Synthesis of polymorph A-enriched beta zeolites in a HF-concentrated system†

Guanqun Zhang, Pingchun Wang, Weiping Zhang, Mingrun Li and Zhijian Tian*abcd

Polymorph A-enriched beta zeolites were synthesized by employing high HF concentrations in the synthesis medium. The polytopic compositions of the synthesized beta zeolites were determined by the complementary characterization methods: 1H NMR analysis and PXRD simulation. With a variety of SDAs, a high HF concentration (HF/SDA > 1.0) in the synthesis medium results in the A-rich feature (55–65% A) of beta zeolites, while a moderate HF concentration only results in typical beta zeolites. A systematic study on the synthesis conditions reveals the existence of a buffer system of H+ and F− formed in the highly HF-concentrated medium. This buffer results in a small but continuous supply of F− during zeolite crystallization, in contrast to the conventional fluoride route where all F− are discharged all-at-once at the initial stage.

Introduction

Zeolites are crystalline materials defined by ordered micro-porous pores or cavities. For some zeolites like beta, ITQ-39, SSZ-26 and SSZ-33, more than one form of crystal structure (known as polymorphs) is capable to exist and inter-grow in the zeolite. The different inter-growing extents of polymorphs would undoubtedly change the pore/cavity arrangement in the zeolite structure and hence influence the stability and catalytic properties of zeolites. Beta zeolites are among the first synthetic zeolites with three-dimensional large pores and high Si/Al ratios, and are widely applied in catalysis, separation and other fields. Structural elucidation shows that beta zeolites are an intergrowth of three closely related polymorphs, i.e. polymorphs A, B and C. These polymorphs are built from epistaxis stacking of identical layer units. The different stacking ways of the neighboring layers build up these three polymorphs that possess similar twelve-ring pore sizes but different channel features: polymorph A has one chiral and two straight channels, polymorph B has one achiral sinusoidal and two straight channels, whereas polymorph C has three straight channels. The different channel structures of the three polymorphs endow them with different properties. The intrinsic chiral channel systems of polymorph A may be useful in chiral sorption and catalysis. For instance, using the polymorph A-enriched beta zeolite as the catalyst, Tong has reported a higher product enantioselectivity than by the typical beta zeolite. The three-dimensional straight channels of polymorph C would remarkably enhance the diffusion of reactants. Preceding research by Tomlinson and Li showed that the structures of polymorphs A and B are almost thermodynamically equivalent while the structure of C is slightly less stable, indicating that those polymorphs tend to grow together instead of separately. For decades endeavors towards the synthesis of beta zeolites enriched in specific polymorphs have never stopped. Nevertheless, despite the diversity of synthesis conditions employed, usually the synthesized beta zeolites contain about 45% A, 55% B and a trace amount of C (which is referred to as “typical beta”). The generally constant polymeric composition of beta zeolites makes the enrichment of a specific polymorph quite a challenging task. In 2001 by introducing Ge atoms in the synthesis Corma’s group obtained the pure polymorph C. Later this group synthesized a beta zeolite of 85% polymer B by using a suitable structure-directing agent (SDA) and by adjusting the H2O/Si ratio in the synthesis medium. Very recently, Yan’s group has made great achievements in synthesizing A-enriched beta zeolites containing 65% polymorph A. They demonstrated that the ultra-concentrated synthesis conditions, (H2O/Si ≤ 1.12) and the partial decomposition of tetraethylammonium hydro-
oxide (TEAOH) are crucial to the enrichment of polymorph A in beta zeolites. In these studies, the polymorphic composition was determined by either the PXRD refinement or PXRD simulation method which is suitable when no more than two polymorphs are present in the zeolite.24

In this work, we present the syntheses of beta zeolites at different HF concentrations (defined as HF/SDA ratio) with either pyrrole derivatives or tetraethylammonium hydroxide (TEAOH) as the SDA. Compositions of the three polymorphs in the obtained materials were determined by employing $^{19}$F solid-state NMR analysis and powder X-ray diffraction simulation as complementary characterization methods. When synthesized at high HF concentrations, beta zeolites, directed by either of the SDAs, exhibit remarkable enrichment of polymorph A. Investigation on the fluoride species in the precursor gel and post-synthesis filtrates reveals the presence of a buffered system of H$^+$ and F$^−$ in the synthesis medium, which controls the release of F$^−$ for the crystallization process and is thought to be responsible for the polymorphic enrichment in beta zeolites.

### Experimental section

#### Synthesis of SDAs

Four SDAs were used in the synthesis to evaluate their influence on the polymorphic composition of beta zeolites. Among them three pyrrole-based SDAs, i.e., N-isobutyl-N-methylpyrrolidinium hydroxide, N-isopropyl-N-methylpyrrolidinium hydroxide and N-isopentyl-N-methylpyrrolidinium hydroxide (denoted as iButOH, iProOH and iPenOH, respectively) were synthesized in the laboratory. The synthetic steps are detailed in the ESL† TEAOH, a common SDA in the synthesis of beta zeolites, was purchased as 25 wt% solution from Aladin and used as received.

#### Synthesis of Zeolite

The synthetic procedure of beta zeolites is based on the previous fluoride synthesis route with slight modifications12 (see the ESL† for details). The molar composition of the final mixture is 1SDA : 2SiO$_2$: 10H$_2$O : nHF. A summary of synthesis conditions is listed in Table 1. The products are denoted as iBut-beta(n), iPro-beta(n), iPen-beta(n) and TEA-beta(n), respectively, where the n value represents the HF/SDA ratio.

#### Characterization

Powder X-ray diffraction (PXRD) was performed on a PANalytical X’Pert Pro diffractometer equipped with a Pixel detector using Cu Kα1 radiation ($\lambda = 1.5406 \text{ Å}$) operated at 40 mA and 40 kV with a scanning speed of 5° min$^{-1}$. Scanning electron microscopy (SEM) was carried out on a Hitachi S4800 field-emission scanning electron microscope operating at 20 kV. $^{29}$Si and $^{19}$F solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) data were collected on an Agilent DD2-500 MHz spectrometer with a spinning rate of 13 kHz and 15 kHz, respectively. Liquid $^{19}$F and $^{29}$Si NMR data were collected on a Bruker Avance III 500 MHz NMR spectrometer (frequency 470 MHz). $^{29}$Si and $^{19}$F chemical shifts were referenced to tetramethyldisilane (TMS) and CFCl$_3$, respectively. The $N_2$ isotherm was measured with Micromeritics ASAP 2420 apparatus at 77 K. High-resolution transmission electron microscopy (HRTEM) images was obtained using an FEI Tecnai F30 microscope operated at 300 kV with a point resolution of 0.20 nm.

#### Simulation of powder X-ray diffraction (PXRD) patterns

The powder X-ray diffraction patterns of the inter-grown structure of beta zeolites was simulated using the program DIFFaX_v1813.24–26 The unit cell parameters and planar translations of the building layer of beta zeolites was extracted from the database of international zeolite association (see http://izasc.biw.kuleuven.be/fmi/xsl/IZA-SC/ref.xsl) as the starting model. The simulation was based on the random stacking of layers in the zeolite structure. The instrumental broadening was shaped by the pseudo-Voigt peak shape function wherein the parameters were set as 0.89, −0.32, 0.08 and 0.6 for $u$, $v$, $w$ and $\sigma$ respectively.

#### Results and discussion

The SEM images show that iBut-beta(n), iPro-beta(n) and iPen-beta(n) zeolites have similar prism-like morphologies, whilst TEA-beta(n) zeolites have truncated bipyramidal shapes (see Fig. 1 and S1†). As exhibited in Fig. 1, the crystal of iBut-beta (1.5) is constructed by four smooth convex surfaces with two rough end planes, totally different from the flat planes of TEA-beta(1.5). The curved shape of iBut-beta zeolite is rarely seen in zeolite crystals which are usually characterised by well-formed flat surfaces27,28 and is a sign of the unique faceting process of iBut-beta.

The PXRD patterns of iBut-beta(n) and TEA-beta(n) are shown in Fig. 2. In the high-angle region (2θ > 10°), both iBut-beta(n) and TEA-beta(n) show characteristic diffraction peaks

<table>
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<tr>
<th>SDA</th>
<th>n</th>
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<th>A%$^b$</th>
<th>B%$^b$</th>
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<td>8</td>
<td>45–55</td>
<td>35–45</td>
</tr>
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<td>35–45</td>
</tr>
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<td>TEAOH</td>
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<td>4</td>
<td>40–50</td>
<td>45–55</td>
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<tr>
<td>TEAOH</td>
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<tr>
<td>TEAOH</td>
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<tr>
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<td>2.0</td>
<td>2</td>
<td>55–65</td>
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</table>

$^a$Values derived from the $^{19}$F MAS NMR spectra. $^b$Values estimated from the DIFFaX simulation.
of “typical beta” despite the increase of HF concentration during the synthesis. On the other hand, in the low angle range ($\theta < 10^\circ$), as the HF concentration increases in the synthesis a significant peak change is present for both iBut-beta (n) and TEA-beta(n). More specifically, when the synthesis was performed at a low HF concentration (HF/SDA ≤ 1/1), the PXRD patterns of either iBut-beta or TEA-beta displayed only one broadened peak around 7.6°, which is in accordance with that of “typical beta”; however, as the HF concentration increases, the PXRD patterns exhibit a sharp peak at 7.03° with a shoulder at 7.68° for iBut-beta(n) and a sharp peak at 7.08° with a shoulder at 7.68° for TEA-beta(n). For iPro-beta(n) and iPen-beta(n) the peak features with increasing HF concentrations is similar to that of iBut-beta(n), as is shown in Fig. S1.†

![Fig. 1 SEM images of (a) iBut-beta(1.5) and (b) TEA-beta(1.5).](Image)

The $^{29}$Si solid-state MAS NMR spectra of iBut/iPro/iPen/TEA-beta(1.5) display no resonances below $-105$ ppm (see Fig. S2†), indicating the absence of $Q^3$ Si species.‡ This spectral feature, together with the presence of only well-formed crystals in the SEM images of iBut/iPro/iPen/TEA-beta (1.5), confirms that the unusual PXRD patterns of these beta samples arise from the intrinsic zeolitic structures rather than from impurities or structural defects.

Treacy$^2$ and Newsam$^{10}$ attributed the presence of sharp and broadened diffraction peaks of beta zeolites to the polymorphism of the zeolite framework. Herein, by using the program DIFFaX, we simulated a series of PXRD patterns for beta zeolites containing different proportions of polymorphs A, B and C (see Fig. S3†). Having different polymorphic compositions, these PXRD patterns basically are the same in the range of 20 > 10° but are quite different in the 5–10° range. Analysis of the simulated PXRD patterns further reveals that, if a beta zeolite is rich in polymorph A, a sharp peak will be present near 7.08° (the position of the characteristic peak of polymorph A); if rich in B a sharp peak will be present near 7.41°, and if rich in C a sharp peak will be present near 6.99°. Thus the presence of sharp diffraction peaks for iPro/iBut/iPen/TEA-beta implies the enrichment of polymorph A and/or C in these beta zeolites.

**Structural analysis of beta zeolites**

Structurally, polymorph A is constructed by alternate stacking of building layers in either a right-handed or left-handed manner around a four-fold screw axis; polymorph B is constructed by recurrent alternation of building layers in a right- and left-handed fashion, and polymorph C is constructed by stacking of neighboring building layers with no lateral translations.¹¹ The different stacking manners of identical building layers generate $[4354]$ cages in polymorphs A and B and the $[46]$ cage in polymorph C. When beta zeolites crystallize in fluoride medium, the $[4354]$ and $[46]$ cages accommodate one $F^-$ per cage. Based on the type of cage that occludes $F^-$, $^{19}$F NMR spectra show two resonances at $-56$ to $-59$ ppm and $-65$ to $-69$ ppm for $F^-$ in $[4354]$ and $-36$ to $-39$ ppm for $F^-$ in $[46]$.¹⁶ Therefore $^{19}$F NMR spectroscopy is a useful tool to probe the existence of polymorph C in beta zeolites. Additionally, Blasco⁰ showed that the proportion of polymorph C calculated from PXRD analysis agrees well with the ratio of $[4354]/[46]$ from $^{19}$F NMR spectra. Accordingly, the proportion of polymorph C of iBut/TEA-beta(n) samples was estimated and listed in Fig. S5 and S6.† The result shows that at a higher concentration iBut-beta has a significantly higher content of polymorph C than TEA-beta. Additionally, the proportions of polymorph C estimated from iPro/iPen-beta(n) samples also show the high concentration of polymorph C (not shown).

After estimating the proportion of polymorph C, the proportions of polymorph A and B in iBut/TEA-beta(n) samples were determined using the PXRD simulation program DIFFaX (see Fig. S8 and S9†). We took the case of iBut-beta(1.5) as an example. The sample contains 19% C as acquired via $^{19}$F MAS NMR analysis. The PXRD pattern of iBut-beta(1.5) was compared with a series of simulated PXRD patterns containing 19% C and different proportions of polymorph A and B (see Fig. 3 and S7†). As Fig. 3 shows, the simulated pattern that
contains 55–65% of A, 20–30% of B and 19% of C fits best with iBut-beta(1.5).

Fig. 4 shows the HRTEM image of iBut-beta(1.5) viewed along the [100] direction. The HRTEM image actually presents the projection of the zeolite framework in the [100] direction. In this projection, the chiral channel of polymorph A, the achiral zig-zag channel of polymorph B and the straight channel of polymorph C appear as the abab, abcabc, and aaaa arrangement of the twelve-ring pores, respectively. The intergrown domain contains all the three polymorphs as delineated by white lines. The boundaries of every two polymorphs contain large amounts of structural defects. From this domain ten layers of A, four layers of B and three layers of C are observed, which agrees with the polymorphic composition estimated from the $^{19}$F NMR spectrum and PXRD simulation.

The estimated polymorphic compositions of all iBut-beta($n$) and TEA-beta($n$) samples are listed in Table 1. It turns out that at low HF concentrations (0.4 ≤ HF/SDA ≤ 1), all iBut-beta($n$) and TEA-beta($n$) zeolites contain similar polymorphic compositions to that of the “typical beta”, and the choice of either TEAOH or iButOH has little influence on the polymorphic composition of beta zeolites. However, at a high HF concentration the polymorphic composition of beta zeolites is influenced both by the choice of SDA and by HF/SDA ratios. For iBut-beta($n$), when HF/SDA reaches 1.2 the proportion of A rises to 55–65% and stays unchanged despite further increase of HF concentration, while the proportion of C continuously ascends from 7% to 19%. Similar polymorphic compositions are also estimated for iPro-beta and iPro-beta. For TEA-beta($n$), when HF/SDA reaches 1.5 the proportion of A rises to a constant value of 55–65% whereas the proportion of C is basically unchanged (~2%) within the HF/SDA range of 0.8–2.0. Therefore the polymorph A-enriched iBut-beta is obtained from the synthesis with HF/SDA ratios larger than 1.0, and A-enriched TEA-beta is obtained from the synthesis with HF/SDA ratios larger than 1.2. In Yan’s report, the A-enriched beta zeolite contains approximately 60–65% polymorph A, which is similar to the proportion of A of iBut/iPro/iPen/TEA-beta($n$) synthesized in our work. However, the iBut/iPro/iPen-beta($n$) synthesized at high HF concentrations also contains a large proportion of polymorph C.

**Fluoride species in zeolite synthesis**

In zeolite synthesis HF acts both as the mineralizer and as the pH adjustor, and thus the increase in HF concentration not only increases the amount of fluoride in the synthesis medium but also decreases the overall pH value. The change of the pH value would further influence the state of fluoride species in the synthesis medium. In the conventional fluoride-route beta zeolites crystallize in neutral medium produced by an equivalent amount of HF and alkaline SDA in the synthesis medium. Sano studied the state of fluoride species in the precursor gel are $\text{F}^−$ in the form of TEAF. Nevertheless, as stated by Cundy and Koller, as the synthesis medium becomes acidic, $\text{F}^−$ reacts with silicate in complicated ways forming various fluoride species such as $\text{Si(OH)}_4\text{F}^{3−}$ and $\text{SiF}_6^{4−}$, Guth et al. also concluded that $\text{SiF}_6^{2−}$ becomes more prominent in the synthesis as the fluoride concentration increases. Fig. 5a shows the $^{19}$F solid-state MAS NMR spectra of the precursor gel of iBut-beta($n$). Two resonances can be observed corresponding to the presence of two different fluoride species in precursor gels. The first species, having a $^{19}$F NMR resonance at $−118$ ppm, is ascribed to $\text{F}^−$ in the form of iBut$\text{F}_3^{15,16}$ and denoted as free-$\text{F}^−$ (and $\text{F}^−$ entraped in [4]$^3$ or [4]$^4$) cage is denoted as entrapped-$\text{F}^−$). The second species has a $^{19}$F NMR resonance at $−128$ ppm; furthermore, the gel of iBut-beta(1.5) which only presents the $^{19}$F NMR resonance $−128$ ppm was subjected to $^{29}$Si solid-state MAS NMR and shows a resonance at $−188$ ppm$^{17,18}$ corresponding to hexa-coordinated $\text{Si}^4+$ in $\text{SiF}_6^{2−}$—(see Fig. 5b). So the second species in $^{19}$F NMR spectra is unambiguously assigned as $\text{SiF}_6^{2−}$ in the
form of iBut$_2$SiF$_6$. No other fluoride species, such as SiF$_5^-$ or Si(OH)$_2$F, are detected in these precursor gels. As Fig. 5a shows, when the HF/SDA ratio in the synthesis is smaller than 0.6 (with the synthesized zeolite being typical beta), only free-F$^-$ is present in the gels; as the HF/SDA ratio grows larger (with the synthesized zeolites being A-enriched beta), SiF$_6^{2-}$ appears and grows with F$^-$ progressively disappearing. The case of the precursor gels of TEA-beta(n) is similar: as HF/SDA grows SiF$_6^{2-}$ becomes prominent over F$^-$ and eventually exists as the only fluoride species (see Fig. S10†). In summary, the enrichment of polymorph A in beta zeolites coincides with the formation of SiF$_6^{2-}$ in the precursor.

Fig. 6 displays the correlation between the input HF/SDA ratio in the synthesis of iBut/TEA-beta(n) and the pH values of the corresponding post-synthesis filtrates. As the input HF/SDA increases, the pH value of the filtrates first descends drastically (within the pH range where all the crystallized products are typical beta) but then descends in a much gentler way (within the pH range where all the crystallized products are A-enriched beta), implying the existence of a pH buffer within the HF/SDA range of 1.0–1.5 for iBut-beta(n) and 1.2–2.0 for TEA-beta(n). In addition, the presence of this buffer parallels the predominance of SiF$_6^{2-}$ in the filtrates, as evidenced by $^{19}$F liquid-state NMR (Fig. S11†).

An equilibrium can explain the correlation between F$^-$ and SiF$_6^{2-}$ under slightly acidic conditions:40–42

$$\text{SiF}_6^{2-} + 4\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 + 6\text{F}^- + 4\text{H}^+ \quad (K_d \approx 10^{-30})$$

This equilibrium indicates that a buffer of H$^+$ and F$^-$ could be produced in the presence of SiF$_6^{2-}$. In a recent research, Corma’s group discovered a buffer of F$^-$ formed by K$_2$SiF$_6$ in the synthesis medium and proved that this buffer is key to formation of the pure polymorph C.43 We thought that the presence of such a F$^-$-buffer in our work is responsible for the polymorphic enrichment of beta zeolites.

**Evolution of fluoride species during crystallization**

Fluoride species plays a crucial role in the nucleation and crystal growing processes of beta zeolites. Studies by Camblor,44 Barrett45 and Larlus42 et al. show that fluoride helps in mobilizing silica species, stabilizing small subunits like [4$f$] cages, pairing with the OSDA cation and decreasing the crystallization rate. Due to the large size, SiF$_6^{2-}$ is not likely to enter and stabilize framework subunits like [4$^3$] as F$^-$ does. In fact, as we discovered, with high HF/SDA input the fluoride species in the precursor gel of beta zeolites are exclusively SiF$_6^{2-}$, however the only fluoride species detected in the cleansed zeolite are F$^-$. Thus there should be a transport route of fluoride from SiF$_6^{2-}$ to entrapped-F$^-$ in the zeolite structure. Barrett46 and Zones47 discussed the role of SiF$_5^-$ and SiF$_6^{2-}$ as dynamic species in the break-formation of Si-O-Si bonds during crystallization, and proposed that such species helps in transporting highly fluorinated silicate species to solution, resulting in the slowdown of the nucleation rate of the zeolite. Similarly, the replacement of F$^-$ by SiF$_6^{2-}$ in the starting materials should lead to a different crystallization process of beta zeolites from that of the conventional fluoride synthesis route. The unwashed products of iBut-beta(1.5) were synthesized at different times and then dried at 353 K and subject to $^{19}$F solid-state MAS NMR (see Fig. 7) to track the evolvement of SiF$_6^{2-}$ along zeolite crystallization.

As shown in Fig. 5a, in the precursor gel of iBut-beta(1.5) SiF$_6^{2-}$ is the only fluoride species. However, since the initial stage of crystallization, a small part of free-F$^-$ is also present in reaction materials. The presence of F$^-$ in the materials is attributable to the condensation of the silanol groups during crystallization, which generated OH$^-$46,48 to shift the equilibrium between F$^-$ and SiF$_6^{2-}$ in favor of F$^-$. At a longer crystallization time the F$^-$ entrapped in [4$f$] and [4$^3$5$^3$] cages starts to emerge. It can be inferred from Fig. 7 that during the whole crystallization process (note that iBut-beta(1.5)) is of high crystallinity in 24 h) the vast majority of fluoride is stored in the form of SiF$_6^{2-}$ rather than F$, and the transfer of fluoride follows a “SiF$_6^{2-}$ → free-F$^-$ → entrapped-F$^-$” route. At a high HF concentration the F$^-$-buffer maintains a relatively constant
and low concentration of F$^-$ in the synthesis medium. Thus a small but continuous amount of F$^-$ is released in the synthesis medium, in contrast to the all-at-once discharge of F$^-$ in the conventional fluoride route. Owing to the insufficient supply of F$^-$ the nucleation process of beta zeolites should be relatively slow. Probably such a slow nucleation allows for a more ordered successive stacking of building layers and results in the enrichment of polymorphs A and C in iBut/iPro/iPen-beta and the enrichment of polymorph A in TEA-beta.

**Conclusions**

In summary, we have presented a novel synthesis route to A-enriched beta zeolites. The polymorphic composition of the synthesized materials was determined by using the complementary characterization methods $^{19}$F MAS NMR analysis and PXRD simulation. Investigation on the synthesis conditions reveals that when a large amount of HF is present in the synthesis medium, a vast majority of F$^-$ converts to SiF$_6^{2-}$ and a buffered system of H$^+$ and F$^-$ is formed in the synthesis medium. This buffer restricts the release of F$^-$ to a small but continuous supply for the crystallization process, which may be the reason for the polymorphic enrichment in beta zeolites.

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**Notes and references**


