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Al-Rich Zeolite Beta by Seeding in the Absence of Organic Template

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Low- and no-template precursor suspensions are studied to clarify the effects of Si/Al ratio, seed content, heating temperature, and crystallization time on the syntheses of Al-rich zeolite Beta. Syntheses using 2.5 wt % seeds resulted in well-shaped octahedral Al-rich Beta crystals with sizes between 0.4 and 1 μm after either 6 days hydrothermal treatment at 125 °C or 12 days at 100 °C. The crystalline Beta product has Si/Al ratios as low as 3.9 (16.4 Al atoms per unit cell), which are comparable to the natural counterpart of zeolite Beta, the mineral Tschernichite, and give the material high hydrophilic properties. The tetrahedral coordination of aluminum in the Al-rich Beta and their stability upon calcinations is demonstrated by NMR spectroscopy and TG analysis. The seed method opens new perspective in the development of economically and environmentally friendly synthesis approach for Al-rich zeolite Beta, where the amount of organic template is reduced significantly.

Introduction

The synthesis of zeolites, crystalline aluminosilicate framework type materials, has been extensively investigated for a long time; a small part of these investigations are carried out with basic zeolites, and from these even a smaller fraction concerns Al-rich materials. The term "Al-rich" depends on the framework types under consideration and is generally used for materials with a Si/Al ratio below 5. To date, only nine zeolite structures with large pore openings (> 5 Å) have been synthesized with a high content of framework aluminum.[1]

BEA-type zeolite possesses a three-dimensional system of intersecting channels with pore openings with size of 6.6 × 6.7 Å.[2] The intriguing structural and chemical properties of zeolite Beta make it an important material in diverse acid-catalyzed reactions including FCC processes.[3,4] Since its first synthesis by Wadlinger et al. in 1967, this zeolite has been prepared exclusively from precursor gels or suspensions with organic structure directing agents (SDA) such as tetraethyl ammonium hydroxide (high-silica product) and dibenzyl-dimethy-

lammonium hydroxide (pure-silica product).[5,6] Because of the abundant use of organic additives in the precursor mixtures, zeolite Beta is obtained as a high-silica material with crystallite sizes in the nanometer range. The typical Si/Al ratio of synthetic zeolite Beta is in the range of 12 to 30.[7]

However, in 1991, the discovery of the mineral Tschernichite, with an Al-rich BEA-type structure (Si/Al = 3.3), expanded the possibilities for using a broader chemical compositions and synthesis conditions to prepare materials with increased aluminum content.[8,9]

High- and pure-silica zeolites have found applications where the hydrophobicity and high acidity of the material are of significant importance. On the other hand, high aluminum content in zeolites results in a higher density of the acid sites, high hydrophilicity, and large ion-exchange capacity. In addition, acid/base pair sites are available in Al-rich zeolites, and their strength can be tuned by ion-exchange of the charge balancing cations, and thus the base strength increases in the sequence Li < Na < K < Rb < Cs.[10,11] Besides, the applications requiring high hydrophilicity such as removal of water and ion-exchange,[12,13] Al-rich zeolite Beta is a promising candidate

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as a shape selective basic catalyst for reactions such as Knoevenagel condensation,[14] transesterification,[15] hydrocarbon oxidation,[16] and alkylation.[17] Moreover, through ion-exchange with transition metal cations Al-rich zeolite Beta may increase the repertoire of basic catalyst supports.[18]

Steaming and acid leaching have been used for the dealumination of zeolite Beta.[19] The counterpart to these procedures, desilication in basic media has been applied to introduce additional mesoporosity in the materials.[20] However, this procedure results in only a marginal increase of the Al content. Thus, the increasing of framework aluminum is usually carried out during syntheses. Vaudry et al. have achieved Si/Al ratios for zeolite Beta as low as 7.7,[21] later other groups have reported materials with ratios of 5 from low-SDA thick gels and by addition of Al species during the synthesis process.[22,23] As stated by Gabelica et al., the template content plays a crucial role in aluminum insertion during the synthesis of Al-containing zeolites.[24] Nonetheless, for counterbalancing the charge of more Al framework atoms, more and smaller cations are needed, and thus the replacement of organic cations by alkali-metal cations is expected to increase the aluminum content in the structure. This is achieved with Ca^{2+} cations in the case of Tschernichite (BEA-type structure).[21−23] However, calcium-governed hydrothermal synthesis of zeolites is usually performed at very high temperatures (> 300 °C), which is not favorable from a practical point of view. In fact, there is a limit on lowering the organic SDA content in the synthesis of zeolites with big pore openings, which is caused by the difficulty of alkali cations to stabilize the zeolite channel (voids) because of their size. For instance, the bulky tetraethyl ammonium cations can be decreased to a R/SiO_2 ratio of 0.10 for obtaining of pure BEA phase, while below this value only amorphous products have been obtained.[25,26] Recently, Xie et al. have claimed a template-free synthesis of zeolite Beta; regretfully, no comment about aluminum content is given.[27] A very interesting approach for preparation of zeolite Beta with low Si/Al ratio by using nucleation gel is reported by Zhou.[28] In this case, the very low amount of TEA.OH is introduced not in a direct form, but as a complex precursor gel containing all the sources (silica, alumina and sodium), which are needed for the synthesis of zeolite Beta. It is clearly demonstrated that this precursor gel did not contain any crystalline phase, but did, however, stimulate the crystallization of high alumina zeolite Beta at a very low consumption of organic template.

In this work, we present the crystallization of Al-rich zeolite Beta (Si/Al ratios as low as 3.9) in the absence of organic structure-directing agent (template) by use of nanosized zeolite Beta seeds. The reactivity of the silica source and synthesis conditions have been varied in order to obtain highly crystalline zeolite Beta.

Experimental Section

Colloidal silica solution or freshly freeze-dried powder (Aldrich, SM-30 30 wt. % in water) as silica source and aluminum isopropoxide (Aldrich, 99.99%) as aluminum source were used for preparation of precursor suspensions. Tetraethyl ammonium hydroxide (TEAOH, Aldrich, 35 wt. % in water) as organic SDA for the preparation of Beta seeds, and sodium hydroxide (NaOH, 85%, Riedel de Haën) for the preparation of Al-rich precursor suspensions were applied.

Synthesis of Zeolite Beta Seeds. Zeolite Beta is prepared from precursor suspensions containing organic template with following compositions (samples denominated **A**-*b*)

$$a\mathrm{Na_2O} : b\mathrm{TEAOH} : 0.25\mathrm{Al_2O_3} : 25\mathrm{SiO_2} : 297\mathrm{H_2O}$$

where *a* is 7.65, 6.7, 1.6, and 0.35, whereas *b* is 1, 3, 5, and 9, respectively. Initially, aluminum isopropoxide was dissolved in a solution containing NaOH, TEAOH, and distilled water, and finally the silica source was added to the clear suspensions and stirred for 30 min. The obtained precursor suspensions were hydrothermally treated in static conditions at 100 and 130 °C for > 4 and 3 days, respectively (Table 1). The crystalline materials were purified in three steps consisting of high-speed centrifugation at 20 000 rpm for 45 min, removal of the mother liquor, and redispersion in double deionized water using an ultrasonic bath. The concentrated zeolite Beta suspensions were freeze-dried prior to characterization.

Synthesis of Al-Rich Zeolite Beta. Precursor suspensions with following chemical compositions were prepared and used for crystallization of Beta zeolite

$$7.5\mathrm{Na_2O} : a\mathrm{Al_2O_3} : 25\mathrm{SiO_2} : 375\mathrm{H_2O}$$
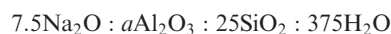
where *a* is 0.25, 0.5, and 0.75. The silica source (B syntheses, freeze-dried silica powder; and C syntheses, colloidal silica solution) was dissolved in a solution of NaOH, aluminum isopropoxide, and distilled water. Dry nanosized zeolite Beta (sample A-9) synthesized and purified through the procedure described in section 2.1 was added as seeds (2.5, 0.5, and 0.1 wt % in relation to SiO_2 content in the precursor reacting mixtures). The mixtures were agitated until a fluid gel was obtained and then hydrothermally treated in static conditions at 100−125 °C

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Table 1. Synthesis conditions and physicochemical characteristics of zeolite Beta synthesized from precursor mixtures containing 2.5 wt. % seeds

sample	conditions	SiO$_2$/TEA$_2$O[a]	phase	crystallinity (%)[b]	yield (%)[c]	Si/Al[d]	Na/Al[d]	surface area (m^2/g)
A-9	100 °C, 4 days	6	BEA	100	40	26	0.07	500
A-5	130 °C, 3 days	10	BEA	100	39	22	0.3	583
A-3	130 °C, 3 days	17	BEA	100	29	13	0.3	524
A-1	130 °C, 3 days	50	BEA	100	28	11	0.8	538
B-0	125 °C, 9 days	∞	BEA + MOR	61		4.8	1.1	376
B-1	125 °C, 6 days	∞	BEA	100	24	4.5	1.2	425
B-2	150 °C, 2 days	∞	MOR+ECR-1			5.6	1.2	
B-3	150 °C, 18 h	∞	amorphous			9.0	2.3	
C-1	100 °C, 12 days	∞	BEA[e]	98−99	10	3.9	1.2	355
C-2	100 °C, 9 d	∞	BEA	32		4.6	1.1	221
C-3	125 °C, 9 days	∞	BEA	87	26	5.4	1.3	284
C-4	125 °C, 6 days	∞	BEA	35		5.6	1.6	112
C-5	125 °C, 4 days	∞	BEA	35		5.9	1.9	81
C-6	125 °C, 2 days	∞	BEA	23				
C-7	130 °C, 3 days	∞	BEA + GIS + MOR			8	2.4	131
C-8	140 °C, 3 days	∞	GIS + MOR			5.4	1.5	
C-9	160 °C, 3 days	∞	MOR			6.2	1.2	
C-10	90 °C, 28 days	∞	BEA		15			

[a] initial precursor suspensions. [b] A-9 is used as reference sample. [c] Calculated on the basis of the crystalline solid in relation to SiO$_2$ + Al$_2$O$_3$ in the initial mixture. [d] Final solid product. [e] Traces of GIS.

for 2−12 days (Table 1). The obtained materials were purified according to the procedure described above and freeze-dried.

Characterization

The crystallinity and phase purity of the samples were determined by X-ray powder diffraction using a PANalytical X'Pert Pro diffractometer in Debye−Scherrer geometry with Cu Kα radiation. Information for the crystal size and morphology of the samples was obtained by scanning electron microscopy (SEM) using a Phillips XL 30 microscope. The porosity of the samples is probed by nitrogen sorption measurements carried out on a Micromeritics ASAP 2040 instrument (the Al-rich BEA samples were measured without calcination). Prior to the measurements, all samples were degassed at 90 °C for 1 h and then at 300 °C for 15 h in a vacuum.

Infrared analysis of Beta samples was performed with a Bruker Equinox 55 FRA106/S spectrometer (32 scans, 4 cm^{-1}). Solid-state ^{27}Al and ^{29}Si MAS NMR spectra were collected with a Bruker Avance^{II} 400 FT spectrometer. The ^{29}Si MAS, ^{1}H decoupled, NMR spectra were recorded at 79.495 MHz with a pulse length of 2.08 μs, a recycle time of 80 s and a spinning rate of 4 kHz; the ^{27}Al MAS NMR spectra were recorded at 104.261 MHz with a pulse length of 0.65 μs and a spinning rate of 25 kHz. Prior to ^{27}Al NMR measurements, zeolite Beta powders were saturated with water in order to reveal all Al species (24 h in desiccators with a saturated solution of NH$_4$Cl in water).

Elemental analyses of all samples were performed using a Phillips MagiX X-ray fluorescence spectrometer. The stability and thermal behavior of zeolite Beta were investigated on a Setaram Labsys analysis instrument with a heating ramp of 5°/min under air flow.

Pyridine adsorption measurements were carried out on sample A-9 after calcination at 550 °C for 10 h in air with a ramp of 1°/min. Samples A-9, B-1, and C-3 (Table 1) were stirred 6 h in excess of a 1 M ammonium nitrate solution, followed by centrifugation at 20 000 rpm and redispersion in distilled water. The procedure was carried out three times and finally the materials were freeze-dried and calcined at the conditions described above.

Results and Discussion

Synthesis conditions, phases and characteristic properties for the most relevant samples described in the present work are summarized in Table 1. The template commonly used for synthesis of zeolite Beta, TEAOH, was progressively replaced by sodium in the samples A-9 to A-1. Inclusion of other cations such as Li$^+$ and K$^+$ in compositions B and C showed a drastic detrimental influence on the crystallization process producing either amorphous material, Mordenite (MOR) or mixtures with Analcime (ANA).[29] It is reported that in the natural Tschernichite, the Ca^{2+} plays a crucial role in the stabilization of the structure.[30] Nonetheless, seeded syntheses with calcium cations were unsuccessful and hindered the growth of any phase in the precursor suspensions. Most probably, the low crystallization temperatures employed for this study were the reason for the absence of structure directing effect of the calcium cations. Therefore, Na$^+$ was used as charge balancing cation in all investigated systems. Fully crystalline samples were obtained after 6 days treatment of the precursor mixtures at temperatures below 125 °C (Table 1). Faster crystallization was achieved by using the more reactive freshly freeze-dried silica (B samples), whereas the precursor suspensions prepared with the colloidal silica solution (C samples) required 3 more days to reach a similar degree of crystallinity. Thus, the colloidal silica (C- type samples) was chosen for further study of the crystallization kinetics of zeolite Beta free of organic additive, because the very fast crystallization of B-type results often in formation of side phases. Furthermore, the use of other alumina sources such as Al(OH)$_3$ and NaAlO$_2$ caused a faster crystallization but also gave MOR as an impurity. For further discussion, mainly samples A-9 (used for seeding) and B-1, C-1, and C-3 will be considered (Table 1).

The crystalline yield from the syntheses batch (amount of solid obtained in relation to SiO$_2$ and Al$_2$O$_3$ used for

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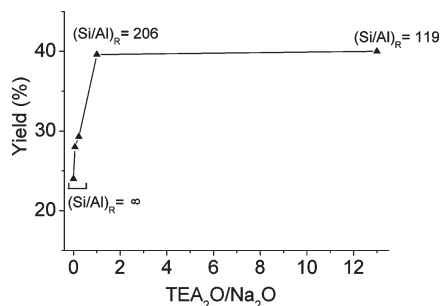
Figure 1. Relation between the crystalline yield of Beta zeolite and TEA_2O/Na_2O ratios of the precursor suspensions; 2.5 wt % Beta seeds were used for the syntheses below a TEA_2O/Na_2O ratio of 0.2 (Si/Al_R is the ratio of the remaining mother liquor after synthesis).

Figure 2. XRD patterns of Beta sample used for seeding (A-9) in comparison to Al-rich Beta (samples B and C) and starting mixture. Dotted line denotes the position of the peaks at 7.0 and 22.1° 2θ (asterisks mark GIS impurity).

preparation of the initial mixture) is about 25−30% and remains mostly unaffected by changing the water content in the reaction mixture and the ratio TEA_2O/Na_2O below 0.2 (for A samples), as can be seen from Figure 1. Only at low crystallization temperature (100 °C, sample B-1) does the yield of zeolite Beta decrease below 10%. It is important to notice that the aluminum content in the mother solution is the limiting factor for the crystallization of Beta zeolite as seen from the Si/Al ratios of the remaining mother liquors (see Figure 1). In all cases, the homogeneity of the mixture was particularly important, as any nondissolved silica easily starts to transform into MOR instead of BEA type molecular sieve.

Different factors influencing the crystallization process related to the presence of seeds were studied, including the seed content, particle size, chemical composition, calcination of seeds, and the impact of the TEA^+ trapped inside the noncalcined seeds. It is found that the crystallite size increases with lowering the seed and template contents in the reacting mixture, and some crystallites even reach the micrometer size range. Between the precursor mixtures containing 10 and 2.5 wt % seeds, no remarkable change in the crystallite size was observed, whereas the use of 0.5 wt % seeds result in octahedral crystals with sizes around 1 μm. For further discussion only the systems containing 2.5 wt. % seeds will be considered, as this quantity is found to be favorable for further optimization of the synthesis process. Beta seeds (Si/Al = 26) in colloidal suspensions (50 nm) were also used in order to obtain less aggregated samples and more homogeneous precursor suspensions. In addition, Al-rich Beta seeds (Si/Al < 4.5) were used for the synthesis; however, no crystalline product was obtained.

The samples seeded by calcined Beta nanoparticles (Si/Al = 26) did not yield any crystalline phase. A possible reason can be a deactivation of the crystalline surface by additional condensation of the high silica seeds upon calcination but not because of the absence of TEA^+ in the seed crystals. The presence of TEA^+ from the seeds was considered to have a negligible impact on the crystallization process because of its extremely low concentration and limited liberation into the synthesis mixture. To verify this, a modified synthesis of template-containing sample A-1 was carried out. In this synthesis, the seed content was lowered to 0.1 wt % while retaining the same
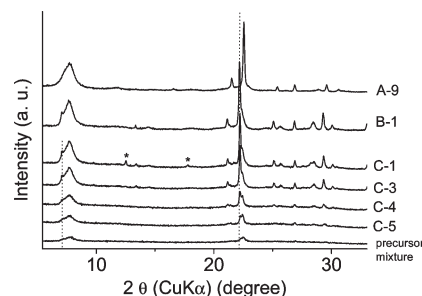
amount of TEAOH ($SiO_2/TEA_2O = 50$) in the precursor suspension. When the template in the seeds is taken into account, then the quantity of template used in the aforementioned synthesis is several times more than in syntheses carried out only with uncalcined seeds (syntheses of samples B and C with 2.5 wt %). However, this experiment gave poor crystalline yield (< 5%). The purpose of this experiment was to simulate a partial dissolution of the seeds (low seed content) and an integration of the template (high template content) into the reacting system. Thus, this demonstrates that the presence of seeds with active surfaces promotes the crystallization of BEA phase and not the low amount of organic template occluded in the channels of the seeds.

An increase of aluminum in the precursor mixtures slowed down the crystallization process. Using a suspension with SiO_2/Al_2O_3 ratio of 100, it was possible to prepare zeolite Beta without giving any nondesired phase. However, the increase of the starting SiO_2/Al_2O_3 ratio above 250 resulted in the crystallization of MFI phase.

X-ray diffraction patterns of high-Al BEA samples along with the parent A-9 seeds and selected samples of series B and C are depicted in Figure 2. All samples show the characteristic zeolite Beta peaks. The highest crystallinity was achieved by sample B-1 after 6 days, followed by C-1 (12 days) and sample C-3 (9 days). An induction period of several days is observed for all samples as seen in the case of composition C, where the same degree of crystallinity was measured for a crystallization period of 4 days. XRD patterns of Al-rich samples show a competition between the Bragg reflections of the Si-rich phase at 22.5° 2θ with the ones of the Al-rich phase at 22.1° 2θ. The position of the signal of the Al-rich Beta has also been observed in the X-ray pattern of natural zeolite Tschernichite.[31] The change of the position of these peaks can be attributed to the higher amount of framework aluminum in comparison to the synthetic zeolite Beta, but also to the open channel network of Beta samples without any organic additives. The XRD diffractograms of Beta samples free of template are also characterized by a sharpness of the peaks at lower 2θ degree (7.05° 2θ) in comparison to the standard sample A-9. This indicates larger crystalline domains in the Al-rich Beta samples

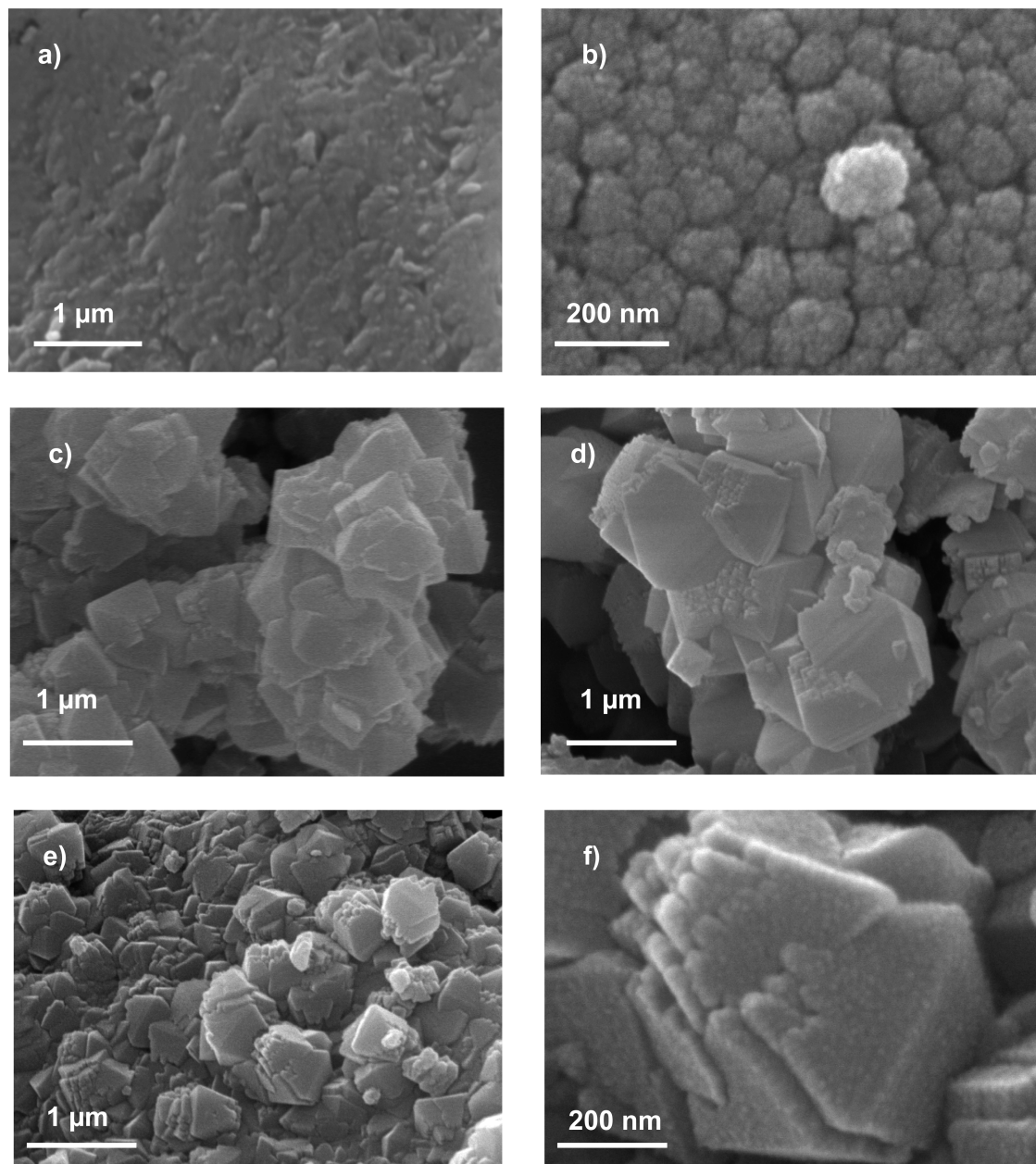(31) Szostak, R.; Lillerud, K. P.; Stöcker, M. *J. Catal.* **1994**, *148*, 91.

Figure 3. SEM micrographs of (a) amorphous precursor gel for sample B-1, (b) A-9 seeds, and Al-rich BEA samples (c) B-1, (d) C-3, and (e) C-1 at low magnification and (f) C-1 at high magnification.

and an approximate ratio of polymorphs A and B of 0.5 in comparison to the standard sample A-9 with a ratio of 0.6.[32]

The morphological features of the precursor mixture and the crystals used as seeds (sample A-9) for the synthesis of Al-rich Beta are shown in Figure 3. The crystalline seeds with size of 100 nm are composed of smaller individual particles with size around 10−20 nm, which during further crystallization fuse together and give the final crystals smoother features. This has been previously observed in the crystallization of templated zeolite Beta.[33] These seeds can hardly be seen in the

precursor mixture because of the small amount and well-disintegrated aggregates during the agitation and aging of the precursor mixtures prior the hydrothermal treatment. The obtained products from syntheses B-1, C-1, and C-3 (Figure 3c−f) are very homogeneous and consist of intergrown crystals possessing a truncated octahedral morphology, typical for zeolite Beta. The individual size of these crystals lies between 400 and 600 nm, and seem to be composed of smaller particles of the same size as the seeds (Figure 3f).

All samples show sorption isotherms characteristic of microporous materials, as can be seen from the N_2-sorption data depicted in Figure 4. No calcination was performed prior to nitrogen sorption measurements of Al-rich samples. Samples B-1 and A-9 exhibited surface areas of 425 and 500 m^2/g, respectively (Table 1). The

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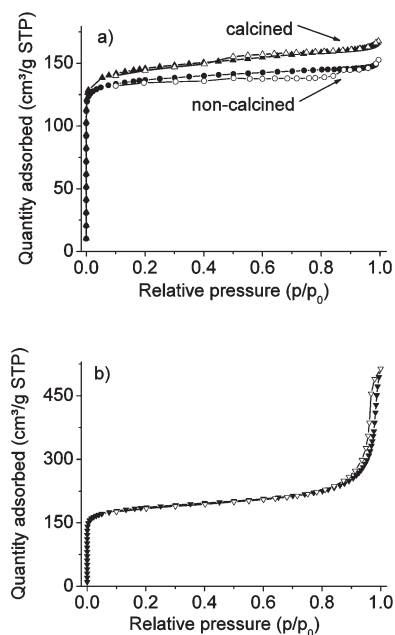(33) Hould, N. D.; Lobo, R. F. *Chem. Mater.* **2008**, *20*, 5807.

Figure 4. Nitrogen adsorption−desorption isotherms for samples (a) B-1 and (b) A-9 seeds.

Figure 5. TG-DTA analyses of as-synthesized samples (a) B-1 and (b) A-9 seeds.

nitrogen sorption isotherms for the Al-rich Beta samples show no textural porosity due to intergrowth and large zeolite crystals (Figure 4a). The surface area of the high-Al Beta samples gradually increases with improving crystallinity of the samples from 81 to 425 m^2/g (Table 1). The contribution of the template from the seeds to the Al-rich material is minimal as seen in Figure 4a; where the surface area liberated after calcination (550 °C, 10 h in air with a ramp of 1°/min) is about 2.3% (447 m^2/g) in comparison to the noncalcined sample .

To assess the quantity of water and organic template coming from the seeds in the samples, we carried out thermogravimetrical (TG/DTA) measurements on zeolite Beta powders saturated with water (24 h in desiccators with a saturated solution of NH$_4$Cl in water). A TG curve with a steep decrease in the range of 25−250 °C, characteristic of hydrophilic microporous materials was observed in all Al-rich samples. The TG data of sample B1 representative for the whole set of Al-rich materials is shown in Figure 5a. The sample B-1 shows an 11% weight loss with a light endothermic signal until 250 °C assigned to adsorbed water and afterward a 2% weight loss with exothermic response attributed to the elimination of the organic template (TEAOH) from the seeds used in the syntheses of Al-rich Beta samples. In the case of the standard zeolite Beta (sample A-9) the exothermic responses measured are about 3.5% weight loss from adsorbed water and about 13% weight loss with a strong exothermic response coming from the high amount of organic template (Figure 5b). The usual weight loss of high silica zeolite Beta is about 17−18 wt % taking into account the surface water. Thus in the case of sample A-9, the total weight loss is 16.5 wt %, which falls into the range measured for colloidal zeolite Beta synthesized from fluoride-free media.
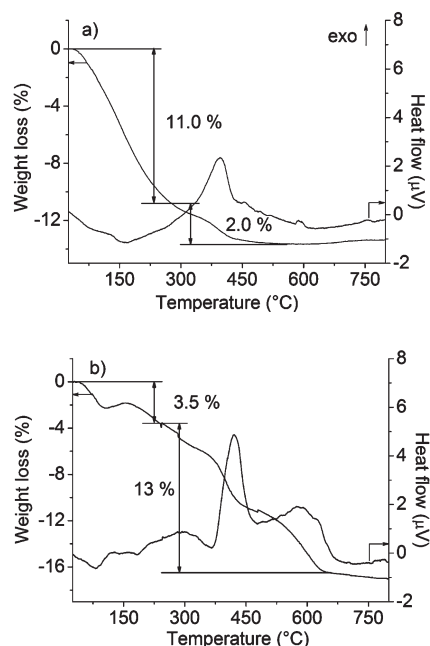
Important conclusions for the assessment of the crystallinity of aluminosilicates are made based on ^{27}Al MAS NMR spectroscopy. All synthesized samples show the presence of only tetrahedrally coordinated aluminum, seen as a signal at 53.4 ppm for the standard high-Si sample A-9, and at 56.6 ppm for all Al-rich samples (Figure 6 A). This low field shift reflects the higher Al content in the second coordination sphere of the framework Al atoms. ^{27}Al spectra of Al-rich BEA also show some asymmetry and peak broadening due to the many different Si−O−Al species present in the samples (see Figure 6Aa, b). The H-form of the standard high-Si (A-9) sample shows a low degree of dealumination due to the calcination process as can be seen from the ^{27}Al NMR spectrum, whereas the Al-rich samples show a small quantity of aluminum at 3.6 ppm that can be due to octahedrally distorted Al and a broad signal related to pentacoordinated aluminum at 28.0 ppm.[34]

^{29}Si MAS decoupled NMR spectra of Al-rich zeolite Beta (Figure 6B a, b) showed four distinct sites for the silicon with different number of Al- neighbors: a) Si-(OAl)$_0$ at −115.5, Si(OAl)$_0$/Si(OAl)$_1$ at −110.0, Si(OAl)$_2$ at −105.2, and Si(OAl)$_3$ at −99.8 ppm.[35,36] As expected, in the case of Al-rich BEA, the peaks related with Al-coordination grew in intensity due to the higher aluminum content. The ^{29}Si spectra of Al-rich samples show an increase in intensity of the signal at −110.0 ppm together with a decrease of the peaks at −105.2 and −98.8 ppm after treatment for conversion into the H-form. The A-9 seeds show also the same behavior but less accentuated,

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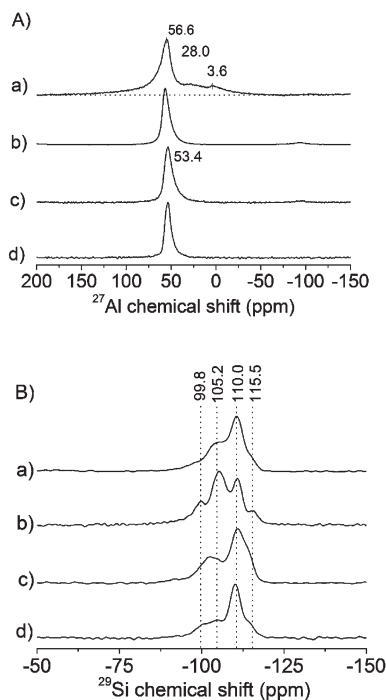(36) Camblor, M. A.; Corma, A.; Valencia, S. *J. Mater. Chem.* **1998**, *8*, 2137.

Figure 6. (A) ^{27}Al MAS and (B) ^{29}Si MAS decoupled NMR spectra of (a) B-1 H-form, (b) B-1 as-synthesized, (c) A-9 H-form, and (d) A-9 as-synthesized Beta samples.

where the signals at -105.2 and -99.8 ppm increase in intensity and overlay into a peak at -102.2 ppm, which can be attributed to dealumination of the sample with an increase of silanol groups (see Figure 6B c). The characteristics of Al-rich BEA samples are also in accordance with the studies made by Szostak on Tschernichite, the natural analogue of zeolite Beta.[31]

X-ray fluorescence spectroscopy measurements show a high aluminum concentration, resulting in Si/Al ratios as low as 3.9 (16.4 Al atoms per unit cell), which is not achievable by templating the zeolite with TEA$^+$, as only 6–8 cations can be accommodated into the unit cell of zeolite Beta. The measured Si/Al ratios for the Al-rich zeolite Beta are very close to the natural Tschernichite possessing a Si/Al of 3.3.[31,37] On the other hand, the crystallization of zone crystals can be expected coming from the seeds, thus higher Si content in the core and high Al concentration in the shell. By closely monitoring the chemical composition of the crystalline products as well as the obtained phases, a good insight into the crystallization process of Al-rich zeolite Beta can be provided. In the initial precursor mixture with a SiO$_2$/Al$_2$O$_3$ ratio of 50, it was possible to generate nucleation sites starting from the high-Si BEA seeds. The inclusion of aluminum was induced by the absence of an organic template in the mixture, as this forces the creation of fresh nucleation sites around the surface of the seeds and thus to counterbalance the Al with sodium. In turn, the abundance of sodium cations induces the inclusion of more aluminum in the BEA structure. Nonetheless, the excess of sodium in the mother liquor is also responsible for the appearance of other phases at higher synthesis temperatures. The speed of crystallization of the metastable BEA phase does not change, as it is dependent on the proximity of seeds, however more stable and denser phases such as Gismondine (GIS) and MOR[2] nucleate in the suspension apart from the seeds, because the composition of the initial mixture fits better the crystallization field of these zeolites at high temperature.

Essentially, zeolite Beta crystallizes first because the initial SiO$_2$/Al$_2$O$_3$ ratio (50) lies outside the typical compositions favoring the growth of competing phases such as MOR (30–40) and GIS (3.5). At temperatures higher than 125 °C, the speed of nucleation for zeolite Beta is slower without any organic template (for instance TEAOH) and the overall composition of the mother liquor starts to change and favor the formation of denser phases. This is supported by the long time syntheses at 100 °C for a period of up to 12 days in which no other phase than BEA is crystallized. At temperatures higher than 150 °C, the formation of MOR as impurity and ECR-1 in very small amount points toward a fast consumption of Si species from the synthesis mixture, this results in products with higher Si/Al ratios (samples B-2 and B-3).[38] The simultaneous formation of MOR phase in the system together with BEA phase after 18 h at 150 °C and further increasing of the MOR phase with further crystallization (48 h) is observed (see Figure A in the Supporting Information). This result shows that high temperature and short synthesis time stimulates the formation of MOR in the investigated system. The GIS phase starts to crystallize before and along MOR phase at intermediate temperatures (130–150 °C) because the lower temperature is detrimental for MOR crystallization.

The acid sides of the Al- and Si- rich zeolite Beta samples have been characterized using pyridine adsorption followed by FTIR spectroscopy. The total number of acid sites was measured by stepwise dosage of pyridine on dried samples in H-form at 200 °C. The acid sites after desorption of pyridine at 200 °C for 1 h were taken into consideration for further quantification following the method developed by Emeis.[39] The Al- rich BEA (sample B-1) shows a higher quantity of acid sites (0.54 mmol/g) than the sample A-9 (0.25 mmol/g) (see the IR spectra in Figure E and Table B in the Supporting Information).

Conclusions

Al-rich zeolite BEA zeolite with Si/Al ratios as low as 3.9 was successfully synthesized starting from precursor suspensions without organic structure-directing agent in the presence of zeolite seeds. It was found that the crystalline yield of zeolite Beta synthesized with seeding is low in comparison to the traditional templated syntheses. The slow crystallization kinetics and narrowness of crystallization

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field for Al-rich zeolite Beta may explain the scarcity of the material Tschernichite in nature.

Our results clearly show that the crystallization of zeolite Beta initiated by seeds (≤ 2.5 wt. %) can only be successfully carried out using low synthesis temperatures (< 125 °C) as higher temperatures easily induce the formation of MOR as seen in samples B-2 and C-7 to C-9. Also, the Beta crystals show large sizes around 400 nm and no crystals with sizes below 200 nm are present. These results are in a good agreement with the work of Kim and Ahn reporting the crystallization of MOR from the unseeded precursor suspensions at high temperatures.[40]

Although the used precursor mixtures and synthesis conditions need further optimization to improve the crystalline yield and decrease the degree of aggregation, the obtained Beta samples show interesting acid/base properties and may be useful for catalytic studies in direct comparison to zeolite Y (FAU-type structure). This synthesis approach also opens new ways for the development of an economic and environmentally friendly synthesis procedure for Al-rich zeolite Beta without the use of template.

Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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