR chemical shift characterizes tetrahedrally coordinated Ga species. Indeed, similar ^{71}Ga NMR shifts were reported in various Ga-substituted zeolites.[35−37] Moreover, as in the case of aluminum, octahedrally coordinated species are always detected around 0 ppm. It was impossible to record a ^{71}Ga NMR spectrum of calcined samples. Indeed, it has been shown that ^{71}Ga NMR lines drastically broaden upon calcination, probably because of modifications of the quadrupolar moment, and that signals are very difficult to observe even in the case of highly crystalline zeolites.[37] Some authors have mentioned that contacting calcined Ga-substituted zeolites with water or acetylacetone could help in recording spectra by decreasing the relaxation time of ^{71}Ga nuclei.[38] However, the procedure also extracted part of the framework Ga species and could not thus be applied to determine the real coordination of these species.[39]

^{29}Si MAS NMR spectra of as-synthesized samples show three distinct peaks at −90, −98, and −109 ppm/TMS (Figure 6). By comparison with data obtained on amorphous silicas, MCM-41, and zeolites,[14,40,41] these peaks can be unambiguously attributed to Q^2, Q^3, and Q^4 species, respectively. Because of the relatively low amount of incorporated metal in the samples, the contribution of Si(OSi)$_3$Me and Si(OSi)$_2$Me$_2$ species to the NMR signal was negligible. The $f_s = (Q^2 + Q^3/Q^2 + Q^3 + Q^4)$ ratio that characterizes the fraction of silanol groups in the samples is close to 0.5 and does not seem to depend on the trivalent metal content. The ^{29}Si NMR spectra of calcined samples are less well resolved and show a single broad band around −107 ppm/TMS (Figure 6). Deconvolution of the spectra into three peaks shows that the above ratio decreases upon calcination to about 0.25, resulting from the condensation of silanol groups to form Q^4 species.

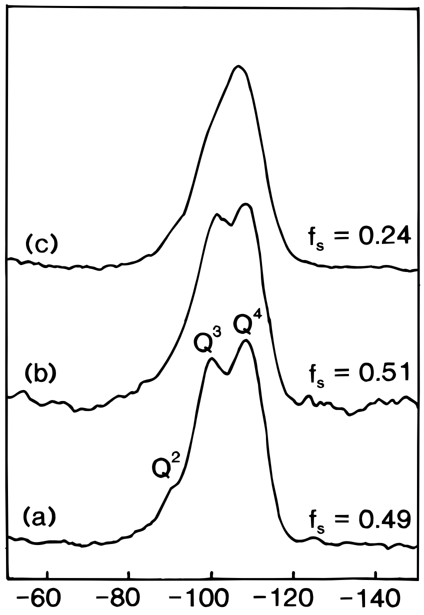

Figure 6. ^{29}Si MAS NMR spectrum of sample 4. As-synthesized form (a), solvent extracted (b), and calcined in air at 650 °C (c). f_s corresponds to the fraction of silanol groups as defined in the text.

EPR Spectroscopy. The EPR spectrum recorded at 77 K of a typical iron-containing mesoporous silica is shown in Figure 7. The spectrum can be deconvoluted into three components I, II, and III, whose g values are 4.4, 2.4, and 2, respectively. Similar spectra were previously reported by Lin et al.[42] on Fe-ZSM-5. Following these authors, site I corresponded to Fe-substituted sites where the negative charge of the Fe atoms were compensated by protons. Site II was attributed to Fe in a trigonal environment Fe(OSi)$_3$, whereas site III characterized tetrahedrally coordinated Fe cations whose charge was compensated by a framework defect. Their assignment was supported by the fact that the relative intensities of sites II and III were approximately 1 for all samples. When the amount of Fe is increased in our samples, we observed an increase of the intensity of sites II and III with respect to site I.

The EPR spectrum is drastically affected by calcination of the sample in air at 650 °C (Figure 7). In contrast to what is usually observed for Fe-containing zeolites, site II almost disappears, whereas site III remains practically unchanged (Figure 7). The disappearance of site II strongly supports the absence of iron

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(35) Timken, H. K. C.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *109*, 7669.

(36) Zhi, Y.-X.; Tuel, A.; Ben Taârit, Y.; Naccache, C. *Zeolites* **1992**, *12*, 138.

(37) Bellussi, G.; Millini, R.; Carati, A.; Maddinelli, G.; Gervasini, A. *Zeolites* **1990**, *10*, 642.

(38) Bayense, C. R.; Kentgens, A. P. M.; De Haan, J. W.; Van de Ven, L. J. M.; Van Hooff, J. H. C. *J. Phys. Chem.* **1992**, *96*, 775.

(39) Bayense, C. R.; Van Hooff, J. H. C.; Kentgens, A. P. M.; De Haan, J. W.; Van de Ven, L. J. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1292.

(40) Tuel, A.; Hommel, H.; Legrand, A. P.; Chevalier, Y.; Morawski, J. C. *Colloids Surf.* **1990**, *45*, 413.

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

(42) Lin, D. H.; Coudurier, G.; Vedrine, J. C. In Jacobs, P. A., Van Santen, R. A., Eds.; *Zeolites: Facts, Figures and Future*; Elsevier Science Publishers, B.V.: Amsterdam, 1989; p 1431.

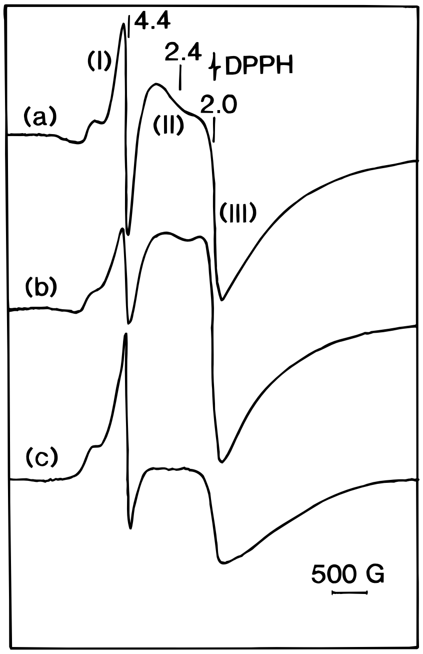

Figure 7. EPR spectra of iron-containing mesoporous silicas. Sample 14 (a), sample 17 (b), and sample 14 after calcination in air at 650 °C (c).

oxide species in the calcined samples as that signal was also attributed by different authors to superparamagnetic tiny oxide particles. That was also confirmed by UV−vis spectroscopy.

Solvent Extraction of the Template. For pure silica materials, Tanev et al.[23] have reported that washing a mesoporous silica with boiling ethanol resulted in the total removal of primary alkylamines from the mesopores. The solvent extraction had the advantage with respect to a conventional thermal treatment to preserve the mesoporosity of the sample and to prevent framework degradation upon burning off the organics. However, that could be possible because of the weak interactions between the neutral organic micelle system and the inorganic framework. When trivalent cations are tetrahedrally coordinated in a silica matrix, they create a charge defect that has to be compensated by cations. In zeolites, these are usually alkali cations like Na^+ or K^+ that can be introduced directly in the synthesis gel. When no cations are present, the charge is balanced by templating molecules, generally tetraalkylammonium cations. Upon calcination, protons formed during the thermal decomposition of the organics maintain the neutrality of the system. As the present mesoporous materials are prepared in the absence of alkali and ammonium cations, the only way to preserve the electrical neutrality is to suppose that primary ammonium cations are formed in situ during synthesis. However, if it is really the case, the interaction between the templating molecule and the inorganic framework will be stronger than in the case of pure silica materials. As a consequence, we may expect the template removal by a solvent extraction to be less efficient. However, it has been recently reported that ionic template recovery was possible, provided that exchange ions or ion pairs are present in the extraction process.[24,25]

We have first followed the recipe of Tanev et al.[23] to try to remove the template, i.e., the dried samples were refluxed twice in ethanol for about 1 h. The removal of templating molecules from the mesopores was monitored by infrared and solid-state NMR spectroscopies. The procedure removes nearly all the organics as evidenced by a strong decrease of specific absorption bands in IR spectra. However absorptions characteristic of templating molecules still persist in the IR spectrum, even after three ethanol extractions. ^{13}C CP/MAS NMR confirms the persistence of organic molecules within the samples. The ^{13}C NMR spectrum shows small differences with respect to that of hexadecylamine in as-synthesized products (Figure 8). The signal-to-noise ratio is low, but that is a consequence of the very small amount of organics remaining in the mesopores after ethanol extraction. More interesting is the presence of a peak at about 41 ppm/TMS, that has been attributed to carbon atoms directly bonded to primary ammonium cations.[43] These cations, that were not removed in boiling ethanol, are more likely in the proximity of Me^{3+} cations and serve to maintain the electric neutrality of the material.

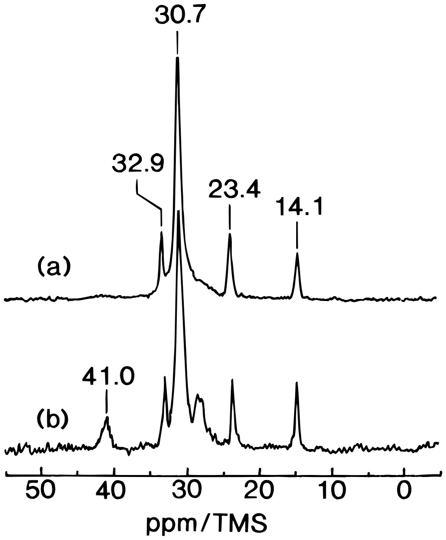

Figure 8. ^{13}C CP/MAS NMR spectra of as-synthesized sample 5 (a) and sample 5 after 3 ethanol extractions (b). To normalize the spectra, the intensity of spectrum (b) was multiplied by a factor of 20.

We can therefore propose that the synthesis of trivalent-metal-containing mesoporous silicas is essentially based on a neutral templating process. The major part of organic species are neutral alkylamines, not strongly bonded to the silanol groups of the inorganic framework and can be easily removed by a pure ethanol extraction. However, the presence of trivalent cations in a tetrahedral coordination necessitates the protonation of a small amount of primary amines to maintain the electrical neutrality of the material. These primary ammonium cations are more strongly retained in the mesopores and difficult to remove by ethanol extraction.

We thus tried to add inorganic cations to the extraction solvent to exchange the primary ammonium cations. The extraction procedure was similar to that previously described except that sodium chloride was preliminary dissolved in ethanol (1 g/100 mL ethanol). IR spectroscopy as well as ^{13}C NMR clearly show that all the organics were then removed, even in samples containing high metal contents (Figure 9). Therefore,

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(43) Boxhoonn, G.; Van Santen, R. A.; Van Erp, W. A.; Hays, G. R.; Alma, N. C. M.; Huis, R.; Clague, A. D. H. Proc. 6th Int. Zeolite Conf., (Reno, 1983); Butterworth: Guildford, 1985; p 694.

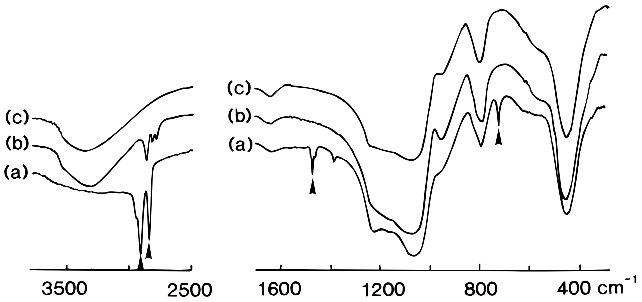

Figure 9. Infrared spectra of sample 5 as-synthesized (a), solvent-extracted (b), and calcined in air at 650 °C (c). Absorption typical of occluded amines are indicated by arrows.

to be sure that all templating molecules were removed, the ethanol/NaCl system was adopted for all the samples. It is interesting to note that the band at 960 cm^{-1} in IR spectra that characterizes Si–O$^-$ groups[44] is much more intense for solvent-extracted samples than for calcined samples (Figure 9). Indeed, calcination at high temperature results in a partial dehydroxylation of the samples due to the condensation of paired silanols.

Even though infrared spectra of the solvent extracted samples show that all the templating molecules have been removed, new adsorptions are observed around 2900 cm^{-1}. These C–H vibrations are characteristic of Si–O–C_2H_5 species, formed after partial esterification of the samples upon solvent extraction. The attribution of these bands was supported by a significant decrease of the intensity of the OH IR band at 3745 cm^{-1}.

Chemical analysis shows that the extraction does not modify the composition of the samples. In particular, and in contrast to previous observations made by Schmidt et al.,[24] the removal of organics is not accompanied by a partial extraction of trivalent cations from the silica framework.

X-ray diffraction patterns of extracted samples are similar to those of calcined samples and exhibit a single diffraction peak corresponding to a *d* spacing of about 4.2 nm. As already mentioned by Tanev et al.,[23] the intensity of the peak of extracted samples is high compared to that of calcined samples, reflecting some degradation of the mesopore system upon calcination in air at high temperature.

N_2 adsorption–desorption isotherms are quite similar to those of calcined samples, but the inflexion point at $p/p_0 \approx 0.4$ is slightly higher for solvent-extracted samples. That indicates that the pore dimension is smaller in calcined samples, thus confirming the partial collapse of the structure upon calcination. This is particularly evidenced in Figure 10 where the Horvath–Kawazoe pore size distribution curves of sample 5 calcined and submitted to a solvent extraction are compared. After removal of the template by a solvent extraction, all samples exhibit high surface areas and pore sizes of about 37 Å (Table 2). This value is relatively high as compared to those reported by Tanev et al.[23] for pure silica materials prepared following a similar recipe. However, incorporation of Al^{3+} in the silica matrix increases the lattice parameter and, thus, the pore dimension.[14] Nevertheless, the value is very close to that reported by different authors on aluminosilicate MCM-41 materials.[14]

Figure 11 compares the ^{27}Al MAS NMR spectra of sample 5 as-synthesized, calcined at 650 °C in air and submitted to a solvent extraction. We had previously observed that calcination of the sample in air resulted

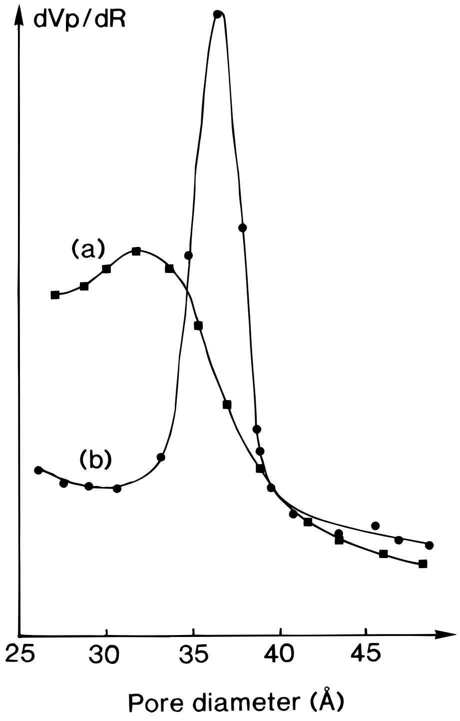

Figure 10. Horvath–Kawazoe pore size distribution curves of sample 5 calcined in air at 650 °C (a) and solvent-extracted (b).

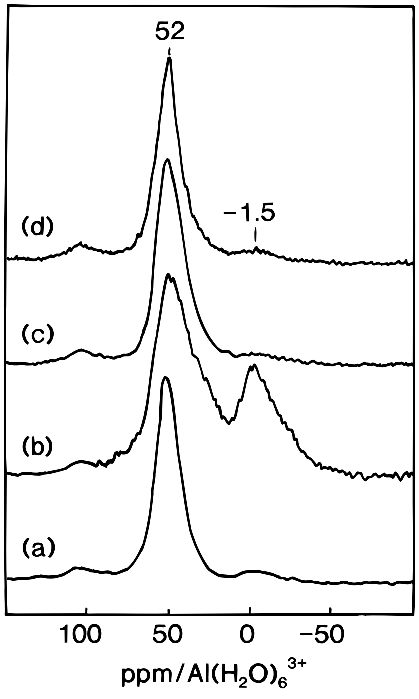

Figure 11. ^{27}Al MAS NMR spectra of sample 5. As-synthesized form (a), calcined in air at 650 °C (b), solvent-extracted (c), and calcined in air at 500 °C after the solvent extraction (d).

in the removal of part of the framework aluminum, evidenced by the presence of an additional NMR line around 0 ppm. As clearly demonstrated in the figure, the solvent extraction method preserves the coordination of the trivalent cation, as no octahedrally coordinated species are detected. The ^{27}Al NMR spectrum is identical to that of the as-synthesized sample. Moreover, the spectrum is unchanged when the solvent extraction is followed by a calcination in air at 500 °C. That confirms that the formation of octahedral alumi-

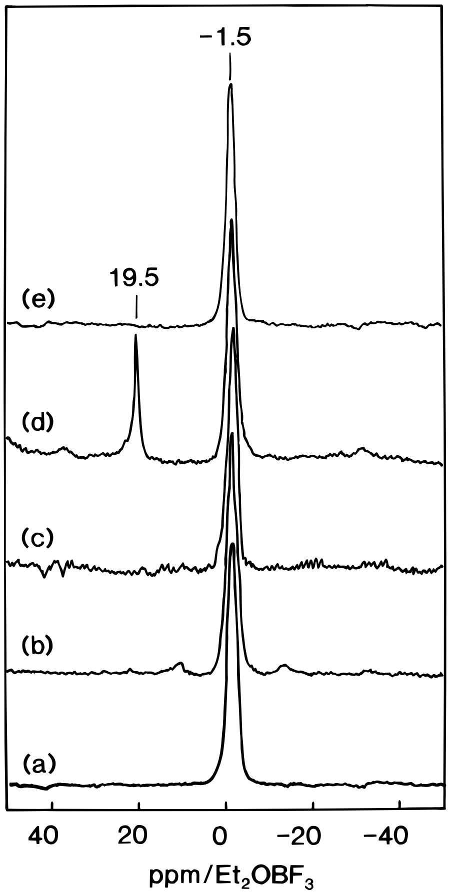

Figure 12. ^{11}B MAS NMR spectra of sample 24. As-synthesized form (a), solvent-extracted (b), solvent-extracted and partially rehydrated (c), solvent-extracted and rehydrated for 24 h (d), and solvent-extracted and calcined at 500 °C in air (e).

num species more likely occurs during the decomposition of organic templating molecules at high temperature.

Similarly, when the template is removed by a solvent extraction from boron-containing mesoporous silicas, the ^{11}B NMR spectrum is very different from that of the corresponding calcined sample. A single narrow line identical in shape and position to that of as-synthesized samples is observed at -1.5 ppm and characterizes B(OSi)$_4$ units (Figure 12). As for aluminum-containing materials, subsequent calcination does not modify the NMR spectrum. When a boron-containing solvent-extracted material is rehydrated with water vapor at room temperature, the peak at 20 ppm that was almost immediately observed on calcined samples is not detected, except for very long periods of exposure (Figure 12). One explanation could be that Si$-$O$-$C$_2$H$_5$ species formed upon solvent extraction increase the hydrophobic character of the material. This may explain why boron sites inside the mesopores are less affected by the presence of water than in the corresponding calcined samples. As in the case of aluminum, calcination of the solvent-extracted samples does not affect the coordination of B^{3+} cations in the mesopores.

EPR spectroscopy shows that the solvent extraction method also preserves the coordination of Fe^{3+} cations in mesoporous silicas. EPR spectra are identical to those of as-synthesized samples and are not affected by a subsequent calcination in air.

The ^{29}Si MAS NMR spectra of solvent extracted samples are strictly similar to those of the corresponding as-synthesized materials (Figure 6). The fraction of silanol groups estimated from these spectra are the same as those of the starting solids, thus confirming the preservation of the framework. However, a small amount of the species observed at -100 ppm/TMS in ^{29}Si NMR spectra are probably Si$-$O$-$C$_2$H$_5$ moities, due to a partial esterification of silanol groups during the solvent extraction.

Conclusion

We have shown that trivalent-metal-containing mesoporous silicas could be prepared using a primary alkylamine as liquid-crystal surfactant molecule. As in the case of pure silica materials, these solids were characterized by the presence of a single X-ray diffraction peak, a system of regular mesopores and high surface areas. The physical properties of the products, and particularly their surface area did not significantly change with the amount of incorporated metal. Following this recipe, mesoporous silicas containing tetrahedrally coordinated trivalent cations could be synthesized with Si/Me ratios as low as 10 without observing the presence of octahedral species.

Removal of the templating molecules by calcination in air resulted in a partial collapse of the mesopores and in the extraction of trivalent cations from their framework positions. A solvent-extraction with pure boiling ethanol removed almost entirely the organics. Nevertheless, primary ammonium cations formed during the synthesis to maintain the neutrality of the system remained. They could however be easily removed by addition of cations, e.g., NaCl, in the extraction system.

That procedure preserved not only the mesoporosity of the materials but also the coordination of trivalent cations. Solvent-extracted materials were thermally stable and could be calcined at 500 °C in air without modification of the cation coordination. The subsequent calcination was actually necessary to eliminate ethoxy groups bonded to the silica framework and formed during the extraction process.

The synthesis route presented is thus very promising for preparing template-free mesoporous silicas containing relatively high amounts of tetrahedrally coordinated trivalent cations.

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