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Ordered mesoporous aluminosilicates with very low Si/Al ratio and stable tetrahedral aluminum sites for catalysis

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Abstract

New and ordered 2D-hexagonal (*p6mm*) mesoporous aluminosilicates (CMI-11) have been synthesized in strongly alkaline media using aluminosilicate ester ($(Bu^sO)_2$-Al-O-Si-$(OEt)_3$) as single-source molecular precursor and CTMABr as surfactant and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption–desorption and ^{27}Al and ^{29}Si MAS NMR spectroscopy. These mesoproous aluminosilicates exhibit a very low Si/Al ratio of 1.9 and highly thermal stable tetrahedral aluminum sites in the mesoporous walls. ^{27}Al and ^{29}Si MAS NMR spectroscopy indicates that the pore walls of CMI-11 are fully condensed with molecular homogeneity of Si–O–Al linkage. These materials are highly important in catalysis, in particular for the petroleum processing and the bulky molecules treatment.

Keywords: Mesoporous aluminosilicate; Synthesis; Strong alkaline condition; Molecular homogeneity; Al–O–Si linkage; Aluminosilicate ester

1. Introduction

The synthesis of mesoporous (2–50 nm) silicas M41S in 1992 using a supramolecular surfactant system as a template provoked a great ''Boom'' in the field of nanoporous materials [1–7]. In particular, a special attention has been devoted to develop mesostructured aluminosilicates since aluminosilicate is one of important chemical compositions in catalysis and separation processes of high molecular weight petroleum fractions [1,2]. There are a number of successful approaches to introduce heteroatoms (T) such as Al and Ti species into mesoporous silica materials by direct-synthesis or post-grafting methodology [3–38]. It is still of a major challenge for the synthesis of mesoporous aluminosilicates with the lowest Si/Al ratio (1), i.e. Al content as high as possible and highly stable tetrahedral aluminum sites, due to the amorphous nature of the mesopore walls and the complexity in the synthesis.

All the actual preparation methods conducting to the incorporation of heteroatoms in mesoporous silica network whatever direct-synthesis or post-synthesis joins to one common point that independent and separated heteroatom sources have to be used either to introduce in the silica gel or to contact with the pre-synthesized mesoporous silica. All these methods which are expected to generate the secondary link between silica source and aluminum source would lead either to relatively low heteroatom content, or to extra framework heteroatom species, or to lower order of mesostructure, or to an anchor of heteroatom species only on the surface of channels. The principle reason of these relevant issues is that a new Si–O–T bond has to be constructed from two independent precursors (direct-synthesis) or from a secondary precursor with the surface of preformed mesoporous silica framework (post-synthesis). The different hydrolysis and condensation rates of any two independent precursors will unavoidably lead to the heterogeneity of Si and T atoms in the framework or to the low organization and to the presence of extra-framework species since the homocondensation of one source predominates over the heterocondensation between two different precursors [36].

Another drawback of actual mesoporous aluminosilicate materials in their applications reside in its amorphous nature of the mesopore walls with heterogeneously distributed Al atoms in the framework, giving the heterogeneity of acid sites, impossible to use as acid catalysts with high selectivity for the efficient reactions. Although zeolite mesoporous aluminosilicate composites [21–23,38–50] can be prepared by quite different routes, the synthesis of one single phase mesoporous

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aluminosilicate materials with homogeneously distributed and accessible acid sites throughout the framework remains a great technical challenge in the field of materials and catalysis.

The question can then arise as to whether a single-source molecular precursor containing already the Si–O–T bonds can be used in the synthesis. We can expect a well organized framework with a Si/T ratio as low as possible up to unit, in another word, the T content as high as possible. Heteroatoms can molecularly and homogenously distributed because the heteroatoms are initial part of the same molecule and their presence in the framework is owing to the existence of Si–O–T linkage in this single molecular source.

The first attempt of this kind was demonstrated by Tilley and co-workers [51,52] using $Zr[OSi(O^tBu)_3]_4$, $(EtO)_2Ta[O\text{-}Si(O^tBu)_3]_3$, $Fe[OSi(O^tBu)_3]_3{\cdot}THF$ and $[Al(O\text{-}i\text{-}Pr)_2O_2P(O\text{-}t\text{-}Bu)_2]_4$ and block copolymer as templates to synthesize mesostructured mixed-element oxides such as $ZrO_2{\cdot}4SiO_2$, $Ta_2O_5{\cdot}6SiO_2$, $Fe_2O_3{\cdot}6SiO_2$ and $AlPO_4$. In spite of the lack of long range order reflected by the relatively poor XRD patterns and TEM images, this is still a nice and elegant idea which can generate a new synthesis route for the design of mesoporous multi component oxides with molecularly homogenous frameworks. Another advantage of this kind of ''single-source molecular precursor'' resides in that the heteroatoms are located in the center of these molecular precursors and Si–O–T bonds can be protected, because the hydrolysis and polycondensation can only occurs in the side of unique alkoxide functionality such as $–OSi(O\text{-alkyl})_n$ and $O\text{-(o)}P(O\text{-alkyl})_n$ ($n \geq 1$). However, the single sources used by Tilley et al. cannot allow to synthesize the compounds with Si/T equal to unit. While in some areas such as catalysis, it is desirable to introduce T atom content in a well ordered framework as high as possible for an optimal activity and selectivity.

In our preliminary study, aluminosilicate ester ($(Bu^sO)_2$-Al-O-Si-$(OEt)_3$) was used as a single source of silicon and aluminum elements for the synthesis of ordered mesoporous aluminosilicates [53]. This single-source molecular precursor, different from those used by Tilley and co-workers [51,52], contains two alkoxide functionalities, one on Si side and another on Al side. Both functionalities can undergo the hydrolysis and polycondensation, which allow to design a nice chemistry to construct a continuous Si–O–Al framework as encountered in low silicon content faujasite X zeolite (LSX, Si/Al = 1.0). The use of aluminosilicate ester containing ordered Al–O–Si linkage on the molecular scale renders possible the precise control of the structure and active sites in the mesoporous materials. However, the hydrolysis and polycondensation rate of aluminium alkoxides is much higher than that of alkoxysilanes in aqueous solution. The polymerization can occur primarily through Al–O–Al bonding, conducting to Al–O–Si linkage cleavage [24,36,54]. The great challenge in the synthesis of high Al content and highly ordered mesoporous aluminosilicates using this single molecular precursor is therefore to balance the hydrolysis and polycondensation rates of two alkoxide functionalities. Thus, we have used acetone and alkylacetone to slow down the hydrolysis rate of metal alkoxides [53], resulting in the successful synthesis of highly ordered mesoporous silicoaluminates CMI-10 with the lowest Si/Al of 1.0 [53]. However, the synthesis of ordered mesoporous materials under organic solution cannot be extended to alkaline condition, because the triblock copolymer surfactants are not ordered micelle under alkaline media. Li et al. and Amorós et al. [24,54] have reported the synthesis of mesoporous materials under alkaline condition using aluminosilicate ester. However, the lack of long range mesostructured order is still a crucial point, because the hydrolysis rate of aluminosilicates ester is too fast under weak alkaline media [24,54].

The present work demonstrates the fine tuning of the hydrolytic rate under strongly alkaline media (pH > 14) to prevent the Si–O–Al bond cleavage and using CTMABr as surfactant instead of P123. The highly ordered mesoporous aluminosilicates labeled as CMI-11 with very low Si/Al ratio of 1.9 are successfully synthesized. This suggests that the synthesis route of mesoporous silicoaluminates using Si–Al ester as single molecular precursor is versatile both under acidic and basic conditions with either neutral (CMI-10) or cationic (CMI-11) surfactants. More importantly, tetrahedral aluminum sites in CMI-11 are also highly stable after calcination, long period immersion in boiling water and steaming treatment, which is quite essential for catalysis.

2. Experimental

2.1. Materials

Di-*s*-butoxyaluminoxytriethoxysilane ($(Bu^sO)_2$-Al-O-Si-$(OEt)_3$) was purchased from Gelest, and other chemicals from Aldrich. In a typical synthesis of ordered hexagonal mesoporous aluminosilicates, the following procedure was used: (1) 1.2 g of CTMAB were mixed with 38 g of pH 14 NaOH aqueous solution under stirring for 30 min, followed by the addition of 6 g of Di-*s*-butoxyaluminoxytriethoxysilane. (2) After stirring at room temperature for 24 h, the solution was transferred to Teflon lined autoclaves and aging for 72 h at 80 °C. (3) The solid product was filtered, washed with water and dried in air for 12 h. Finally, the calcination was carried out at 550 °C for 5 h in a flow of oxygen to remove the organic templates. The sample obtained will be labeled as CMI-11 (14). For a comparison, the synthesis was also realized in a pH 11 aqueous solution. The sample obtained will be labeled as CMI-11 (11).

2.2. Characterizations

X-ray diffraction patterns (XRD) were obtained with a Panalytical X'Pert diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) experiments were performed on a Philips TECNAI-10 at an acceleration voltage of 100 kV. The nitrogen adsorption–desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010 M system. The samples were outgassed for 10 h at 300 °C prior to the measurements. The Si/Al ratios of the samples were determined by the inductively coupled plasma analysis (ICP, Perkin-Elmer 3300 DV). ^{29}Si

and ^{27}Al MAS NMR spectra were recorded on a Bruker MSL-500WB spectrometer, fitting the samples in a 7 mm ZrO_2 rotor, spinning at 8 kHz.

3. Results and discussion

Fig. 1 shows XRD patterns of as-synthesized and calcined CMI-11 (14) (Fig. 1A and B, respectively) and CMI-11 (11) samples (Fig. 1C and D, respectively). The as-synthesized CMI-11 (14) (Fig. 1A) exhibits three well-resolved peaks in low angle zone that can be indexed as the (1 0 0), (1 1 0) and (2 0 0) diffractions associated with the *p*6*mm* hexagonal symmetry with a lattice constant a_0 = 56.6 Å. After calcination in air at 550 °C for 5 h, these three diffraction peaks become even sharper due to the removal of surfactant molecules (Fig. 1B), suggesting the good thermal stability of our sample. In contrast, the mesostructured order of CMI-11 (11), both as-synthesized and calcined (Fig. 1C and D, respectively), is significantly reduced with only one diffraction line which appears at much lower angle range. This suggests that the mesostructure becomes less uniform because very high condensation rate of the aluminosilicate ester cannot allow an optimal interaction between inorganic source and surfactant array to conduct to a polycondensation of aluminosilicate ester around of surfactant edifices to generate an ordered mesostructure in weak alkaline aqueous solution [24,54]. This clearly demonstrates the important role of strongly alkaline media as inhibitor to slow down the hydrolysis rate of metal alkoxides.

Fig. 2 shows TEM images of calcined CMI-11 (14) (Fig. 2A) and CMI-11 (11) (Fig. 2B) samples. The observation of a highly ordered hexagonal arrays of mesochannels further confirms the 2-D hexagonal (*P*6*mm*) mesostructure (Fig. 2A) of CMI-11 (14). In contrast, CMI-11 (11) shows wormhole-like mesostructure (Fig. 2B) as previously observed for those synthesized in weak alkaline conditions [24,54].

Fig. 3 shows N_2 isotherms of calcined CMI-11 (14) (Fig. 3A) and CMI-11 (11) (Fig. 3B). The textural characteristics are presented in Table 1. CMI-11 (14) after calcination at 550 °C

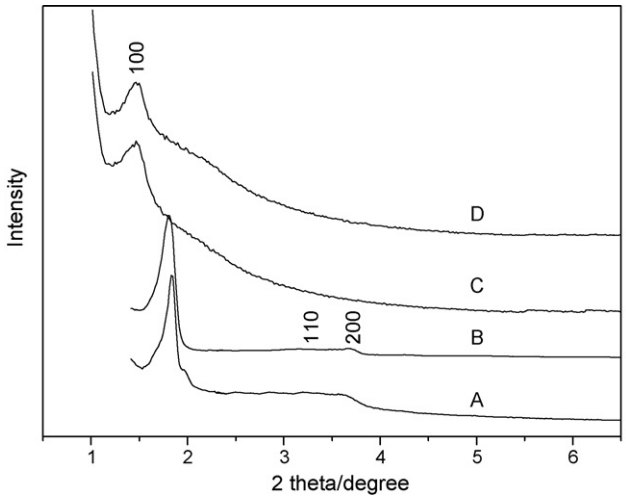

Fig. 1. XRD patterns of CMI-11 (14) sample: as-synthesized (A), calcined (B) and of CMI-11 (11) sample: as-synthesized (C) and calcined (D).

for 5 h exhibits type IV isotherm, typical for a 2-D hexagonal (*P*6*mm*) mesostructure with a BET surface area of 474 $m^2\ g^{-1}$ and pore volume of 0.74 $cm^3\ g^{-1}$. The very narrow pore size distribution, calculated from the adsorption curve using Barrett-Joyner-Halenda model, shows an average pore size of about 2.9 nm (Table 1). The wall thickness estimated from the lattice constant of hexagonal symmetry (a_0) and pore size gives a value of 3.4 nm. In contrast, the CMI-11 (11) exhibits a not well defined isotherm and has a larger pore size (4.2 nm) and thicker wall (9.9 nm), which is in good agreement with the results by XRD and TEM. These results imply that the CMI-11 (11) tends to have much thicker wall comparing with that of CMI-11 (14), indicative of the very fast condensation rate of the aluminosilicate ester, rendering difficult the self-assembly between inorganic species and surfactant micelles in weak alkaline aqueous solution.

Fig. 4 shows ^{27}Al MAS NMR spectra of as-synthesized and calcined CMI-11 (14) (Fig. 4A and B, respectively) and CMI-11 (11) samples (Fig. 4C and D, respectively). ^{27}Al NMR

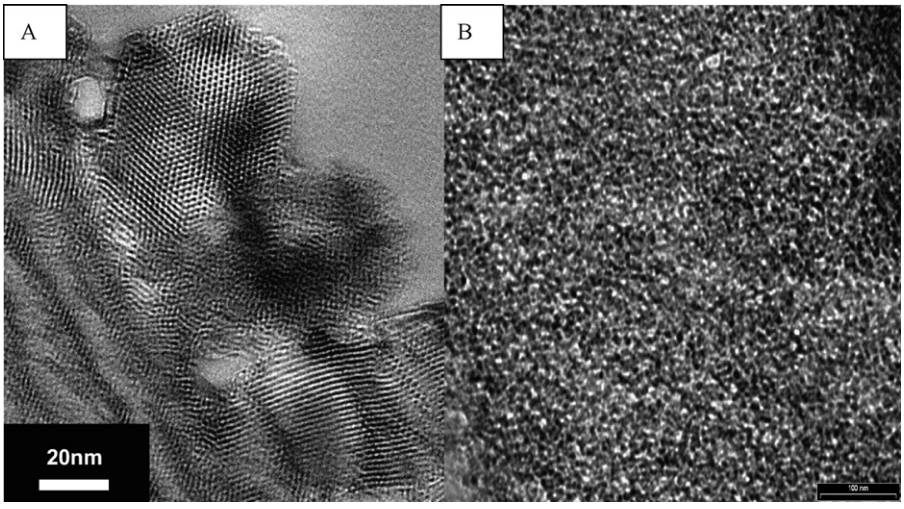

Fig. 2. TEM images of calcined (A) CMI-11 (14) taken in the (1 0 0) and (1 1 0) directions, and calcined (B) CMI-11 (11).

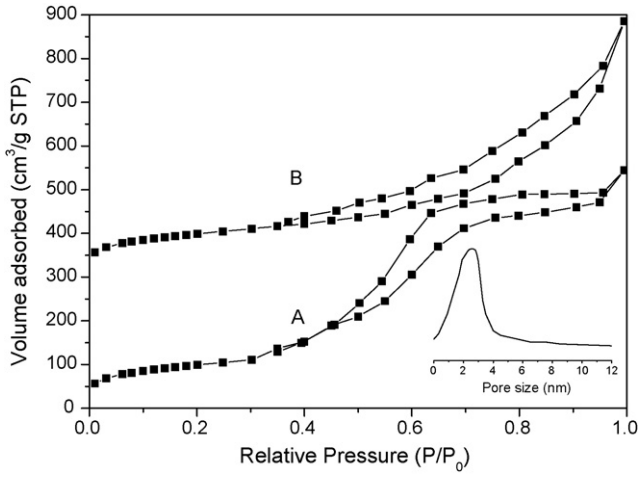

Fig. 3. N_2 isotherm and the corresponding pore size distribution (inset) of calcined CMI-11 (14) (A) sample and N_2 isotherm of CMI-11 (11) (B) sample. The isotherm for (B) is offset from 300 cm^3/g to begin for clarity.

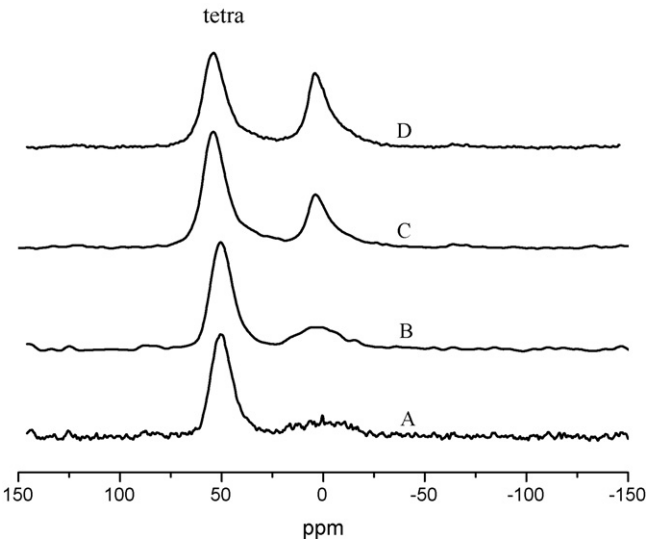

Fig. 4. ^{27}Al MAS NMR spectra of as-synthesized (A), calcined (B) CMI-11 (14) and of as-synthesized (C) and calcined (D) CMI-11 (11) sample.

spectrum of as-synthesized CMI-11 (14) shows a sharp and symmetrical signal centered at 53 ppm (Fig. 4A), indicating that aluminum atoms have successfully been incorporated into the mesoporous framework in tetra coordinated position. The very good symmetry of this signal implies that aluminum atoms in tetrahedral position are located at the same chemical environment. Only a very small resonance of Al atoms located in octahedral position at 0 ppm can be observable, suggestive of the presence of a very small amount of extra framework Al species. The presence of practically only Al atoms in tetrahedral position illustrated by ^{27}Al MAS NMR spectrum indicates that all the Al atoms are linked with Si atoms and there is no cleavage of Si–O–Al linkage present initially in single-source molecular precursor. Very interestingly, after calcination at 550 °C for 5 h, the spectrum remains quasi unchanged and almost aluminum species are tetrahedral (53 ppm, Fig. 4B).

However, the ^{27}Al MAS NMR spectrum of as synthesized CMI-11 (11) (Fig. 4C) shows an important resonance at 0 ppm due to the Al atoms in octahedral position in addition to the tetrahedral position signal at 53 ppm. The calcination to remove surfactant molecules provokes a significant increase of this signal in intensity, indicating the formation of more octahedral Al atoms. This part of the result suggests not only that the synthesis under weak alkaline condition (pH 11) with aluminosilicate ester will generate a significant amount of octahedral Al atoms, but also that the Al atoms in tetrahedral position are not stable and a simple calcinations at 550 °C will extract a significant amount of tetrahedral Al atoms from framework to give a considerable quantity of octahedral Al atoms. This further implies that during the synthesis, Al–O–Si linkage of aluminosilicate ester will suffer an important cleavage. The transformation of Al atoms from tetrahedral to octahedral position upon calcination reveals a less complete condensation occurred in CMI-11 (11), rendering Al atoms in tetrahedral position instable. Our present observation is in good agreement with results reported by Li et al. [24,54]. The ^{27}Al MAS NMR experiments demonstrate that strongly alkaline media is in favor of the preparation of ordered mesoporous materials with more complete Al–O–Si linkage frameworks, resulting in the formation of much more stable tetrahedral aluminum sites in CMI-11 (14). The molecular-level homogeneity of Si–O–Al linkages and tetrahedral aluminum sites are essential and very important in catalysis for activity, selectivity and stability.

The high stability of tetrahedral aluminum sites in CMI-11 (14) can be reasonably attributed to molecular order and full condensation of mesoporous walls, which is further evidenced by ^{29}Si MAS NMR spectroscopy (Fig. 5). In general, ordered mesoporous aluminosilicates exhibit three signals centered at chemical shifts of −92, −102 and −112 ppm, which can be

Table 1
Physical parameters of mesoporous aluminosilicates (CMI-11(A) and CMI-11(H))

Sample	d (100) (nm)	Pore size[a] (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)	a_0[b] (nm)	Wall thickness[c] (nm)	Si/Al[d]
CMI-11 (14)	4.9						
Calcined	4.9	2.9	0.74	474	5.66	3.36	1.92
CMI-11 (11)	12.2						
Calcined	12.2	4.2	0.47	402	14.1	9.9	1.21

[a] Pore size obtained from BJH analysis of desorption data.
[b] a_0 (lattice parameter) = $2d_{100}/3^{1/2}$.
[c] Wall thickness = a_0 − pore size.
[d] The Si/Al ratios in the calcined materials were obtained by ICP-AES method and the all Si/Al ratios in synthesis gel are 1.

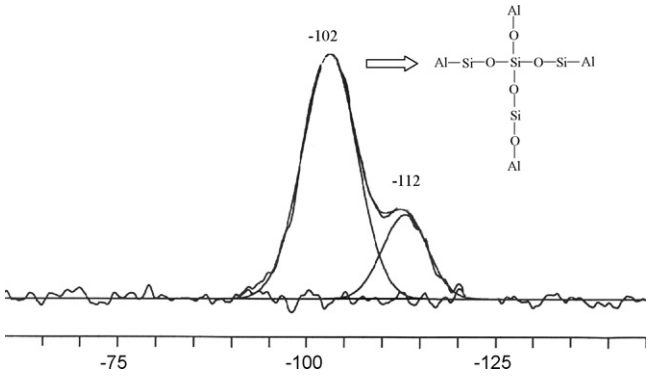

Fig. 5. ^{29}Si MAS NMR spectrum of as-synthesized CMI-11 (14).

attributed to $Si(OSi)_x(OH \text{ or } OAl)_{4-x}$ framework units where $x = 2$ (Q^2), $x = 3$ (Q^3) and $x = 4$ (Q^4), respectively. As-synthesized CMI-11 (14) gives a highly intense resonance at −102 ppm and a small shoulder at −112 ppm and is thus primarily made up of cross-linked Q^3 silica units [−102 ppm, $Si(OSi)_3(OAl)$] with a very small contribution from Q^4 [−112 ppm, $Si(OSi)_4$]. Our elemental analysis indicates that the Si/Al ratio is around 1.9 for CMI-11 (14) (Table 1). The observation of the shoulder at −112 ppm assigned to Q^4 [$Si(OSi)_4$] suggests also the presence of some Si–O–Si linkages in the framework, being in agreement with the Si/Al = 1.9 measured by chemical analysis. However, the presence of practically only Al atoms in tetrahedral position and their good thermal stability indicate that no cleavage of Si–O–Al linkage during the synthesis which could be owing to the strongly alkaline media and adjustor of hydrolysis and polycondensation [53,55–57].

The aluminosilcate ester has two different functional groups ($–OSi(O\text{-alkyl})_3$ and $–OAl(O\text{-alkyl})_2$) in one single molecule and two different hydrolytic rates in solution. It is well known that metal alkoxides have a higher hydrolysis rate compared with that of alkoxysilanes. In our previous work [53], to avoid the cleavage of Si–O–Al linkage due to the different hydrolysis rate of two functionalities in aluminosilcate ester, acetone was used as complexing agent since the aluminium alkoxide part due to the presence of the vide case in the external electronic shell can act as a Lewis acid with a positive charge to coordinate with one molecule of the acetone. This concept has been largely used in Tishchenko disproportionation reaction [58]. The hydrolysis rate of $–OAl(O\text{-alkyl})_2$ group is inhibited by reducing the possibility of nucleophilic attack of H_2O molecule at the positively charged aluminium atom and could be now even slightly lower than that of $(–OSi(O\text{-alkyl})_3$ group. The interaction between two Al sides is thus hindered due to the presence of acetone. The Si–O–Al linkage in aluminosilicate ester is well preserved and the heterocondensation between Si side of one ester molecule with Al side of other molecule can only be envisaged since neither Si–O–Si nor Al–O–Al linkage was observed in the final product, leading to CMI-10 with the lowest Si/Al ratio of 1.

In our present case, we used strong alkaline condition, we found the same effect. Only, other than Si–O–Al linkages in the framework, we found also some Si–O–Si linkages, leading to a material with a Si/Al of 1.9. It is well known that the hydrolysis and condensation of $Si(OR)_4$, R = alkyls, in aqueous solution can be acid-catalyzed or base-catalyzed reactions. The choice of acid catalysis or base catalysis has only a substantial influence on the nature of the gel formed. However, it should be noted that the redissolution of silica gel can occur in highly alkaline conditions [59,60]. The behavior of aluminium alkoxides can be different since the hydrolysis in an acidic medium results in stable sols and the decrease in acidity will lead to the amorphous hydroxide precipitate with considerable content of residual alkoxides, indicating that the stability of aluminium alkoxides increases or its reactivity decreases with the decrease in acidity [59,60]. Thus, strong alkaline condition plays a role in reducing significantly the hydrolysis and condensation rate of aluminium alkoxide part of silicoaluminium ester. However, the behavior of $Si(OR)_3$ part is less affected by pH value, the possibility to form Si–O–Si linkage on the basis of two ester molecules is enhanced. That is why Q^4 contribution is observed in addition to the strong contribution of Q^3 in ^{29}Si MAS NMR spectrum (Fig. 5). Due to no occurrence of Si–O–Al linkage cleavage and the hindrance of Al–O–Al formation, all Al atoms are in tetrahedral coordination and each Al atom will have at least one Si atom as neighbor to generate a molecular-level homogeneity of Si–O–Al linkages and a very low Si/Al ratio of 1.9. The full condensation of the walls made up of Al–O–Si linkages would greatly increase stability of tetrahedral aluminum species.

Under pH 11, the hydrolysis and condensation rate of the aluminium alkoxide part still predominates and the formation of Al–O–Al linkage between two aluminosilicate ester molecules induces the important cleavage of pre-existing Si–O–Al linkages, leading to a wormhole like framework with mixed octahedral and tetrahedral coordination of aluminium atoms and even lower Si/Al ratio of 1.2 due to the presence of an amount of Al–O–Al linkages. This has been clearly illustrated by XRD, TEM, N_2 adsorption–desorption measurement and ^{27}Al and ^{29}Si MAS NMR spectroscopy.

4. Conclusions

Ordered hexagonal mesoporous aluminosilicates material (CMI-11) has been successfully synthesized under strongly alkaline condition using aluminosilicates ester as single source and cationic CTMAB as surfactant. The high aluminum content, i.e. low Si/Al ratio of 1.9 and stable tetrahedral aluminum sites in ordered CMI-11 (14) should directly be attributed to the use of unique aluminosilicate ester containing Al–O–Si linkage and the well control of the hydrolysis and condensation rate of two functionalities in this single molecular precursor under strong alkaline condition. The present work demonstrated that the ordered mesoporous silicoaluminates with very low Si/Al ratio can be synthesized using Si–Al ester as single molecular precursor both under acidic (CMI-10) and basic (CMI-11) conditions with either neutral (CMI-10) or cationic (CMI-11) surfactants. More importantly, tetrahedral aluminum sites in these new materials are also highly stable after calcination, long period immersion in boiling water and steaming treatment,

which is quite essential for catalysis. It is believed that our synthesis method can be extended to other surfactants. Various mesostructures (cubic, lamellar and hexagonal) with different pore sizes (2–30 nm) can be obtained. Furthermore, other esters containing M–O–Si linkage such as Ti–O–Si, Zr–O–Si and Ta–O–Si can also be employed in the synthesis leading to the synthesis of highly ordered mesoporous materials with high metal content and stable active sites. We are convinced that the strategy developed here provides a facile, unique but versatile approach for the synthesis of highly organized mesoporous mixed-element oxide materials with defined structure, high heteroatom content and stable active sites.

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