NCL-7, A novel all silica analog of polymorph B rich member of BEA family: Synthesis and characterization

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Abstract

Polymorph B-rich BEA type structure, NCL-7, was synthesized using hydrothermal method in fluoride medium using perchloric acid as promoter. The samples were characterized using XRD, low temperature N_2-adsorption and ^{29}Si MASNMR. As the structure of beta is highly disordered Rietveld refinement of powder XRD patterns is precluded. Phase composition is derived using the simulated patterns for the random intergrowths of polymorph A and B by DIFFaX. The stacking direction c' is perpendicular to the $a'b'$ plane of the layer. The composition of polymorph B is found to be ca. 60–65%. Two other structures namely NCL-5 and NCL-6 with varying degree of polymorph B enrichment were also synthesized. Synthesis parameters such as effect of H_2O/SiO_2, $TEAOH/SiO_2$, $HClO_4/SiO_2$ and crystallization temperature were studied thoroughly. The present article explains for the first time the synthesis and characterization of NCL-7, an analog of BEA type family with enrichment of polymorph B and its comparison with normal beta (*BEA).
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1. Introduction

Zeolite beta firstly synthesized by Wadlinger et al. [1], is one of the most useful high silica zeolite, its interconnected large pore network and strong acidity giving it special catalytic properties [2–6]. It is highly disordered, made of the random intergrowth of polymorph A and polymorph B in the ratio ca. 45:55 respectively. Both the polymorphs A and B are constructed from the same centrosymmetric, tertiary building unit (TBU) arranged in layers successively which interconnect either left handed (L) or right handed (R) manner. Polymorph A represents uninterrupted sequence either left handed or right handed, whereas the polymorph B has alternative stacking sequence. TBU has no preference for the either mode of connection leading both to occur with almost equal possibility in the structure of Beta,

which enhances the growth of faulty structure. Polymorph A (with space group symmetry $P4_122$ and $P4_322$) and polymorph B (with space group $C2/c$), were theoretically proposed by Newsam et al. [7]. Though none of these polymorphs was synthesized till date, another analog of BEA family, polymorph C was reported by Corma and his co-workers using 1 benzyl-1,4-diazabicyclo[2.2.2]octane as a structure directing agent in presence of Germanium [8–10a]. Liu et al. reported the synthesis of pure silica Beta polymorph C using tetramethylene bisquinuclidinium diquaternary cation [10b]. Though elucidation of structure of zeolite beta solved a long lasting problem in zeolite crystallography [11,12], realizing the synthesis of Polymorph A and B or even to significantly alter the concentration of polymorphs has eluded the scientific community over 20 years.

Most of the zeolites synthesized by hydrothermal method suffer the hurdle of long crystallization period. Previously, we had reported chemical method to reduce the crystallization time of zeolite using oxyanions as promoter,

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which not only speed up the crystallization but also stabilizes the less metastable phase [13–15]. It is in this context that we have endeavored use of promoter for controlling the faulting in zeolite beta. We herein, report the use of perchloric acid as promoter in the synthesis of B-rich BEA type material (NCL-7) in fluoride medium. We also studied the effect of different synthesis parameters such as template concentration, water content, promoter and temperature to understand the role of individual.

2. Experimental

2.1. Materials and synthesis

Tetraethyl orthosilicate (TEOS, 99+%, Aldrich), tetraethylammonium hydroxide solution (TEAOH, 35% aqueous solution, Aldrich), hydrofluoric acid (HF, 40% aqueous solution, Loba-Chemie, India Ltd.), perchloric acid ($HClO_4$, 70% aqueous solution, Loba-Chemie India Ltd.) were used as a raw material for the synthesis.

The syntheses were carried out hydrothermally at 408 K by following similar procedure as described earlier [16]. Different gels were prepared having molar gel compositions $SiO_2:xTEAOH:0.57HF:yHClO_4:zH_2O$, where $0.38 < x < 0.98$, $0.0 < y < 0.15$ and $7.6 < z < 50$ and then subjected for hydrothermal treatments under pre-decided set of synthesis conditions. In a typical synthesis of NCL-7, 62.4 g of TEOS was slowly added at room temperature to 85.7 g aqueous TEAOH solution under vigorous stirring. In order to remove the ethanol liberated, stirring was further continued till 37.6% weight loss was achieved. To this mixture, 8.53 g of 40% aqueous hydrofluoric acid was added with constant stirring and stirring was further continued for 30 min. Finally 3.88 g of 70% aqueous perchloric acid was added to the above mixture with vigorous stirring and stirring was continued till homogeneous gel was formed. The pH of the homogeneous gel thus formed was 7.5 ± 0.2. Based on the extent of weight loss due to escaped ethanol, the resultant gel has a molar composition $SiO_2:0.68TEAOH:0.57HF:0.09HClO_4:9.5H_2O$. The gel was then transferred into 300 mL capacity batch autoclave. The stirring speed was maintained at 160 ± 10 rpm. The crystallization kinetics was studied by comparing the extent of the crystallization as a function of time at 408 K. The solid product was separated from mother liquor by filtration and washed thoroughly with distilled water. The product obtained was dried at 383 K under vacuum for 2 h. The fully crystalline phase obtained after 120 h was further calcined at 833 K for 12 h in presence of air. All-Silica Beta (*BEA) sample was obtained from the same molar gel composition without $HClO_4$ after crystallization period of 142 h at 408 K.

2.2. Characterization

The calcined samples were scanned on a Philips X'Pert Pro powder X-ray diffractometer using Co Kα radiation

($\lambda = 1.7903$ Å) on a flat sample stage in the reflection mode. The diffractometer was equipped with a Fe filter and X'celerator as detector. The samples were scanned in the range 5–60° 2θ and the scans were collected for 6 h to increase the intensity of weak and overlapping reflections. The Rietveld refinement of the powder XRD pattern of NCL-7 was attempted using the X'Pert Plus software. The simulation studies were carried out using the DIFFaX code [17]. In this the solid is treated as a stacking of layers and are interconnected by appropriate stacking vectors and this operation results in the stacking of layers in either at random or in some particular manner with certain probability. The XRD pattern is then simulated by integrating the diffraction intensities layer by layer. By changing the layer composition or the stacking sequence, it is possible to build in different types of disorder into the lattice and compute the changes in the pattern. During the simulation of powder pattern using DIFFaX, we have changed only the stacking probabilities of the different layers, while standard stacking vectors were used. The simulation yields Bragg maxima, which is suitably broadened using a Lorentzian line shape to incorporate the instrumental broadening before a comparison is made with the experimental pattern. The low temperature nitrogen adsorption and desorption isotherms were obtained using Omnisorb 100 CX Coluter instrument. Prior to measurement, sample was degassed for 12 h under vacuum at 573 K. The specific surface areas were determined by BET method. Solid-state ^{29}Si MAS NMR spectra were recorded on Bruker MSL-300 NMR spectrometer at 59.595 MHz. The finely powdered calcined samples were placed in zirconia rotor and spun at 4 kHz. The chemical shifts were referred with respect to tetraethyl orthosilicate ($\delta = -82.4$ ppm from TMS).

3. Result and discussion

3.1. Characterization of NCL-7

3.1.1. X-ray diffraction

Fig. 1, depicts the powder XRD patterns of calcined NCL-7, All Si-beta (*BEA), and simulated pattern of pure polymorph B of *BEA family. The X-ray profile consists of mainly sharp reflections and some broad peaks indicative of the inherent faulting characteristic of the *BEA. In comparison to the reported powder patterns of zeolite beta, our sample yield fairly good powder pattern indicating the predominant phase of polymorph B. Although, the Rietveld refinement of the powder pattern of disordered zeolite beta is not appropriate for structural studies, yet we have made an attempt to do structural refinement till the model was steady and the phase composition of polymorph B was found to be 80%. Coordinates for the polymorphs A and B were taken from the reported data by Higgins et al. [11], the R values could not be improved since the atoms could not be stably refined due to the inherent disorder present in the sample. Hence, the simulations of powder
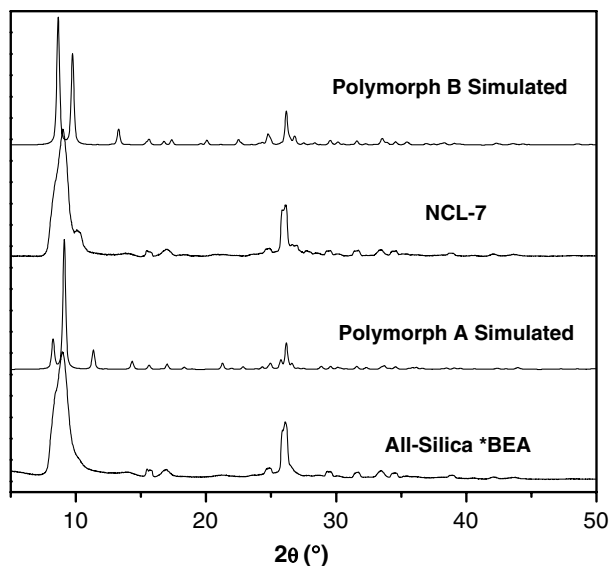
Fig. 1. Powder X-ray diffraction patterns of *BEA, NCL-7 and simulated polymorph A and polymorph B.
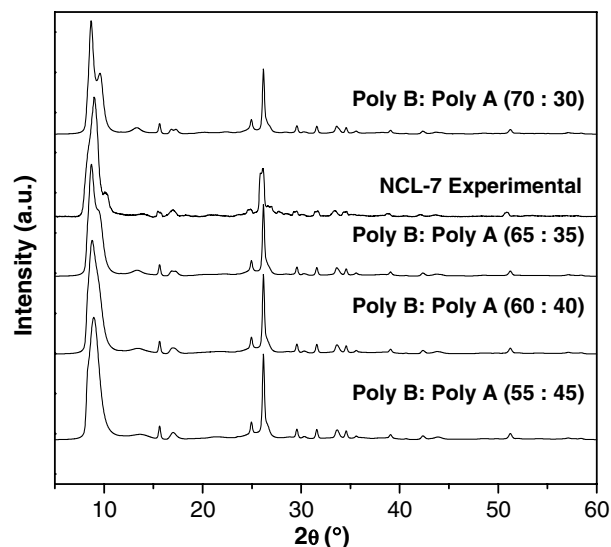

Fig. 2. Comparison of simulated patterns of zeolite beta with different proportion of polymorph B and polymorph A with NCL-7 where the values in the parenthesis indicate the proportion of polymorph B and polymorph A respectively.
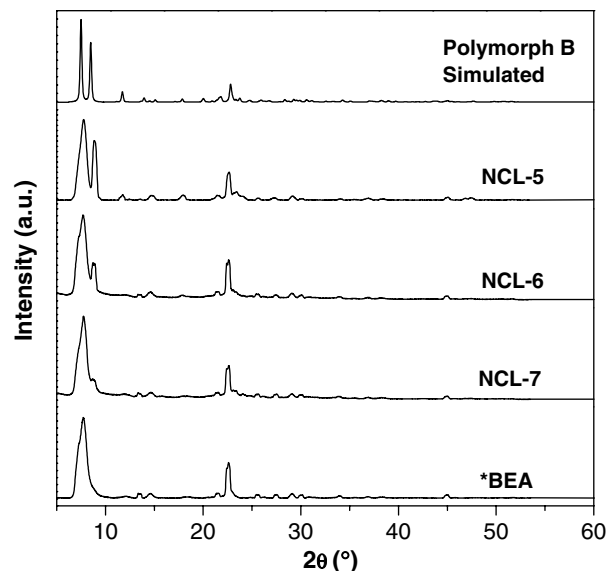

Fig. 3. The powder XRD patterns of simulated polymorph B and experimentally obtained NCL-5, NCL-6 and NCL-7 and *BEA (standard Si-Beta).

patterns of zeolite beta for different ratios of polymorphs A and B have been carried out using DIFFaX code. The stacking direction c' is perpendicular to the $a'b'$ plane of the layer. For comparison with the observed pattern of NCL-7, the intensity values of simulated patterns for random intergrowths of polymorphs A and B were normalized. On comparison of the simulated patterns with the experimental pattern of NCL-7, the best agreement was found with ca. 65% of polymorph B. This can be more clearly seen in Fig. 2 where NCL-7 experimental XRD pattern is compared with simulated XRD patterns of various intergrowth of polymorph B: polymorph A in the ratio

of 55:45, 60:40, 65:35 and 70:30. Broadening in the reflections of the observed patterns is due to the heavy faulting/disorder in the material. In Fig. 3, the powder XRD patterns of experimentally obtained samples of Si-Beta, NCL-5, NCL-6 and NCL-7 are plotted along with simulated XRD pattern of polymorph B indicating that NCL-5, NCL-6 and NCL-7 consists of the intergrowth of polymorph B (vis-à-vis polymorph A) as ca. 95%, 75% and 65%, respectively. The detailed characterization of NCL-5 and NCL-6 is in progress.

3.1.2. Low temperature N_2-adsorption–desorption

Fig. 4 shows the low temperature N_2-adsorption–desorption isotherms for *BEA and NCL-7 samples. The *BEA sample has exhibited BET surface area of the magnitude 618 $m^2 g^{-1}$. After employing t-method, the values for external surface area, microporous surface area and cumulative micropore volume were approximated to 43 $m^2 g^{-1}$, 575 $m^2 g^{-1}$ and 0.228 cc/g respectively. However, NCL-7 has not only shown the lower value of BET surface area but also for external surface area, microporous surface area and cumulative micropore volume as compared to *BEA. These observations provide the base, at least partly, to believe that there is higher concentration of B polymorph in NCL-7 as compared to *BEA, as hypotheticated by Newsam et al. [7]. The BET surface area, external surface area, microporous surface area and cumulative micropore volume of NCL-7 were found to be 539 $m^2 g^{-1}$, 26 $m^2 g^{-1}$, 513 $m^2 g^{-1}$ and 0.206 cc/g respectively.

3.1.3. ^{29}Si MAS NMR

^{29}Si MAS NMR spectra of calcined *BEA and NCL-7 samples are depicted in Fig. 5. Both the spectra show no distinctive peaks in the ppm range of 95–100. Thus, it
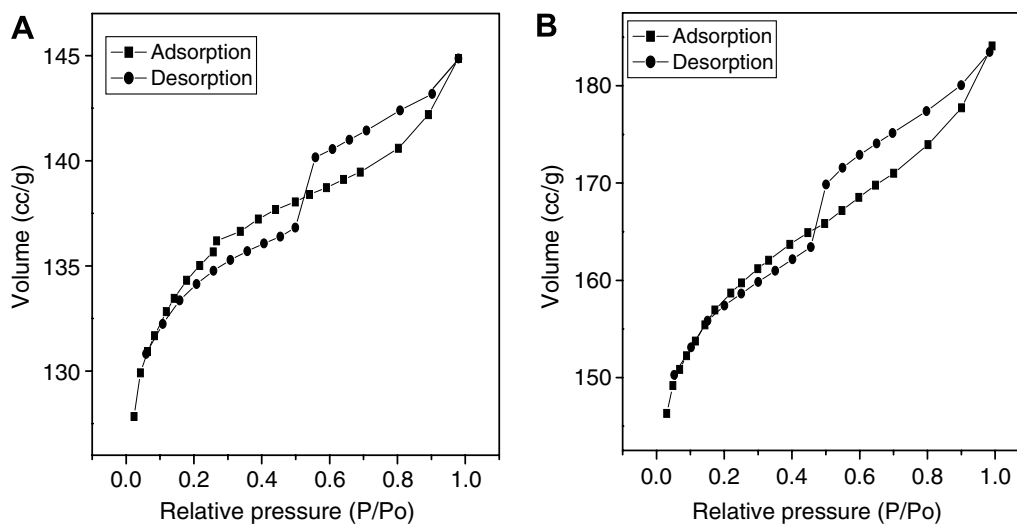
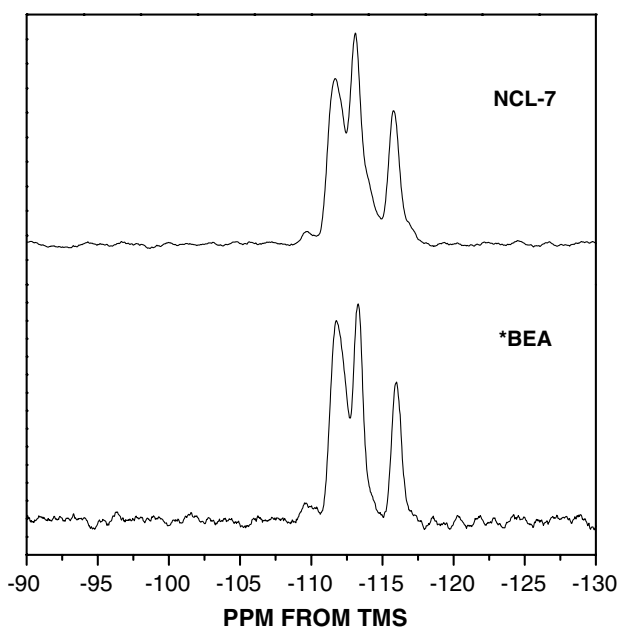Fig. 4. N_2-adsorption–desorption isotherm for *BEA (A) and NCL-7 sample (B).

Fig. 5. ^{29}Si MAS NMR spectra of *BEA (zeolite beta with polymorphic proportion of polymorph B:polymorph A 55:45) and NCL-7 (zeolite beta with polymorphic proportion of polymorph B:polymorph A 70:30).

can be concluded that, irrespective of variation in polymoph B concentration, defectless structures can be obtained by fluoride-mediated syntheses under mentioned conditions. The ^{29}Si MAS NMR spectra of the calcined samples were deconvoluted in five different T sites in the range of −111.46 to −115.98 ppm, which have been assigned to Q^4 sites [18–20]. The data for different Q^4 site population for these samples are provided in Table 1. It can be clearly seen from this table that, no any regular trend was observed in the population of different sites. However, NCL-7 has shown higher population of T_C, T_D and T_E sites as compared to *BEA. Although, no meaningful conclusion can be drawn from this observation at current stage, further investigations are in progress.

3.2. Optimization of synthesis parameters

The synthesis parameters for the B-rich analog of zeolite beta, NCL-7 were optimized. Influence of different synthesis variables such as temperature, structure directing agent, promoter and its concentration, and water was studied thoroughly. One parameter was changed at one time keeping other parameters and addition sequence constant.

3.2.1. Effect of temperature

Influence of temperature on the phases formed and the proportion of B:A polymorphs in pure crystalline beta phases was studied thoroughly in the range of 373–423 K. Table 2 depicts the influence of temperature on the crystallization and the phase formed. The samples were

Table 1
^{29}Si MAS NMR data for Q^4 site distribution in *BEA and NCL-7

Sample name	Lattice site T_A (−111.58 ± 0.2 ppm)			Lattice site T_B (−112.20 ± 0.2 ppm)			Lattice site T_C (−113.15 ± 0.2 ppm)			Lattice site T_D (−113.9 ± 0.2 ppm)			Lattice site T_E (−115.88 ± 0.1 ppm)		
	Cs^a	Lw^b	P^c	Cs^a	Lw^b	P^c	Cs^a	Lw^b	P^c	Cs^a	Lw^b	P^c	Cs^a	Lw^b	P^c
*BEA	111.72	0.76	34.82	112.39	0.51	12.07	113.27	0.49	27.94	113.74	0.80	4.12	115.98	0.58	21.06
NCL-7	111.46	0.68	21.72	112.06	0.68	12.71	113.08	0.65	34.52	113.96	1.08	8.87	115.81	0.75	22.17

[a] Chemical shift assignment in ppm.
[b] LW = Line width in ppm.
[c] Relative population of lattice sites in the sample (normalized to 100) in ppm.

Table 2
Influence of temperature on crystallization time and obtained phase with molar gel composition $1.0SiO_2:0.68TEAOH:0.57HF:0.09HClO_4:9.5H_2O$

Entry no.	Temperature (K)	Duration (h)	Phase
1	373	336	NCL-7
2	383	228	NCL-7
3	393	216	NCL-7
4	403	144	NCL-7
5	408	120	NCL-7
6	413	108	NCL-7
7	423	95	*BEA

collected at regular interval till the crystallization is completed. As evident, B-rich NCL-7 phase was obtained in the temperature range 373–413 K. When the synthesis was carried out at 423 K the *BEA phase is formed. In order to study the transformation of phase, the synthesis of NCL-7 at 408 K (Table 2, Entry 5) was continued further for 96 h after obtaining the NCL-7 phase. However, it is paramount to mention that the no phase transformation was observed. Therefore, the transformation of NCL-7 to *BEA could be easily ruled out at temperature 423 K. As expected, the crystallization period decreases with the increase in temperature. BET surface area of NCL-7 synthesized at 373, 383, 393 and 408 K was found to be 583, 572, 568 and 539 $m^2\,g^{-1}$ at the crystallization temperature respectively.

3.2.2. Effect of structure directing agent (SDA)

The structure directing agent (SDA) contributes to the stability of the solid and allows the formation of the desired phase. Effect of template (TEAOH) concentration NCL-7 studied to provoke its effect on the phase formed and crystallization kinetics is tabulated in Table 3. Concentration of TEAOH was systematically varied in the range of the TEAOH/SiO_2 = 0.38–0.98 keeping other parameters constant. It was observed that NCL-7 phase was obtained in the range of TEAOH/SiO_2 = 0.68–0.98 (Table 3, Entries 3–5). However, when concentration of TEAOH was >0.68 *BEA phase was obtained. At the same time the decrease in the crystallization time was observed from 120 h for (TEAOH/SiO_2 = 0.68) to 78 h for (TEAOH/SiO_2 = 0.98). This could be attributed to the increase pH due to presence of more OH^- from TEAOH and amount of more TEA^+ cations available for nucleation as reported

earlier [21]. Also SDA contributes the structure by formation of template–template bond and/or template framework bond that leads to the different stabilizing interaction of the charge density of the framework and shape of the desired phase(s). BET surface area of the samples was found to be 539, 527, 571 and 560 $m^2\,g^{-1}$ when the TEAOH/SiO_2 ratio was varied from 0.68, 0.78, 0.88 and 0.98 respectively.

3.2.3. Effect of promoter

Oxyanions such as perchlorate, phosphate and bromate act as a promoter for the enhancement of the nucleation and crystallization. It is reported that the polarising ability and charge to radius ratio are the key factors for the enhancing crystallizaton rate and stabilizing the phases [13]. Table 4 outlines the effect of oxyacids, $HClO_4$ and H_3PO_4 and their concentration on the phase formation and duration required to obtain the crystalline phase. The concentration of $HClO_4$ as promoter was varied from 0.0 to 0.18 with stepwise increase, keeping H_2O/SiO_2 and TEAOH/SiO_2 molar ratio constant. It was observed that at lower $HClO_4$ concentration ($HClO_4$/SiO_2 = 0.0–0.045) *BEA was obtained (Table 4, Entries 9 and 2). At moderate $HClO_4$ concentration ($HClO_4$/SiO_2 = 0.08–0.12), B-rich structure (NCL-7) was obtained (Table 4, Entries 1, 3–4 and 7). However, further increase in $HClO_4$ concentration (0.15 and 0.18) *BEA containing MFI impurity (Table 4, Entries 5 and 6) was obtained. Similarly, when the synthesis trials were carried out using the H_3PO_4 as promoter keeping the H^+ ion and PO_4^{-3} concentration same (Table 4, Entries 7 and 8) the B-rich phase could not be obtained. This may be probably due to the phosphoric acid is having the lower nucleation and crystallization energy compared to perchloric acid. However, no B-rich phase was obtained for any synthesis trial conducted in the absence of promoter. Probably, the use of perchlorate oxyanion in concentrated fluoride medium (at lower H_2O/SiO_2 molar ratio) may facilitate the overlapping of the TEA-enclathrated oxofluorosilicate species. Such overlapping forms composite species at the onset of crystallization process. Thus kinetic effect seems to be responsible for the phase formation [13,14].

Table 3
Effect of TEAOH concentration on crystallization time and obtained phase with molar gel composition: $SiO_2:xTEAOH:0.57HF:0.09HClO_4:9.5H_2O$ at 408 K

Entry no.	x	Duration (h)	Phase
1	0.38	170	*BEA
2	0.48	154	*BEA
3	0.68	120	NCL-7
4	0.78	84	NCL-7
5	0.88	77	NCL-7
6	0.98	72	NCL-7

Table 4
Effect of promoter on crystallization time and obtained phase using molar gel composition: $SiO_2:xTEAOH:0.57HF:xHClO_4:yH_3PO_4:9.5H_2O$ at 408 K

Entry no.	x	y	Duration (h)	Phase
1	0.09	0	120	NCL-7
2	0.045	0	160	*BEA
3	0.08	0	126	NCL-7
4	0.12	0	115	NCL-7
5	0.15	0	102	*BEA
6	0.18	0	96	*BEA + MFI impurity
7	0	0.09	148	*BEA
8	0	0.03	196	*BEA
9	0	0	186	*BEA

3.2.4. Effect of H_2O/SiO_2 ratio

Table 5 outlines the influence of H_2O/SiO_2 molar ratio in the range of 7.5–50 on crystallization keeping other synthesis parameters same. The water concentration in the gel is already limited by the water content in the TEAOH (35% aqueous solution) HF (40% aqueous solution), $HClO_4$ (70% aqueous solution) without adding any extra water, the lower water gel compositions particularly $H_2O/SiO_2 = 7.5$ and 8.5 were achieved by removing the water from the synthesis gel at room temperature under mild vacuum. At lower water concentration ($H_2O/SiO_2 = 7.5$–9.5 Table 5, Entries 1–3), the polymorph B-rich zeolite beta phases namely NCL-7, NCL-6 and NCL-5 with ca. 60–65%, 70–75% and 90–95% enrichment of polymorph B were obtained. The percent composition of intergrowth for NCL-5, NCL-6 and NCL-7 was obtained by comparing their XRD patterns with those simulates for these compositions. At moderate water concentration (up to $H_2O/SiO_2 = 20$ Table 5, Entries 4 and 5) *BEA phase was obtained and above this the obtained phase was *BEA with MFI impurity (Table 5, Entries 6 and 7). These observations can be related to the nucleation step and hence, is probably a kinetic effect. As all the synthesis trials are carried out in fluoride medium, the soluble species more probably seems to be oxofluorosilicate around neutral pH. As the H_2O/SiO_2 ratio decreases the corresponding F^- concentration increases which in tern likely to increase the fluoride to oxygen ratio of the silicate species in the solution. As the crystallization takes place by condensation of silicate species in the solution, the decrease in water content increases the concentration of occluded F^- which requires higher concentration of SDA. It may be recalled that the amount of SDA required to obtain NCL-7 phase is higher in comparison with normally used for the synthesis of *BEA in hydroxide medium. It is important to note that with decrease in the water content in the gel the relatively high dense phase is obtained. Camblor et al. have reported that different phases can be prepared by using the same template with varying the H_2O/SiO_2 ratio [18]. The more metastable phases occurs at more concentrated condition (low H_2O/SiO_2 ratio). The above statement resembles with the proven fact that increase in H_2O/SiO_2 the phase is obtained with the increasing time (Ostwalds ripening) or temperature, which suggests the kinetic control outlined above. However, it is pertinent to note that the Ostwalds ripening is normally a slow process probably due to the low solubility of crystalline phases. Henceforth, it could be concluded that water content in the gel plays an important role in the direction of structure. The effect of water content in the synthesis mixture can modify in some extent the structure directing ability of the SDA and very different phases can be obtained using the same SDA. Transport properties within the gel and the viscosity of the reacting gel vary with the variation in the water content. Even though the phase selectivity is largely going to be dependent on the structure-directing agent, water too can tip the balance of, which phase to crystallize [19].

4. Conclusion

The synthesis of novel B enriched zeolite BEA (NCL-7) could be achieved by using perchlorate oxyanion as promoter in fluoride medium. The synthesis parameters such as $TEAOH/SiO_2$, H_2O/SiO_2, effect of promoter and temperature are optimized. Synthesis of NCL-7 can be achieved in the temperature range 373–413 K, $TEAOH/SiO_2$ molar ratio 0.68–0.98, $HClO_4/SiO_2$ molar ratio 0.08–1.2 and H_2O/SiO_2 molar ratio 9.5. The key factors, which enabled to get preferentially higher concentration of polymorph B of zeolite beta family, are the use of perchlorate as promoter oxyanion in fluoride medium and the H_2O/SiO_2 molar ratio. Two other structures namely NCL-5 and NCL-6 with varying degree of polymorph enrichment were also synthesized and their detailed characterization is in progress.

Table 5
Influence of H_2O/SiO_2 on the crystallization time and obtained phase using molar gel composition: $SiO_2:0.68TEAOH:0.57HF:0.09HClO_4:xH_2O$

Entry no.	x	Duration (h)	Phase
1	7.62	96	NCL-5
2	8.52	110	NCL-6
3	9.50	120	NCL-7
4	14.0	144	*BEA
5	20.0	156	*BEA
6	25.0	168	*BEA + MFI impurity
7	50	190	MFI + *BEA impurity

$T = 408$ K.

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