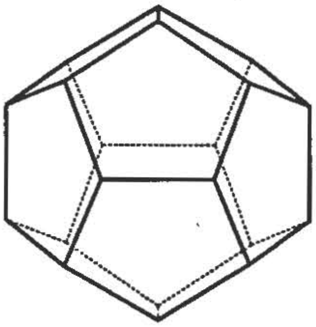
Growth and Characterization of Centimeter-sized Crystals of Pyridine Dodecasil-3C

Todd A. Marquart Final Seminar August 31, 1994

Zeolites are host/guest complexes composed of open framework host structures and guest ions or molecules residing in channels or cages formed by the host lattice. Traditionally they are aluminosilicates, but the term also applies to other systems with aluminum phosphate and pure silica frameworks. Until recently the optical and electrical properties of zeolites have been largely overlooked, with most research focusing on molecular sieve, ion exchange and catalytic properties. Zeolites containing organic guest molecules are attractive candidates for high-technology materials, since their materials properties can be fine-tuned through systematic variation of the guest molecule within a given framework [1-9]. In order for optical and electrical properties to be exploited, large, high-quality single crystals of these materials must be available. Recent attempts to grow such crystals have been hindered, however, by co-crystallization, low thermodynamic stability and the presence of volatile organic guest species.

The zeolite selected for this study is the synthetic, all-silica zeolite ZSM-39 [10], also known as dodecasil-3C (D3C) [11]. Its silicate framework contains two types of cages, a pentagonal dodecahedral cage, **1**, and a larger hexadecahedral cage, **2**. The organic guest molecules are trapped in the larger hexadecahedral cages. The extended structure is formed by linking the large hexadecahedral cages through sharing of the four tetrahedrally arranged hexagonal faces to form "supertetrahedra" that link to form a diamond lattice. An extra atom must be placed in between the supertetrahedra to form the smaller dodecahedral cages).



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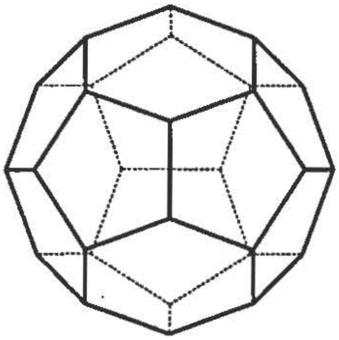

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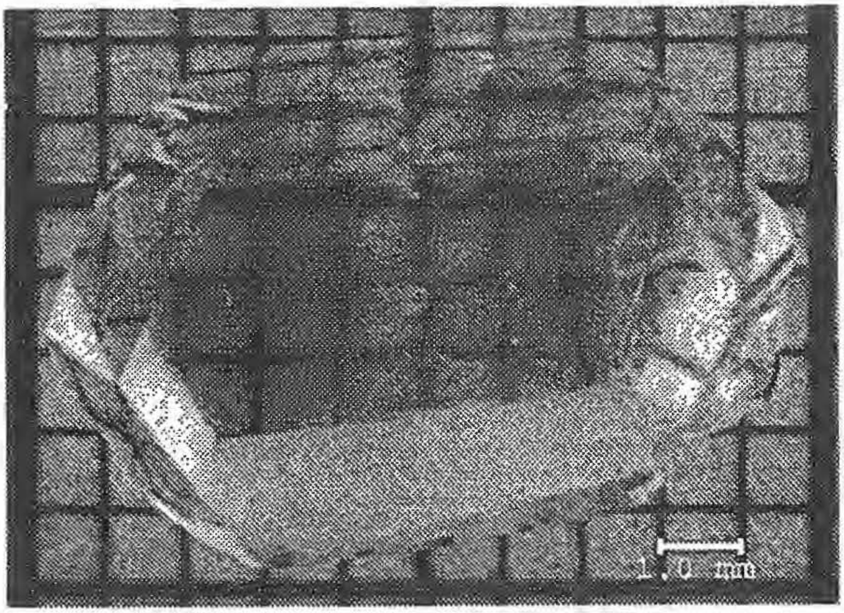
A modified hydrothermal seeded growth method has been used to prepare centimeter-sized crystals of pyridine D3C (**3**) at a mean linear rate of 0.3 mm/day. Formation of pyridine D3C depended upon numerous variables including time, temperature, reagent concentration and the identity of the silica sources. The silica source proved to be particularly critical. Fumed silica supported the highest growth rates (>0.8 mm/day), but favored the formation of competing phases in short reaction times. Fused silica supported steady, albeit lower, growth rates while favoring the formation of pyridine D3C, but its low reactivity did not allow for formation of D3C in the early stages of the reaction resulting in dissolution of the seed crystals. These factors necessitated the use of both forms of silica in order to promote steady, long-term growth of pyridine D3C crystals. The fumed silica acted to bring up the initial concentration of silica, but was quickly depleted. Fused silica then became the primary silica source, supporting long-term reactions capable of producing large crystals.



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Pyridine D3C, like many other zeolites, suffers the handicap of severe transformation twinning [12]. This twinning has hindered attempts to determine the true room-temperature structure. Optical crystallography carried out on a single twin domain revealed that pyridine D3C possesses orthorhombic, or lower, symmetry. However, single-crystal X-ray diffraction could not be used to determine the actual ambient-temperature structure until untwinned crystals were available. Twinning in D3C crystals could be eliminated by thermal annealing, and systematic single-crystal X-ray diffraction studies carried out on detwinned crystals, coupled with optical crystallography studies, were used to determine the true room-temperature orthorhombic structure. Single crystal X-ray crystallography carried out above the phase transition temperature was used to determine the high-temperature cubic structure.

The methods developed for growing large crystals of pyridine D3C represent a general procedure for preparing other zeolitic materials in the form of large crystals. Work is currently under way to apply these methods to other zeolite systems. Future exploration of the twinning in pyridine D3C crystals is necessary for a complete understanding of the structural details of this material. TEM is the logical choice for such a study, however less harsh techniques, such as AFM, are currently being used to examine the twinning in D3C crystals.

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