Real-space Imaging of Offretite and the Identification of Other Coexistent Zeolitic Structures

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Ultrahigh resolution electron microscopic images can be taken of offretite and other beam-sensitive zeolites by first dealuminating the specimens; comparison of the observed and calculated real-space images of the resulting siliceous framework enables structural faults and coherent intergrowths of zeolitic structures to be detected.

Such is the resolving power of the modern electron microscope[1,2] that relatively open solids, provided they survive electron bombardment, can be 'seen' directly at the sub-nanometre level in projection down one or more appropriate crystallographic axis. This convenient fact has led to the clarification of numerous, otherwise intractable, structural and mechanistic problems,[1—4] as well as to the discovery[5] of hitherto unknown structures.

Offretite,[6] a catalytically significant zeolite [idealized formula $(Na_2, Ca, \ldots)_2Al_4Si_{14}O_{36}\cdot 14H_2O$], is a member of an extensive family[7,8] of zeolites which are based, structurally, upon the regular stacking of sheets of corner-linked TO_4 tetrahedra (T can be either Si^{4+} or Al^{3+}). The projection perpendicular to the sheets, composed of six-membered rings, is shown in Figure 1(a). In a direction perpendicular to the sheets, the structure of offretite [Figure 1(b)] may be described as AABAAB . . . . Individual members of the family each possess a characteristic stacking sequence; cancrinite is ABAB . . ., erionite AABAAC . . ., and so on for levyne, afghanite, *etc.* (see ref. 7). Infractions to the regular stacking sequences have been detected, at low resolution, in previous studies.[9] What now appears feasible, given the improved resolving power of electron microscopes and the ability to render (see below) rather beam-sensitive zeolites more resistant to electron-induced decomposition, is the direct identification of local structural variation and intergrowth at the sub-unit-cell level.

Intergrowths in relatively beam-stable zeolitic catalysts such as ZSM-55 and ZSM-11 have been imaged previously.[10] This communication explains how intergrowths and other faults can be identified in a much larger class of zeolitic structures.

The features of the framework structure of offretite likely to be rendered visible in a microscope operating with a point-to-point resolution of 3.0 Å are the tunnels circumscribed by six- and eight-membered rings, here designated S and E, respectively. The computed image[11] [Figure 1(c)] clearly shows [as does the out-of-focus photograph of a structural model, Figure 1(d)] that the relative disposition and sequence of the S tunnels in offretite should be visible in the real-space image taken under the appropriate conditions down the [100] zone axis.

As-prepared samples of offretite (with Si/Al ratios of *ca.* 2.8) are degraded rather rapidly in the electron microscope (JEOL 200 CS, SEG) making high-resolution imaging very difficult. Offretite, like other zeolites, can, however, be 'dealuminated' to an Si/Al ratio of >100, by chemical treatment so as to leave the framework structure intact[12] (essentially all the T sites are now tenanted by Si). In this highly siliceous state the 'offretite' is much more beam-stable (lifetimes improved by factors of up to 10), so that high-resolution images can now be recorded. Note that, as a result of the dealumination, the exchanged cations are eliminated. Our computed images include scattering factors from the framework atoms Si and O only, and are therefore nicely

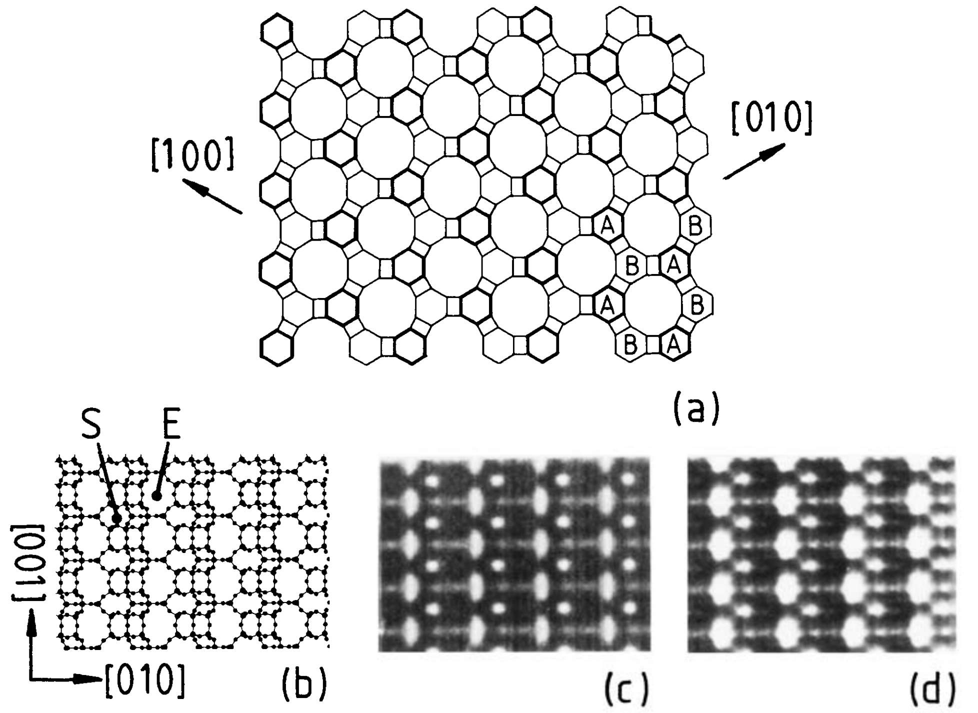

Figure 1. (a) Schematic drawing of the offretite framework viewed along [001] (*i.e.* a plan view of the sheets). Projected positions of the 6-membered rings in A or B sheets (see text) are indicated. (b) Offretite stacking sequence; view of model structure projected along [100] (*i.e.* elevation view of stacks). Tunnels bounded by 6- and 8-membered rings are denoted by S and E respectively. (c) Computer-simulated image for 90 Å thick slab of offretite viewed along [100]. (Spherical aberration 1.9 mm, 800 Å under focus, 200 keV electrons.) (d) Out-of-focus photograph of (b).

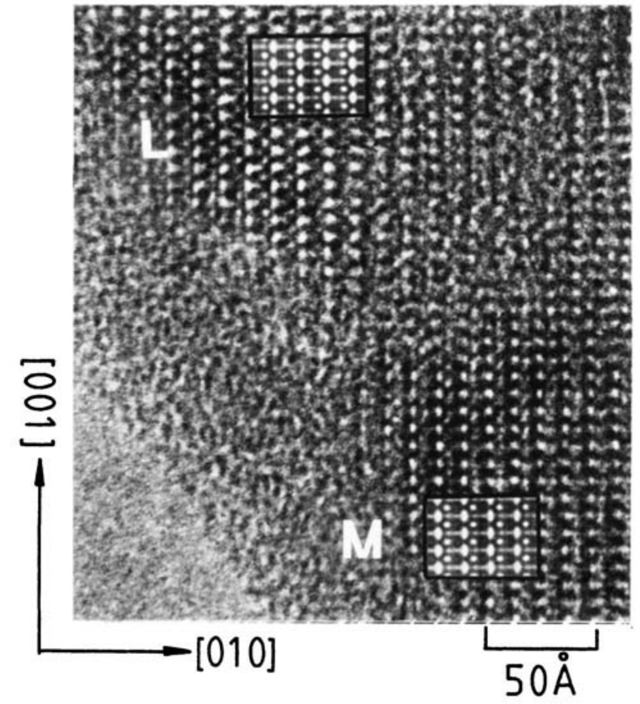

Figure 2. High resolution electron micrograph of offretite viewed along [100]. Insets are matched, computer-simulated images. Regions L and M exhibit an anti-phase structural relationship (see text).

suited for their comparison with the observed images (Figure 2).

The essential features of the offretite structure are clearly visible in the two regions marked L and M (Figure 2). It is noteworthy that these two regions are in anti-phase relationship to one another. One region has undergone a rotation of π radians around the *c* axis relative to the other. This would occur if the intervening region between L and M contains a planar stacking fault. Several plausible local structures could constitute this planar fault. There could be a unit stack of erionite:

$$\underset{\text{Offretite}}{\ldots\mathrm{A\,A\,B\,A\,A\,B}}\,\underbrace{\mathrm{A\,A\,B\,A\,A\,C}}_{\text{Erionite}}\,\underset{\text{Offretite}}{\mathrm{A\,A\,C\,A\,A\,C}\ldots}$$

or a unit stack of cancrinite:

$$\ldots\mathrm{A\,A\,B\,A}\,\underbrace{\mathrm{A\,B\,A\,B}}_{\text{Cancrinite}}\,\mathrm{B\,A\,A\,B\,B\,A\,B}\ldots$$

or a unit stack of chabazite:

$$\ldots\mathrm{A\,A\,B}\,\underbrace{\mathrm{A\,A\,B\,B\,C\,C}}_{\text{Chabazite}}\,\mathrm{B\,C\,C\,B\,C\,C}\ldots$$

or other similar features. Image detail in the region separating L and M (Figure 2) is not, unfortunately, of adequate quality to discriminate between any of these possibilities, or to rule out the additional but less likely possibility that regions L and M are separate subgrains.

The broader implications of this work are clear. With the aid of a library of computed images based on the various kinds of stacking infractions within the respective members of this large family of zeolites, real-space images will afford new insights into the character and extent of minute intergrowths in zeolites of catalytic and other significance. The library of such computed images is currently in course of compilation and its use for diagnostic purposes of the type decribed here is being investigated.

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