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Zeolite Crystal Growth

Fundamental Crystal Growth Mechanism in Zeolite L Revealed by Atomic Force Microscopy**

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Atomic force microscopy (AFM) reveals details of the crystal growth mechanism in the one-dimensional nanoporous aluminosilicate zeolite L. Growth on the side walls of the hexagonal prism-shaped crystals (shown schematically in Figure 1 and in the electron micrographs in the Supporting Information) indicates facile growth of fundamental cancrinite cage units along the length of the crystal but severely frustrated growth in a perpendicular direction. Controlling these relative growth rates is a key to synthesizing high quality crystals with controlled aspect ratio (length *l*/diameter *d*). This is crucial for optimizing diffusion path-lengths within this one-dimensional pore system for catalytic applications such as the dehydrocyclization of light naphtha[1] over Pt functionalized zeolite-Linde-L (LTL). In a one-dimensional pore system diffusion of guest species becomes a problem of molecular traffic-control which is facilitated by short pore lengths and consequently short crystals. Lessons on habit control from this work are also applicable to other types of crystals, such as molecular crystals used in the pharmaceutical industry, where crystal shape can have an affect on physicochemical properties such as solubility and dissolution rate.[2]

The crystal habit of zeolite L can be modified by inhibiting or promoting nucleation in one of the two principal growth directions.[3,4] Habit variations are achieved by compositional changes in the initial synthesis mixture. However, it is still unclear how the preference for growth on one particular face over another switches when such modifications are applied. In previous work, scanning electron microscopy (SEM) was used to image the surface of the (001) face of zeolite L, and showed circular step-like terraces on the face of the crystal.[5] Transmission electron microscopy (TEM) on zeolite L suggests the nature of the likely terminating units on both the (001) and (100) faces, as well as the single unit step height of 0.75 nm on the (001) face.[6] Further, previous studies on zeolite Y using AFM have shown that features on the surface can be used to infer how the whole crystal has grown.[7] To date no previous studies have been carried out utilizing the nanometer-scale resolution of AFM, to study zeolite L. In the current work it has also been demonstrated that sharp nanoscale features of zeolite L serve as excellent probes of the AFM tip shape profile.

AFM images were taken on both the hexagonal (001) face and the (100) side-wall of the three preparations of crystals, and typical micrographs are shown in Figure 1. On inspection, it is apparent that the crystals exhibit significant differences in surface features. At low water content the shortest crystals exhibit signs of frustrated growth on both the (001) face (Figure 1 A,b) and on the (100) face (Figure 1 B,b). On the hexagonal (001) face this is exhibited as holes in the surface that emanate deeper in the crystal but which cause the surface to show both nanometer high terraces as well as large steps. On the side-wall the growth is very rapid along the length of the crystal but very slow, or frustrated, in the orthogonal direction. This results in long terraces, which in many instances run the entire length of the crystal. Such growth will hinder substantially the development of these facets which require both surface nucleation events as well as efficient two-dimensional terrace spreading in order to develop the faces properly. As the water content in the preparations is increased to create longer crystals the growth is progressively less frustrated on both facets. On the (001) hexagonal face this results in fewer defects and the absence of large steps (Figure 1 A,c and 1 A,d). On the (100) side-wall this results in substantial spreading of terraces orthogonal to the long axis of the crystal (Figure 1 B,c and B,d). In other words, more efficient two-dimensional terrace spreading is achieved.

On all AFM images observed on the side-walls of crystals of zeolite L, although the terraces have different lateral width, there is a preponderance of very narrow terraces which all appear to have the same lateral width. The nature of these terraces with different lateral width is explored in the cross-sections taken between the red arrows and between the blue arrows (Figure 2 a). The cross-section between the red arrows explores terraces with variable width and the cross-section between the blue arrows explores only the narrowest terraces. The cross-sections are shown in Figure 2 b and reveal that between the red arrows the heights of terraces are 1.60 ± 0.05 nm, whereas the terrace heights taken between the blue arrows are 1.20 ± 0.05 nm. In other words the narrowest terraces are always significantly less high than all broader terraces. This is an interesting observation and requires careful consideration.

There are two things to explain: first, the nature of the 1.6 nm terraces and the 1.2 nm terraces; second, the reason that there is a minimum lateral width for the 1.2 nm terraces. These observations are almost certainly linked. Considering the latter issue, the minimum terrace width could either be the

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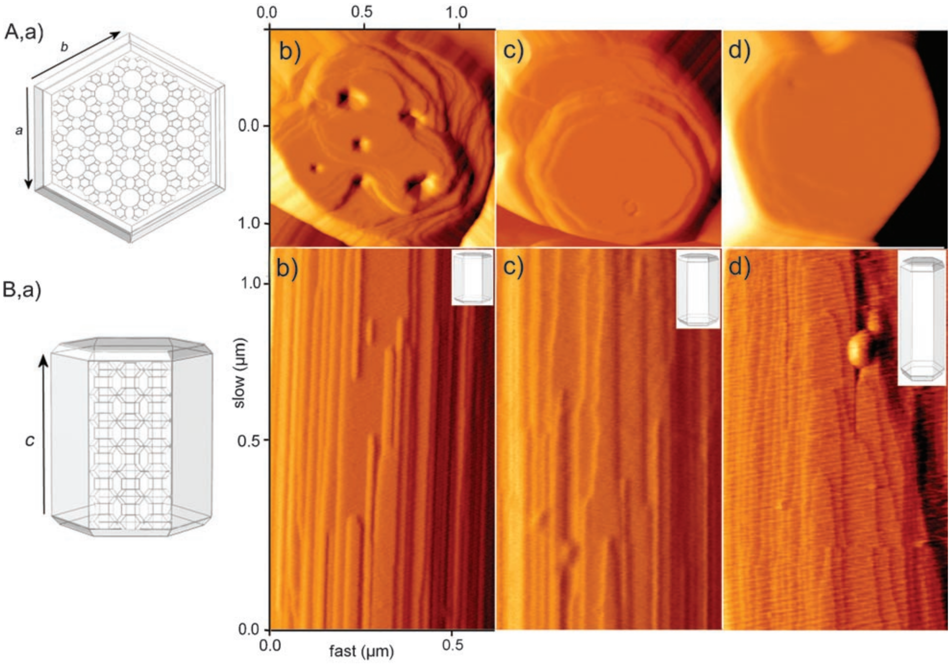

Figure 1. Error signal AFM images of zeolite L with different aspect ratios. A) Hexagonal face down the [001] direction of the crystal; B) side walls down the [100] direction of the crystal. a) Schematic frameworks of the crystal; b–d) crystals with aspect ratio 1.5, 2.3, and 5.1, respectively.

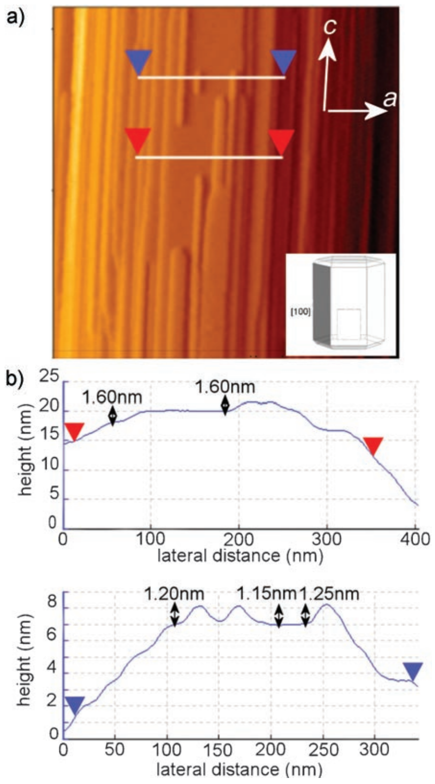

Figure 2. AFM results for the (100) face of crystals with an aspect ratio of 1.5. a) Error signal AFM image of the crystal; b) cross-section between the red and blue arrows, respectively, from (a).

result of a specific structural unit or an artefact produced by the AFM tip profile. The lateral width (baseline-to-baseline) of the narrowest terrace feature is 32 nm. This is equivalent to several tens of unit cells for zeolite L and, consequently, a preferred lateral structural unit is very unlikely to be the explanation for this observation. The lateral spread is, therefore, almost certainly the convolution of the AFM tip-shape with a much narrower surface structural feature. In other words the zeolite surface is mapping the tip shape rather than vice-versa. This is also corroborated by the cross-section profile as the tip traverses the edges of complete terrace steps (Figure 2b lower image at left) which show rounded steps with profiles equivalent to half the tip profile of the narrow terrace features.

The nature of the features giving rise to the 1.6 nm and 1.2 nm terraces can be understood by consideration of the structure of the zeolite L side-wall (Figure 3). It is known from TEM work[6] that the side-wall terminates with complete cancrinite cages. As the first cancrinite cage is formed (Figure 3a) this sits 1.2 nm proud of the side-wall. Lateral addition of subsequent cancrinite cages results in a terrace that sits 1.6 nm proud of the surface (Figure 3b). Consequently, the narrowest terraces observed in Figure 2b are columns of individual cancrinite cages indicating that growth in the *c*-direction (cancrinite cages linking through the double 6-ring) is much more facile than the frustrated lateral growth which requires attachment of cancrinite cages across the large 12-ring. Figure 3c shows how the individual cancrinite cage columns are, in effect, very sharp spikes on the surface of the crystal which image the lateral tip-shape and result in the convoluted cross-section observed. In fact, zeolite L is a useful crystal for accurately measuring AFM tip profiles over the last 1.60 nm at the end of the tip.

Figure 4 shows AFM images of the (001) face of zeolite L. The short cylinders (Figure 1A,b) exhibit a rounded hexagonal face. Layered terraces can be observed on the surface, in addition to six hexagonal-shaped "holes". In some instances, the terraces appear to grow around these holes forming relatively high, non-concentric terraces that contribute to the rounded shape of the overall crystal. A cross-section, taken on the uppermost surface of the crystal shows step heights of 0.73 and 1.39 nm (Figure 4a, lower image), corresponding to one and two cancrinite cage units, respectively. Figure 4b shows schematically the likely unit stabilizing at the (001) surface, which has a corresponding height equal to one cancrinite cage. This result corroborates that observed by Ohsuna et al. by high-resolution electron microscopy (HREM).[6]

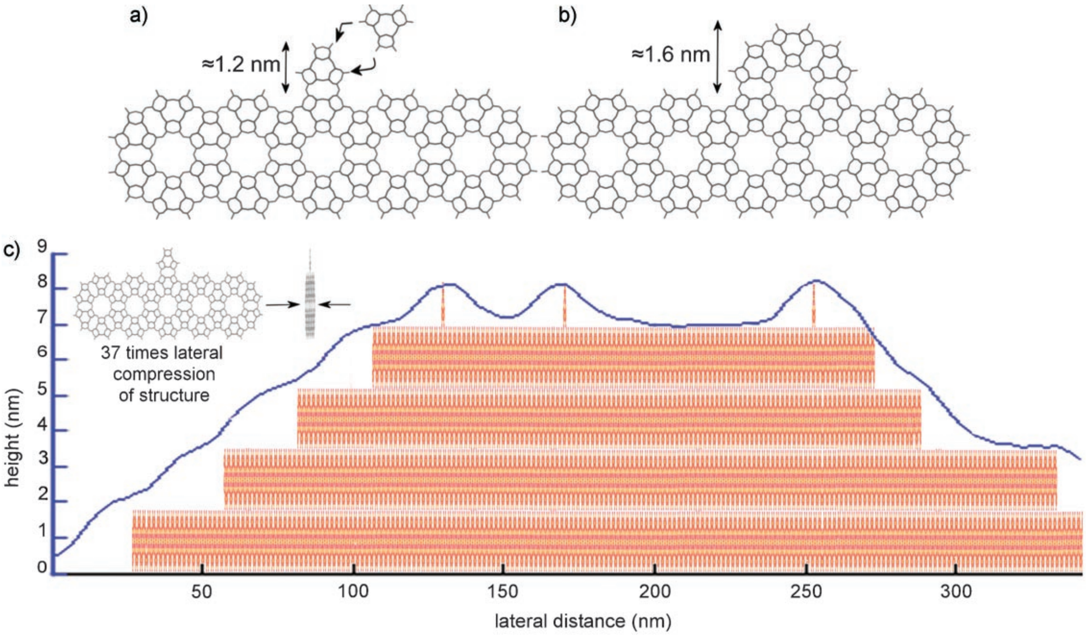

Figure 3. a) An individual cancrinite column sits 1.20 nm proud of the (100) side wall. b) Connected cancrinite columns sit 1.6 nm proud of the (100) side wall. c) Illustration of the 37-fold lateral compression in effect observed by AFM owing to the superior vertical resolution. Superimposed, the blue line shows the AFM cross-section, from Figure 2 b, which is a measure of the surface structure convoluted with the tip profile.

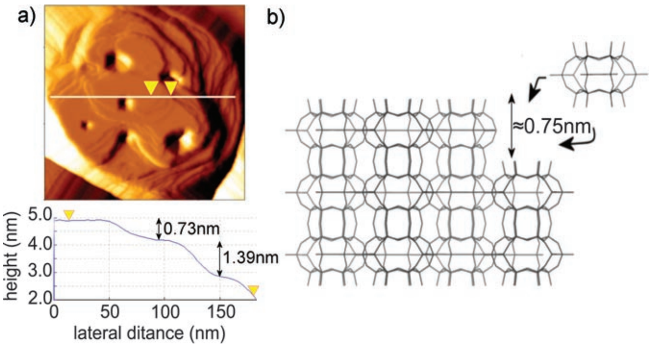

Figure 4. AFM of the (001) face of zeolite L crystals with aspect ratios of 1.5. a) Line of cross-section between the yellow arrows. b) Schematic representation of the structure showing the cancrinite cage unit.

Figure 1 A,c and 1 A,d show typical AFM images of the hexagonal face of the long cylinders and needles of zeolite L. In these images, the face of the crystal appears to become more of a regular hexagonal shape, and growth terraces also follow this morphology. Fewer "holes" are observed compared with the short cylinders. Terraces occur as a series of steps, becoming closer together towards the outer part of the face and are multiples of a single step height (0.75 nm).

There is a consistent trend between the aspect ratio of the crystal and the regularity of the overall crystal habit and the terrace structure. The shorter crystals in these preparations are always associated with more irregular growth and defect structure. Therefore it is possible that the different aspect ratio is also a consequence of frustrated growth as the crystal overcomes gross defect structures.

In conclusion, it has been observed that zeolite L is likely to grow by cancrinite cage attachment onto both principal crystallographic faces. On the side-wall there is a substantial difference in the growth rate in the *a*- and *c*-directions. Cancrinite columns develop rapidly in the *c*-direction but lateral growth of cancrinite cages in the *a*-directions is severely frustrated as the structure builds across the large 12-ring. The relative rate of growth in the *a*-direction appears to increase when the aspect ratio of the crystal increases. There is also a correlation between gross defect structure and the crystal aspect ratio. Finally, the sharp, nanoscale crystalline features on the surface of zeolite L make suitable probes of AFM tip shape at the tip extremity.

Experimental Section

Crystals of zeolite L with different habits were synthesized based on a preparation described by Lee et al.,[3] with molar gel composition: $10.2\,K_2O:1\,Al_2O_3:20\,SiO_2:x\,H_2O$ (where $x = 800$, 1030, and 1200). Once prepared, the gel was stirred for 18 h at room temperature, and then transferred to a teflon-lined stainless steel autoclave. Synthesis took place at 180 °C for 3 days, after which the reaction was quenched by placing the autoclave in cold water. The resulting crystals were filtered with copious amounts of water, before being left to dry at 110 °C overnight.

AFM was carried out using a JPK NanoWizard in contact mode. SEM (see Supporting Information, Figure 1) was carried out using an FEI QUANTA ESEM, and was used to determine the average size of the crystals (both length and diameter). The aspect ratio was 1.5, 2.3, and 5.1 for crystals prepared with 800, 1030, and 1200 moles of water, respectively (described herein as short cylinders, long cylinders, and needles).

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