Chem. Mater. **2005,** *17,* 881−886

Control of the Morphology of All-Silica BEA-type Zeolite Synthesized in Basic Media

Olivier Larlus and Valentin P. Valtchev*

Laboratoire de Matériaux à Porosité Contrôlée, UMR-7016 CNRS, ENSCMu, UHA,
3 rue Alfred WERNER, 68093 Mulhouse CEDEX, France

Received July 23, 2004. Revised Manuscript Received November 23, 2004

All-silica BEA-type (Si-BEA) zeolite readily crystallizes in fluoride quasi-neutral media, while its synthesis under basic conditions is difficult. To compare the morphological features of BEA-type materials synthesized in quasi-neutral and basic media, a two-step nucleation procedure, which allows controlled synthesis of Si-BEA under basic conditions, was developed. The procedure consists of (i) aging of the initial system at a close to neutral pH, and (ii) raising the pH and a secondary aging in basic media. This procedure was further employed to study the effect of the synthesis formulation, especially its sodium and potassium content, on the crystal morphology of Si-BEA. With an increase in the pH of the system, a gradual decrease of the size of the pyramidal (*h*0*l*) face coupled with an increase of the pinacoidal (00*l*) face was observed. Thus, the morphology of zeolite crystals can be varied from well-developed truncated bipyramids to platelike crystals, where the pinacoidal face is dominant. A consequence of this morphological change is the different representation of the channel systems running along the *a* and *c* axes at the crystal surface. Potassium-containing systems provided products with bimodal crystal size distribution without changes in the crystal habit. The amount of K^+ was correlated with the generation of small crystals, indicating its influence on the nucleation process. Small concentrations of sodium did not bring along substantial changes in the morphology of BEA-type crystals. At higher concentration, Na^+ had a pronounced structure-breaking effect, and no crystalline product was obtained. The framework defectness and hydrophobicity of the materials synthesized in basic media were studied by ^{29}Si NMR spectroscopy and TG analyses, which revealed that the alkali-free materials possessed a concentration of defect sites and hydrophobicity similar to that of the sample obtained under fluoride quasi-neutral conditions.

Introduction

The morphology of zeolite crystals is a parameter that substantially influences their performance in the main areas of application of microporous materials, that is, catalytic and separation processes,[1] as well as in new emerging applications, for instance, optoelectronics.[2,3] A number of papers dealing with the effect of synthesis parameters on the morphology of zeolite crystallites have been published. For example, the effect of silica source and its dissolution on the size and morphology of mordenite crystals has been investigated.[4−7] The influence of different synthesis parameters on the crystal habit of MFI-[8−14] and LTL-type[15,16] zeolites has also been carefully studied. Various additives able to form complexes with some of the gel components have been employed to change the equilibrium in the system and, respectively, the morphology of zeolite crystal.[17−22] These studies showed that for a particular zeolite the variation of the gel composition and crystallization temperature has a specific effect on the crystal morphology. In other words, it is difficult to transform merely the knowledge collected in the synthesis of one zeolite to another. This is mainly due to the complexity of the gel systems used in zeolite synthesis. Aluminosilicate zeolites are synthesized under hydrothermal conditions where the reaction variables include time, temperature, pressure, gel composition, the inorganic and organic

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* Corresponding author. E-mail: v.valtchev@uha.fr.

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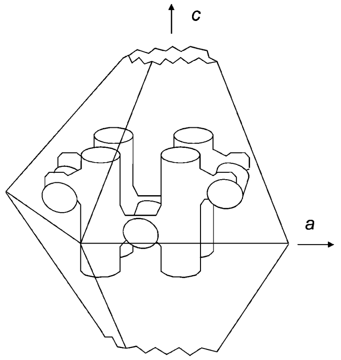

Figure 1. Typical bipryamidal morphology of zeolite Beta with a schematic presentation of the channel system drawn as it is oriented within a crystal.

cations used, reactant source and type, pH, aging time of the gel, reaction cell fill volume, and so on.[23] The effect of varying one of these parameters is difficult to evaluate in a straightforward manner, because it may have an effect on several others. The reaction system is in general inhomogeneous with both liquid and solid components; thus zeolite nucleation and growth involve numerous simultaneous equilibria and condensation steps,[24] which further complicates the analysis and interpretation of the effect of these parameters on the morphology of zeolite crystals. Therefore, to control the morphology of a particular zeolite, a detailed study on the effect of each parameter influencing the crystal growth is required.

The present investigation is devoted to the morphological features of all-silica BEA-type material. The morphology of BEA-type crystals can be varied from well-developed truncated bipyramids to platelike crystals, where the pinacoidal face is dominant. A consequence of this morphological change is the different representation of the channel systems running along the *a* and *c* axes at the crystal surface (Figure 1). The BEA-type framework topology attracts much attention because of the three-dimensional large-pore channel system, which offers numerous advantages for catalytic and separation processes. The Si/Al framework ratio can be easily controlled in the range from 6.5 to 100, thus providing a material with a wide variation in the concentration of the active sites. Although the framework Si/Al ratio may vary over a wide range, the synthesis of all-silica zeolite Beta is difficult, and usually seeding is required. For instance, van Bekkum and co-workers successfully obtained the aluminum-free Ti-beta form of the zeolite by using seeds and a specific template (di(cyclohexylmethyl)dimethylammonium).[25] In contrast, the fluoride route, where the OH^- anions are substituted by F^-, readily provides Si−BEA crystals without seeding of the system.[26] The features of the zeolite product obtained by this synthesis approach are: (i) relatively large individual crystals, and (ii) very few framework defects. The absence of framework defects and the large crystal size change dramatically the properties of zeolite Beta. Such crystals exhibit higher hydrophobicity and increased diffusion limitations as compared to the smaller particles obtained in basic media. These features of the fluoride syntheses are due to the relatively low supersaturation degree in such systems.[27,28] In contrast, the concentration of soluble species in basic media can be varied in a wide range, thus providing an efficient tool for control of the nucleation and crystallization processes.

There are a number of studies on the influence of different synthesis parameters on the formation of zeolite Beta, where the effect of these parameters on the morphology, in particular the crystal size, is discussed. Most of these studies were performed with Al-containing systems in the presence[29−33] or absence[34,35] of alkaline metal cations. On the other hand, the influence of synthesis variables on the crystal morphology of Si-BEA is still not well studied. This fact is mainly due to the very narrow crystallization field of Si-BEA material, which includes crystallization in quasi-neutral alkali-free fluoride media. Consequently, the possibilities for controlling the crystal size and morphology of the zeolite are limited.

We have developed a two-step nucleation procedure that allows the synthesis of all-silica BEA-type zeolite under basic conditions. Thus, the effect of the supersaturation and other chemical variables can be varied in a wide range, which was used to study the effect of synthesis formulation on the morphology of Si-BEA. To study the effect of sodium and potassium cations on the nucleation and crystal growth process was also among the goals of the investigation.

Experimental Section

The reactants used in the present study were pyrogenic silica (Aerosil 130, Degussa), tetraethylammonium fluoride (TEAF) dihydrate (Aldrich), tetraethylammonium hydroxide (TEAOH) (Fluka, 40% in water), and distilled water. A typical preparation procedure included mixing of the silica source with water and TEAF followed by aging overnight at ambient temperature. The second nucleation step consisted of addition of a basic solution to increase the pH and aging of the gel for another night. A reference sample was prepared from the system $0.5TEAF:1.0SiO_2:5.0H_2O$, without secondary aging in basic media. For the other samples, the pH was raised by the addition to the reference gel of TEAOH (40% solution, Fluka), NaOH (98%, Fluka), and KOH (86%, Fluka). The hydrothermal syntheses were performed at 150 °C for different periods of time. The overall compositions, synthesis conditions, and morphological features of the prepared Si-BEA samples are summarized in Table 1. The higher water content in the molar compositions of the samples with respect to the reference composi-

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Table 1. Variation of the Chemical Composition (xROH:0.5TEAF:1.0SiO$_2$:7.0H$_2$O), Synthesis Time, and Morphological Characteristics of All-Silica BEA-type Materials Synthesized in Basic Media

sample	x	R	duration (days)	crystal size distribution	crystal habit b/a
1[a]			7	monomodal	0.58
2	0.1	TEA	10	monomodal	0.55
3	0.2	TEA	17	monomodal	0.63
4[b]	0.3	TEA	23	monomodal	0.65
5	0.1	Na	11	monomodal	0.58
6	0.2	Na	20	amorphous	amorphous
7	0.07	K	11	bimodal	0.52
8	0.15	K	18	bimodal	0.75
9	0.22	K	20	bimodal	0.78

[a] Reference composition: 0.5TEAF:1.0SiO$_2$:5.0H$_2$O. [b] $H_2O/SiO_2 = 9.1$.

tion is due to the addition of the basic solutions. The yield calculation was based on the silica conversion.

The materials were characterized by powder X-ray diffraction (XRD) with a STOE STADI-P diffractometer in Debye−Scherrer geometry equipped with a linear position-sensitive detector (6° in 2θ) and employing Ge monochromated Cu Kα_1 radiation. Micrographs of the samples were taken with a Philips XL 30 LaB$_6$ scanning electron microscope (SEM). The combined thermogravimetrical (TG/DTA) analysis of the samples was performed with a Setaram TG-ATD LABSYS thermal analyzer at a heating rate of 5 °C min^{-1} in an atmosphere containing 80% N$_2$ and 20% O$_2$. ^{29}Si NMR spectra were collected with a MSL 300 Brucker spectrometer at a resonance frequency of 59.6 MHz and magic angle spinning at 4 kHz. The contact time was 4.4 μs for both the as-synthesized and the calcined samples. The recycle times were 10 and 80 s for the as-synthesized calcined samples, respectively. ^{19}F NMR experiments were carried out on a DSX 400 Brucker spectrometer at a resonance frequency of 376.3 MHz. Magic angle spinning was performed at 25 kHz, with 4 μs of contact time and 15 s of recycle time. The elemental analysis of the solids was performed with an X-ray fluorescence spectrometer MagiX (Philips).

Results and Discussion

Our attempts to synthesize all-silica BEA-type material directly in basic media resulted in the formation of a mixture of BEA-, MFI-type zeolites and amorphous material. Keeping in mind that the stabilization of viable nuclei is the key factor in zeolite syntheses and that at room temperature important events are taking place in the synthesis gel, the nucleation procedure was modified to overcome the problem of phase purity. The initial gels were subjected to a two-step nucleation procedure, which includes aging under quasi-neutral and basic conditions of the precursor gel. The viable nuclei that induce zeolite crystallization under hydrothermal conditions were first formed under fluoride media. Subsequently, the pH was raised and the gel system containing the nuclei was aged additionally to reach the new equilibrium under basic conditions. Using this modified nucleation procedure, the system readily converted into highly crystalline and pure Si-BEA (Figure 2). The major difference observed between the formations of the reference sample (no. 1) synthesized under quasi-neutral fluoride media and BEA-type materials synthesized under basic conditions was the synthesis time needed for completion of the crystallization process (Table 1). The increase of the crystallization time for syntheses performed using the modified nucleation procedure is most probably due to the competition between silico-hydroxide and silico-fluoride species, which influence the crystallization rate. On the other hand, the high pH and slow crystallization rate did not influence the yield, which was over 92% for all samples.

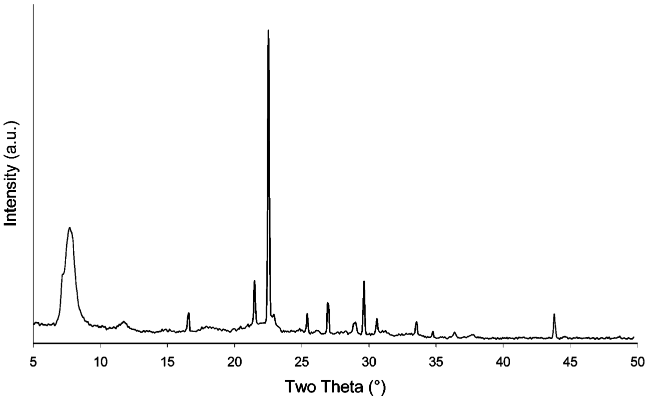

Figure 2. Representative XRD pattern of Si-BEA materials synthesized.

Effect of TEAOH on the Morphology of All-Silica BEA-type Material. The SEM observation showed that the crystals synthesized under quasi-neutral and basic conditions do not differ substantially in size (Figure 3). Both systems yielded relatively large 10−15 μm well-shaped crystals with the typical of BEA-type materials bipyramidal truncated morphology. However, visible changes of the aspect ratio between different faces were observed. For instance, the pyramidal faces of the crystals synthesized in basic media were shorter, whereas the pinacoidal ones (00l) were much better developed with respect to the crystals synthesized in quasi-neutral media. The SEM inspection showed also a partial surface dissolution of the BEA-type crystals synthesized under highly basic conditions, sample no. 4, which is most probably due to the prolonged heating time in highly basic media.

It is worth recalling that the differences in the growth rate of different faces determine the crystal morphology.[36] Thus, faces with a high growth rate are less presented or completely absent in the ultimate crystal morphology, while the ones with slow growth rate are well developed. Therefore, the observed crystal morphology at high pH suggests a relatively high rate of crystal growth of the pyramidal (h0l) face and a slower growth of the pinacoidal (00l) face. The change in the aspect ratio between pinacoidal and pyramidal faces is presented in Table 1 as the ratio between the length of basal (a) and terminal (b) edges of the pyramidal face (Figure 3a). It can be clearly seen that the increase of TEAOH led to a gradual increase of the b/a ratio (Figure 3, bottom).

The pH of the system was increased by the addition of TEAOH. To verify whether the observed effect is due to the synthesis media or the higher content of organic structure-directing agent, a series of experiments, in which TEAOH was substituted by similar amounts of KOH and NaOH, was performed.

Effect of KOH on the Morphology of All-Silica BEA-type Material. The addition of KOH to the reference gel influenced the aspect ratio between pyramidal and pinacoidal faces in a way similar to that of the TEAOH. Therefore, the

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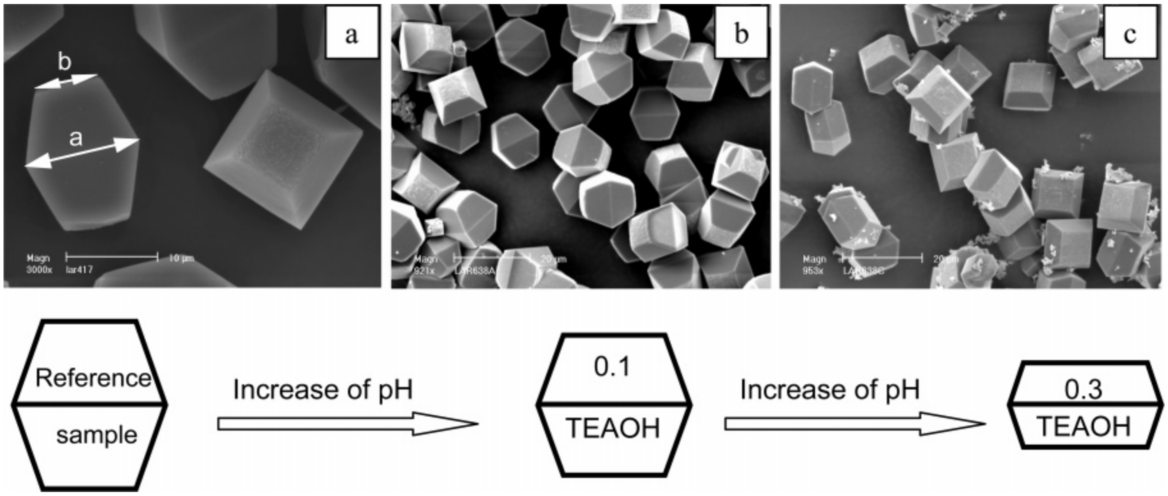

Figure 3. Morphological changes of all-silica BEA-type materials as a function of the synthesis media: reference sample (a) and samples synthesized with 0.1 (b) and 0.3 (c) mol of TEAOH per mol of SiO_2 and schematic illustration of the decrease of the pyramidal face with increase of basicity in the system (bottom).

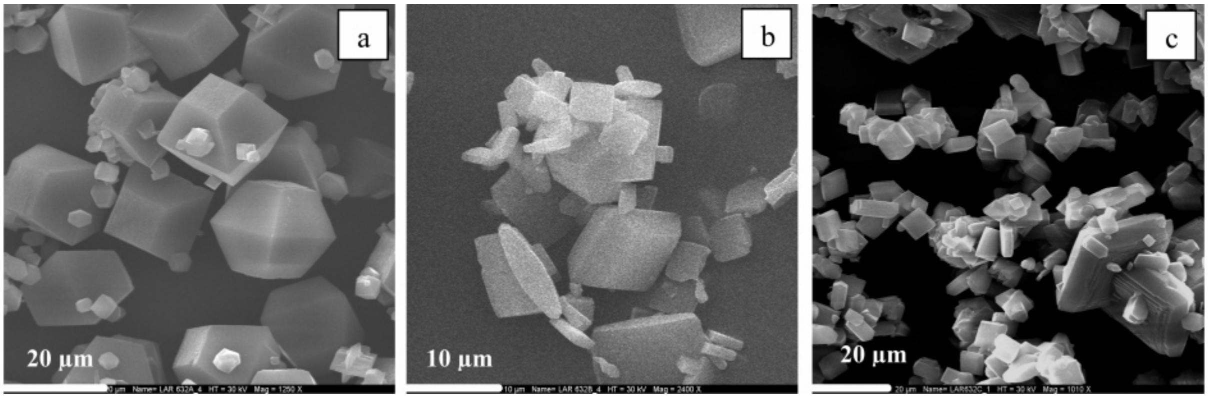

Figure 4. SEM micrographs of the BEA-type crystals synthesized in basic KOH-containing media. The population of small crystals increases with the KOH content in the system, which was varied from 0.07 (a) to 0.15 (b) and 0.22 (c) mol per mol of SiO_2.

observed changes in the morphology of all-silica Beta crystals may be related to the basicity of the system. It is well known that the basicity of a zeolite precursor system influences in a straightforward manner the precursor silica species.[23] With the increase of the pH, the amount of low-weight silica species increases and they become dominant in the nutrient pool. It is difficult, however, to reveal the intimate mechanism that governs the preferential growth of the pyramidal face.

Besides the effect on the aspect ratio between the different faces, the synthesis with potassium hydroxide provided substantial changes in the crystal size. Two populations, consisting of large (10−20 μm) and small (3−7 μm) crystals, were observed in all products (Figure 4). The amount of small crystals was closely related to the potassium content in the initial system. The increase of the population of small crystals with increasing KOH content is evident from Figure 4. Only a few large crystals were observed in sample no. 9 (Table 1), but they exceeded the size of the crystals of the reference sample (no. 1, Table 1).

Keeping in mind that the yield was similar, in the range 93−96 wt %, the decrease in the crystal size is a sound proof that the number of nuclei is increased in potassium-containing systems. The observed effect of potassium is fairly surprising because the previous investigations on aluminum-containing zeolite beta (Al-BEA) did not find a specific structure-directing effect of potassium in the formation of zeolite beta. For instance, Mostowicz et al.[29] showed that Al-BEA cannot be synthesized at higher potassium concentrations. On the other hand, Camblor and Perez-Pariente[30] revealed that an optimum value of (Na+K)/SiO_2 exists, which controls the size and crystallization rate of Al-BEA crystals. They also found that the crystal size of Al-containing beta crystals increased with potassium content in the gel. Therefore, the observed relationship between potassium content and the number of nuclei in Si-BEA precursor system is not likely to be a structure-directing effect of alkaline cation. The addition of potassium hydroxide solution to the reference gel resulted in changes of the physical aspect of the gel, which became nonhomogeneous, containing fairly dense particles and transparent parts with very low viscosity. The subsequent aging made the system more viscous and homogeneous, but still very dense particles difficult to homogenize even by a mechanical treatment were present. We relate different crystal size populations with the inhomogeneities in the precursor gels. The lower viscosity of the gels is due to the partial depolymerization, resulting from the addition of potassium hydroxide solution. The depolymerization includes (i) formation of lower in weight silica species, and (ii) interaction of potassium with negatively charged silica precursors. These changes in the gel system

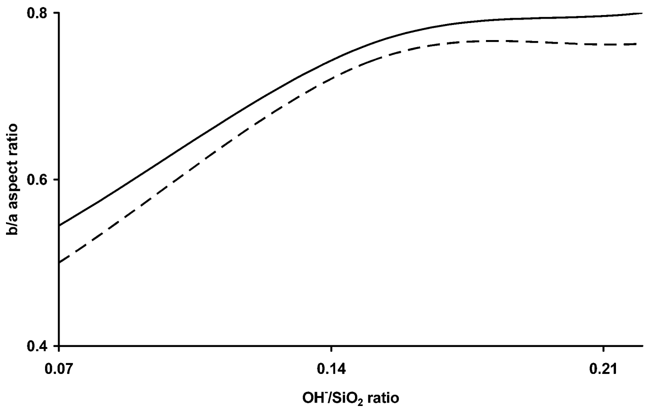

Figure 5. Changes of the *b*/*a* aspect ratio as a function of OH^-/SiO_2 for the K-containing systems with bimodal crystals size distribution: uninterrupted line, large crystals; dotted line, small crystals.

resulted in a larger number of nuclei and smaller ultimate crystal sizes. Thus, the effect of potassium is mainly related to the gel chemistry, without having a real structure-directing function. On the other hand, the crystallization rate in such a system is very low, as discussed above.

The morphological changes due to the synthesis media concerned both large and small Si-BEA crystals. The aspect ratio between the length of basal (*a*) and terminal (*b*) edges of the pyramidal faces of small and large crystals in samples no. 7−9 (Table 1) is depicted in Figure 5. As can be seen, this ratio varies with pH changes in the system, but it is constant for the crystals within a batch. On this basis, one can conclude that the growth mechanism is similar for small and large crystals.

Effect of NaOH on the Morphology of All-Silica BEA-type Material. A small amount of NaOH (0.1 mol of NaOH per 1.0 mol of SiO_2) did not cause changes in the crystal morphology of all-silica BEA-type material, except a slight increase in the size. However, the crystallization time was much longer with respect to the reference synthesis. The increase of sodium hydroxide content in the system suppresses completely the crystallization because any traces of all-silica polymorph were not found after 20 days of synthesis (sample no. 6, Table 1). These are strong indications for the negative effect of sodium on the formation of all-silica BEA-type material. This effect might be related to the strong structure-directing properties of Na^+ cation, which are not favorable for the system under investigation. The small sodium cation with its high charge density interacts strongly with the water molecules in the precursor gel. As a result of this interaction, the original hydrogen bonds formed during the nucleation in neutral media are broken and the water molecules are reorganized around sodium. Sodium hydroxide interacts also with silicon species in the system, breaking the polymer chains. Due to this complex action, the very dense reference gel was transformed into a transparent liquid with low viscosity; that is, the equilibrium in the system was completely perturbed. Thus, sodium demonstrated a pronounced structure-breaking effect in the formation of Si-BEA.

Hydrophobic Properties of All-Silica BEA-type Materials Synthesized in Basic Media. In the Introduction, it was pointed out that all-silica zeolite materials synthesized under basic conditions contain a substantial amount of framework defects, which leads to increased hydrophilicity. The BEA-type materials synthesized in the course of the present work were studied by thermogravimetric (TG) analysis and ^{29}Si NMR spectroscopy to evaluate their degree of hydrophilicity. The TG analysis of the as-synthesized samples showed that the total TEA^+ amount in the framework was constant, close to 19 wt % for the materials synthesized in alkali-free media. This amount corresponds to 6 TEA^+ cations per unit cell, which is the reported maximum for the BEA-type topology. Partial substitution of a TEA^+ cation by K^+ was detected in samples no. 7−9, where the TEA^+ content was evaluated to be 17.5, 16.7, and 15.4 wt. %, respectively. These data were in good agreement with the chemical analysis showing an increase in potassium content (0.105, 0.471, and 1.827 K_2O wt %) from sample 7 to sample 9. According to the chemical analysis, sample no. 9 was richest in potassium, comprising 0.85 K^+ per unit cell. Calcined and rehydrated samples were subjected to TG analysis, which showed that the water adsorbed in the reference sample (no. 1) and materials synthesized in basic alkali-free media is below 0.3 wt %.

The synthesized under basic conditions all-silica BEA-type materials were further studied by ^{29}Si NMR spectroscopy. Similar spectra comprising only Si(4Si) resonance peaks were recorded for the reference sample and material synthesized by the addition of TEAOH (sample no. 4) (Figure 6a). These spectra were carefully inspected for the presence of ^3Q sites indicative of structural defects. No distinctive peak was found in the range 95−100 ppm, which is a proof that BEA-type material with a very low level of defect sites is synthesized under basic conditions. A similar conclusion cannot be made for the potassium-containing sample (no. 9), where a broad peak in the range characteristic for ^3Q sites was observed. The observed difference in the two materials synthesized under basic conditions is due mainly to different properties of TEA^+ and K^+ cations. The high degree of framework perfection of sample no. 4 is due to two main factors, the presence of F^- ions in the synthesis mixture and the slow crystal growth kinetics, which allows the framework to be accomplished with minimum defect sites. Obviously, the F^- ion is able to counterbalance the TEA^+ in basic media, which decreases the interaction of the structure-directing agent (SDA) with the framework. Under similar conditions, K^+ interacts with the framework and provokes framework defects due to its higher charge density.

The NMR spectra of the calcined samples (Figure 6b) were deconvoluted (not shown here) into 11 different T sites from −109.4 to −116 ppm, which can be assigned to Q^4 sites.[26] The only difference observed in the spectra of the calcined materials synthesized under quasi-neutral and basic conditions was the peak at about −109 ppm, which was well established in the former. The −109 ppm peak was very weak in the K-containing sample (no. 9), while the spectrum of sample no. 4 did not comprise such a peak. This peak might be due to F^- attached to the framework as a result of the calcination procedure. The presence of fluorine in the calcined reference sample, identified by ^{19}F NMR, supports this suggestion.

The ^{19}F NMR investigation of the as-synthesized samples showed the presence of fluorine in different chemical en-

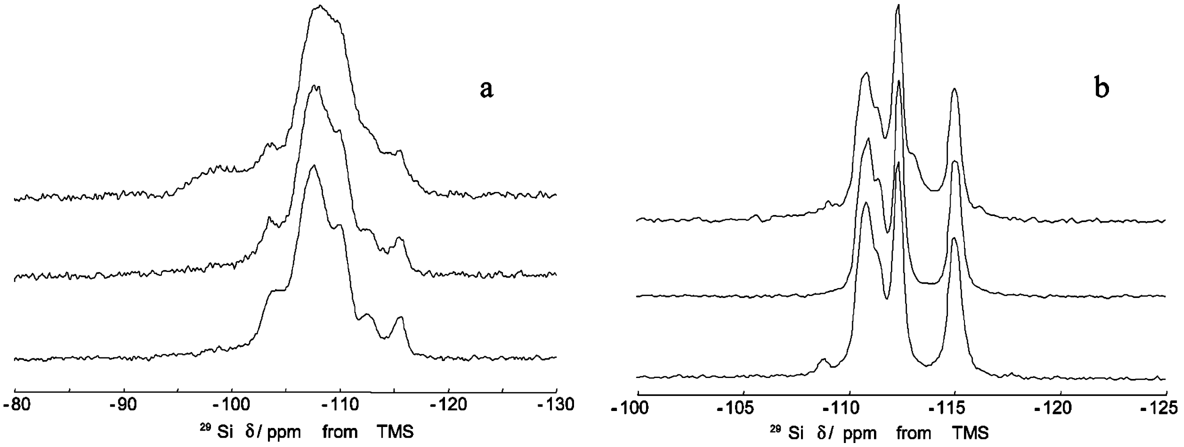

Figure 6. ^{29}Si NMR spectra of: (a) as-synthesized and (b) calcined materials. From bottom to top: reference sample (no. 1), and the samples synthesized in basic media by the addition of TEAOH (no. 4) and KOH (no. 9).

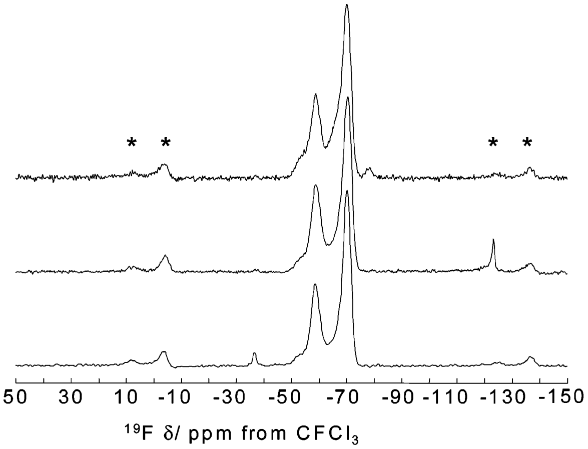

Figure 7. ^{19}F NMR spectra of as-synthesized all-silica BEA-type materials. From bottom to top: reference (no. 1), TEAOH- (no. 4), and KOH-containing (no. 5) samples. (The spinning bands are marked by asterisks.)

vironments (Figure 7). Four distinctive sites, which according to the literature data correspond to fluorine anions not bonded to the framework, plus a strong nonattributed shoulder at −52 ppm, were identified. Thus, the peaks at −58, −65, and −70 ppm were attributed to fluorine in the [4^35^4] cages, while the peak at −38 ppm is often assigned to F^- in a D4R cage.[37,38] The D4R cage is characteristic of polymorph C, whereas such a unit does not exist in the framework topologies of polymorph A and B. Therefore, if the latter assignment is correct, it suggests that polymorph C is indeed present in the materials synthesized under quasi-neutral conditions, while its amount in the materials synthesized under basic conditions is negligible. However, evidence for the presence of polymorph C in the reference sample was not found in its XRD pattern.

Summarizing these data, one may conclude that the BEA-type material synthesized in basic media by the addition of TEAOH possesses a degree of hydrophobicity similar to that of the materials obtained in fluoride media, while the K^+-containing Si-BEA showed a lower degree of hydrophobicity.

Conclusions

The successful synthesis of all-silica BEA-type materials under basic hydrothermal conditions was achieved by a two-step nucleation procedure consisting of: (i) aging of a SDA-containing fluorine-rich silica gel under quasi-neutral conditions, followed by (ii) increase of the pH by the addition of organic or inorganic hydroxides and additional aging. The viable nuclei formed during this pretreatment procedure induced the growth of the BEA-type material during the subsequent hydrothermal treatment. The combined ^{29}Si NMR/TG analysis revealed a very high degree of hydrophobicity of the zeolite crystals synthesized from an alkali-free system, while the alkali-containing systems yielded crystals with a certain amount of framework defects.

The developed nucleation procedure was employed to study the effect of the synthesis media and alkali cations (Na^+ and K^+) on the morphological features of Si-BEA. The change of the synthesis media from quasi-neutral to highly basic resulted in substantial alteration of crystal morphology. Gradual decrease of the size of pyramidal faces with the increase of the pH, coupled with increase of the pinacoidal face, was observed. Thus, the change of aspect ratio between pinacoidal and pyramidal faces caused changes in the number of the pore openings of each of the channel systems (parallel to the *a* and *c* axes) per unit of total external surface.

The introduction of a small amount of sodium increased the size of the crystals without changing the crystal morphology, while a larger amount of sodium ($0.2NaOH/1.0SiO_2$) suppressed the crystallization process and no crystalline product was obtained for 20 days of hydrothermal treatment. Products with bimodal crystal size distribution were found in potassium-containing systems, and the amount of the smaller crystal population was related to the potassium content in the gel.

The obtained data can be used for fine-tuning of the crystal morphology and physicochemical properties of all-silica BEA-type crystals.

Acknowledgment. V.P.V. thanks the CNRS-DFG bilateral program for financial support.

CM048799R

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