ABSTRACT

Zeolites are a class of crystalline aluminosilicate materials that form the backbone of the chemical process industry worldwide. They are used primarily as adsorbents and catalysts and support to a significant extent the positive balance of trade realized by the chemical industry in the United States (around $19 billion in 1991). The magnitude of their effects can be appreciated when one realizes that since their introduction as "cracking catalysts" in the early 1960's, they have saved the equivalent to 60 percent of the total oil production from Alaska's North Slope. Thus the performance of zeolite catalysts can have a profound effect on the US economy. It is estimated that a 1 percent increase in yield of the gasoline fraction per barrel of oil would represent a savings of 22 million barrels of crude oil per year, representing a reduction of $400 million in the United States' balance of payments. Thus any activity which results in improvement in zeolite catalyst performance is of significant scientific and industrial interest. In addition, due to their "stability," uniformity, and, within limits, their "engineerable" structures, zeolites are being tested as potential adsorbents to purify gases and liquids at the parts-per-billion levels needed in today's electronic, biomedical, and biotechnology industries and for the environment. Other exotic applications, such as host materials for quantum-confined semiconductor atomic arrays, are also being investigated. Because of the importance of this class of material, extensive efforts have been made to characterize their structures and to understand their nucleation and growth mechanisms, so as to be able to custom-make zeolites for a desired application. To date, both the nucleation mechanics and chemistry (such as what are the "key" nutrients) are, as yet, still unknown for many, if not all, systems. The problem is compounded because there is usually a "gel" phase present that is assumed to control the degree of supersaturation, and this gel undergoes a continuous "polymerization" type reaction during nucleation and growth.

Generally, for structure characterization and diffusion studies, which are useful in evaluating zeolites for improving yield in petroleum refining as well as for many of the proposed new
applications (e.g., catalytic membranes, molecular electronics, chemical sensors) large zeolites (>100 to 1000X normal size) with minimum lattice defects are desired. Presently, the lack of understanding of zeolite nucleation and growth precludes the custom design of zeolites for these or other uses. It was hypothesized that the microgravity levels achieved in an orbiting spacecraft could help to isolate the possible effects of natural convection (which affects defect formation) and minimize sedimentation, which occurs since zeolites are twice as dense as the solution from which they are formed. This was expected to promote larger crystals by allowing growing crystals a longer residence time in a high-concentration nutrient field. Thus it was hypothesized that the microgravity environment of Earth orbit would allow the growth of large, more defect-free zeolite crystals in high yield.

I. CRYSTALLIZATION IN SPACE

The environment of low-Earth orbit makes it a potentially interesting environment for crystal growth from the melt and from solution. Typically the gravity levels in a manned spacecraft are $10^{-5}$ to $10^{-6}$g residual accelerations and $10^{-4}$ to $10^{-3}$g impulsive accelerations. These substantially reduced levels dramatically reduce gravity-driven convection. In addition, in the case of solution crystal growth, crystals will stay essentially suspended in the nutrient pool under a diffusion-limited growth condition. The "folklore" of crystal growth would then predict more uniform (fewer defects), and larger crystals will be produced in this environment. To date, the results have been interesting but inconclusive.

II. BACKGROUND: GAS1-PRELIMINARY RESULTS

The Get Away Special (GAS) program allows low-cost access to space. The "can" itself is 2 cubic feet, must weigh under 200 pounds, has its own power, and all systems must be activated by a single switch. WPI was given a GAS can by the Mitre Corporation and designed and built a number of experiments that flew on STS-40 in June of 1992. One of those experiments was the growth of zeolite A. Details of the furnace used and the control and archiving equipment are given elsewhere. Basically it consisted of two 10 ml chambers that housed two premixed zeolite A solutions that were heated to 96°C under their own autogenous pressure. Triethanolamine (TEA) was added to control the initial nucleation and to slow the growth of those crystals already formed. Research had shown that the "gel" formed from this formulation appeared to be "stabilized" for 21 to 30 days at ambient conditions (i.e., if heated within this time, a uniform population of crystals having a cubic morphology were formed).

As a result of flight delays, the premixed zeolite solutions were not launched into space for
110 days after they were initially mixed. After approximately one day on orbit, the furnace was activated and performed perfectly, maintaining the 96°C reaction temperature for 72 hours, after which the solutions convectively cooled. Typical results are illustrated in Figures 1 and 2. Figure 1 presents two micrographs representing crystals from a ground (terrestrial) control sample (also premixed and held at ambient conditions for 110 days) and the crystal from one of the reaction chambers activated (heated) in orbit. The heat-up profiles and cool-down profiles for the control samples were essentially identical to those produced during flight. As illustrated, the crystals are virtually identical in size (25-35 μ) and appear in both cases to be intergrown. Figure 2 confirms these results, showing two populations with identical nucleation and growth histories.

Prior ground-based studies had shown that if these solutions were heated immediately on mixing or after only 21 days, they formed a uniform population of well-formed cubes (typical of zeolite A) with little or no intergrowths. In order to try to understand the discrepancies, an investigation was performed on premixed mixed solutions at room temperature and after heating to 80°C using both small-angle neutron diffraction and small-angle X-ray diffraction. Preliminary results indicated that similar solutions without TEA (solutions with TEA were difficult to analyze due to the low number of scattering centers) began to form prenuclei at room temperature immediately after mixing. Thus it can be hypothesized that prenucleation occurred during the 110 delay period and that this phase of the nucleation event was complete prior to flight and furnace activation. The crystal morphology observed can be rationalized if one postulates that these precursor nuclei settle and interact to produce the intergrowths seen in both the flight samples and the control. This would be consistent with the observation that well-formed crystals are produced when the solutions were processed prior to 21 days and with the NIST results that suggest "nucleation" proceeds immediately on mixing and can explain the intergrowths observed in both the flight and ground-control systems, which are likely to be the prenuclei growing together. These conclusions led to an extensive development program to create a crystallization vessel (autoclave) which would allow the precursor solutions to be loaded 48 to 72 hours prior to launch and held unmixed until activation on orbit. In addition, in order to ensure that the solutions were uniformly mixed, different nozzle designs and mixing protocols were developed (glovebox experiment) to test on orbit.

III. USML-1 THE GROWTH OF ZEOLITES A, X AND MORDENITE

Three different zeolites were chosen to be crystallized in space: zeolite A, zeolite X, and mordenite. Due to the furnace configuration, multiple A and X solutions were flown, but only one mordenite formulation was processed. Two of each formulation were processed in orbit to provide reproducibility. The zeolite solution formulations were chosen to test the hypothesis that
larger, more defect-free crystals could be made in orbit. However, no attempt was made to
determine the best solution to maximize growth or to minimize defect formation.

A. Zeolite Flight Facilities

The Zeolite Crystal Growth (ZCG) furnace was designed to process 19 autoclave units, each
unit consisting of two separate autoclaves, each of which houses two 10 ml sample chambers.11
The furnace is cylindrical in shape and configured in three concentric zones. The central zone was
used to process mordenite (experiment temperature 175°C) and could achieve a temperature of 200
°C with a negligible radial temperature gradient and less than a 1°C axial gradient across the sample
chambers. The middle zone could process six autoclave units at temperatures of 105°C to 150°C
with the same precision as the central zone. Zeolite X was processed within this middle zone, and
these samples were processed at 105°C. The outer zone (used to process zeolite A at 96°C)
consisted of 12 furnace tubes, and each could be controlled to the same axial and radial precision in
the temperature range 90°C to 110°C. The entire unit (furnace module and control system) was at
steady state in under 8 hours and used 200 watts of power during heat-up and 91 watts during
steady-state operation. The furnace was controlled with its own independent CPU. All furnace
tubes and all control and heating subsystems were at least single-fault tolerant. A Ground Control
Experimental Laboratory (GCEL) was built to process the terrestrial control experiments. It was
identical in every way to the flight unit except the GCEL had no redundant CPU. In addition to the
furnace and control system, four different autoclave nozzle designs were tested on orbit, and
several operational protocols were utilized.

B. Zeolite Glovebox Experiment (GBX-ZCG)

It is well known that zeolite precursor solutions (e.g., aluminum solutions and silicate
solutions) must be well mixed (homogenous) in order to maximize product purity. In addition, for
those solutions which form a viscous "gel," if the solution is excessively sheared, the product purity
may also be affected. Nuclear Magnetic Resonance Imaging (NMRI) studies were performed in
order to test (evaluate) many proposed nozzle designs and mixing protocols.12,13 The suggested
mixing protocols, which were nozzle and solution dependent, were further tested on low-gravity
aircraft. These combined tests formed the basis for the nozzles and activation procedures for the
on-orbit observation protocol used to establish how best to mix the zeolite solutions to be
processed in the ZCG facility. The results from the glovebox experiment illustrated that real-time
observation of the mixing process is necessary to ensure gel uniformity without excessive shear.
Also bubble formation, inherent in the mixing process, was minimized through real-time observation, analysis, and the resulting crew-initiated corrective actions. This on-orbit intervention helped to minimize impurity phases formed and guaranteed that few, if any, nuclei were formed by excess surface area as the result of bubbles or foaming.

IV. RESULTS AND DISCUSSION

The samples flown on STS-50 and the control solutions were all from a common batch prepared for each zeolite formulation. Eighty-eight autoclaves were loaded, representing five zeolite A formulations, five zeolite X formulations, and one mordenite formulation. Forty-four autoclaves were randomly selected for flight, and the remaining autoclaves were used as controls. These forty-four autoclaves represented nineteen duplicate experiments and six spares. Two autoclaves in the control group and in the flight group represented a zeolite A formulation where no nucleation control agent (Triethanolamine, TEA) was present; this represented an on-orbit control to test the hypothesis that to grow large zeolites in space the nucleation event must be controlled. How each autoclave was activated and what, if any, actions were necessary to minimize bubble formation (based on GBX-ZCG) were recorded on video and evaluated real-time prior to activation of the flight and control autoclaves. Also the heat-up and eventually the cool-down thermal profiles were downloaded during the flight and were duplicated in the GCEL control experiment.

In order to quantitatively determine if, and how, low gravity affected the crystallization of these zeolite formulations, the following analysis procedure was performed on all samples. The crystals from the flight and control samples were observed and photographed using optical and scanning electron microscopy, and a particle-size distribution (PSD) was developed for each. Following this documentation, control and flight samples were sent to the University of Connecticut to measure their surface area (BET), lattice parameters (XRD), X-ray photoelectron spectra (XPS), and the associated surface Si/Al ratio. The samples sent to the University of Connecticut were not identified as to which were flight and which were terrestrial controls. This was done to eliminate any unintentional bias.

A. Zeolite A

Figure 3 compares the flight and terrestrial control for zeolite A where no nucleation control agent was used. This experiment was performed to test the hypothesis that if the nucleation event was not controlled, then the resulting burst of nuclei would drop the degree of supersaturation below the point where growth would be possible or of an acceptable rate. As the micrographs illustrate, there is no substantial difference in either size or morphology. In all cases (four
autoclaves: two processed in space and two processed as terrestrial controls), the size is between one and three micrometers, and the growth of the [110] planes in both samples is evident. The PSD presented in Figure 4 confirms the visual observations. The tail at three to four micrometers on the terrestrial PSD represents precipitate Al(OH)₃. At this time, no explanation can be given for this precipitate. No Al(OH)₃ was found in any of the other flight or control samples. The results represented by Figures 3 and 4 suggest that the hypothesis that in order to grow large crystals from solution in space, the nucleation event must be controlled appears to be correct. X-ray data of these samples indicate that with the exception of the Al(OH)₃, the samples are essentially pure zeolite A.

Figures 5, 6 and 7 are typical of the results observed when nucleation control was present. The micrographs in Figure 5 represent a typical flight and control sample. As illustrated, the flight crystals are 10 to 25 percent larger in linear dimension, do not show the characteristic [110] plane observed on the control sample, and, in general, appear to have fewer intergrowths. Figure 6 illustrates the PSD’s for these flight and control samples. As was suggested by Figure 5, the entire population is shifted to higher average sizes (approximately 10 to 25 percent). The micrographs in Figure 7 represent a comparison for a different zeolite A formulation between crystals made in space, their terrestrial control (both crystallizations were performed with a nucleation control agent), and commercial crystals (no nucleation control). The largest crystals produced in orbit were 10 to 40 percent larger in linear dimension than the largest crystals found in the control and 35 to 40 times as large as those produced commercially. Also as illustrated by the high magnification insert, the morphology of the crystals formed under nucleation control approaches the cubic morphology of an ideal zeolite A crystal. Tables 1 and 2 and Figure 8 represent comparisons of the binding energies, associated spectra, and the resulting Si/Al ratio between flight and control samples for a typical zeolite A experiment. As illustrated in Table 1, the binding levels for the Si KLL and Al KLL transitions for both flight and terrestrial are consistent with literature values. The shape of the peaks and their relative location is illustrated in Figure 8. The arrow shows a satellite peak that represents the mounting medium and is not representative of the samples. Table 2 presents the resulting Si/Al ratios for these samples. As indicated, the crystals produced in space typically gave the same or higher Si/Al ratios than did their control samples. As illustrated in Table 2, flight sample A1 gave the theoretical Si/Al ratio of 1.00. To the authors’ knowledge, this is the only time this has been reported. Examples of XRD data are presented in Table 3. As illustrated, the lattice parameters and, thus, the unit cell volumes for the flight samples were frequently less than for the terrestrial controls. This is consistent with fewer lattice defects in the structure. Finally, CO₂ adsorption studies were performed on the flight and terrestrial controls. All samples, both terrestrial
and flight, displayed Type I adsorption isotherms. In general, but not in every case, the flight samples were smaller in surface area. Once again, this is consistent with a crystal structure that has fewer lattice defects.

B. Zeolite X

Figure 9 illustrates typical results from the zeolite X formulations. As shown, the larger crystals of zeolite X were as much as 50 percent longer in linear dimension than their controls. The PSD for this formulation is depicted in Figure 10. As indicated, the terrestrial controls typically had two different populations. The micrographs in Figure 9 suggest this is likely to be an impurity phase: zeolite P. This is an indication of possible poor mixing. The PSD for the flight sample could not be fully characterized due to size restriction in celloscope available to do the analysis. Another formulation used for zeolite X produced the crystals shown in Figure 11. Again, as was most often the case, the crystals grown in space were larger. It is interesting to note that the PSD from this formulation indicates a nonuniform shift in size; a population of larger crystals was produced in space relative to the terrestrial control population (Figure 12). The initial characteristics of the flight-grown crystals relative to their terrestrial controls were similar to the zeolite A samples. Table 4 lists the Si/AI ratio based on XPS. Here, as in the zeolite A case, the Si/AI ratios of the flight samples are greater on average than their controls. Since zeolite X has a range of Si/AI ratio, no conclusions are possible on the defect content from these data alone. The XRD pattern again resulted in significantly smaller lattice parameters and a smaller cell volume for the flight samples versus the ground controls (Table 5). BET analysis, using N2 as an adsorbent, shows once again these materials produced a Type I adsorption isotherm, characteristic of materials with a high level of microporocicity (Figure 13). In Figure 13, the data are presented in pairs: X1 and X2 represent one control and flight pair, while X3 and X4 represent another. As presented, the even-numbered samples (flight) are significantly different from their controls (odd). The surface areas that have resulted from these isotherms are listed in Table 6. In a similar manner to the zeolite A samples, the zeolite X samples that were prepared in flight had smaller surface areas than their terrestrial counterparts. In the cases illustrated here, these differences in surface areas were between 15 percent and 30 percent. The XRD and BET data taken together with the XPS results suggest, once again, that the larger crystals grown in orbit have fewer lattice defects.

C. Mordenite

Analysis continues on the Mordenite samples. To date, the following has been observed: The physical state of the flight samples was powder-like, while what is normally observed is a
compressed mass of individual crystals. The crystals are not unsimilar in morphology and appear on average to be similar in size. At present, the characterization work on the mordenite has not been completed.

CONCLUSIONS

The results from USML-1 were consistent with the hypothesis that larger, more defect-free zeolite crystals can be grown in high yield in space. The size increase for zeolite A and zeolite X varied between 10 to 50 percent for the formulations flown. Mordenite crystals did not increase in size, on average, when processed in space. Characterization of the flight samples versus their controls indicates that the lattice defect concentration is reduced when these crystals are produced in space.

ACKNOWLEDGMENT

Thanks are extended to NASA through the Battelle and Clarkson University CCDS for funding, to Teledyne Brown Engineering for the furnace fabrication, to Intek, Inc., for the design and building of the control system, and to the crew of USML-1 for the great job they did in orbit. In addition, thanks are given to Mr. Jack Ferraro and the graduate students of Worcester Polytechnic Institute who worked on this project. Lisa McCauley of Battelle deserves special thanks for her support.

REFERENCES


Table 1: XPS Binding Energies for typical Zeolite A Flight and Control Samples

Zeolite A Binding Energies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si KLL*</th>
<th>Al KLL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1(F)</td>
<td>1711.46</td>
<td>1460.23</td>
</tr>
<tr>
<td>A2(T)</td>
<td>1711.56</td>
<td>1460.45</td>
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<tr>
<td>A3(F)</td>
<td>1711.53</td>
<td>1460.37</td>
</tr>
<tr>
<td>A4(T)</td>
<td>1711.49</td>
<td>1460.38</td>
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* - in eV, X-ray Excited Auger Transitions.

Table 2: Si/Al Ratios by XPS for typical Zeolite A Flight and Control Samples

Zeolite A Si/Al Ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
</tr>
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<tbody>
<tr>
<td>A1(F)</td>
<td>1.0</td>
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<tr>
<td>A2(T)</td>
<td>0.97</td>
</tr>
<tr>
<td>A3(F)</td>
<td>0.96</td>
</tr>
<tr>
<td>A4(T)</td>
<td>0.96</td>
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Atomic %.

Table 3: XRD Data comparing Flight (A1, A3) and Control (A2, A4) Samples

Zeolite A

<table>
<thead>
<tr>
<th>Sample</th>
<th>a*</th>
<th>EDS</th>
<th>Volume**</th>
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</thead>
<tbody>
<tr>
<td>A1(F)</td>
<td>24.639</td>
<td>0.0110</td>
<td>14,958</td>
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<tr>
<td>A2(T)</td>
<td>24.672</td>
<td>0.0254</td>
<td>15,018</td>
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<tr>
<td>A3(F)</td>
<td>24.130</td>
<td>0.291</td>
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<td>A4(T)</td>
<td>24.575</td>
<td>0.065</td>
<td>14,842</td>
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* - in Å.
** - in Å³.
JCPDS Zeolite A = 24.64 Å.
Table 4: Si/Al Ratios by XPS for typical Zeolite X Flight and Control Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
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<tbody>
<tr>
<td>X1(T)</td>
<td>1.24</td>
</tr>
<tr>
<td>X2(F)</td>
<td>1.30</td>
</tr>
<tr>
<td>X3(T)</td>
<td>1.31</td>
</tr>
<tr>
<td>X4(F)</td>
<td>1.38</td>
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</table>

Atomic %.

Table 5: XRD Data comparing Flight (X2, X4) and Control (X1, X3) Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>a*</th>
<th>EDS</th>
<th>Volume**</th>
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<tbody>
<tr>
<td>X1(T)</td>
<td>24.992</td>
<td>0.0387</td>
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<td>X2(F)</td>
<td>24.900</td>
<td>0.00718</td>
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<td>X3(T)</td>
<td>24.985</td>
<td>0.170</td>
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<td>X4(F)</td>
<td>24.470</td>
<td>0.132</td>
<td>15,652</td>
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</table>

* - in Å.
** - in Å³.

JCPDS Zeolite X = 24.99 Å.

Table 6: BET Surface Areas comparing Flight and Control Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SA (m²/g)</th>
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<tbody>
<tr>
<td>X1(T)</td>
<td>870</td>
</tr>
<tr>
<td>X2(F)</td>
<td>735</td>
</tr>
<tr>
<td>X3(T)</td>
<td>685</td>
</tr>
<tr>
<td>X4(F)</td>
<td>460</td>
</tr>
</tbody>
</table>

T = Terrestrial.
F = Flight.
Type I Adsorption Isotherms.
N₂ Adsorption.
Figure 1 GAS-1: Zeolite A from STS-40 (Premixed 110 days before launch).
Figure 2  PSD's of Zeolite A (GAS-1).
Figure 3  Zeolite A USML-1 (No Nucleation Control).
Figure 4  PSD's of Zeolite A USML-1 (No Nucleation Control).
Figure 5  Zeolite A USML-1 with Nucleation Control (5.5 TEA, Piston, 5 Activations).
Figure 6  PSD's of Zeolite A with Nucleation Control (5.5 TEA, Piston, 5 Activations).
Figure 7  Comparison between Flight, Terrestrial (Control) and Commercial Zeolite A.
Figure 8: XPS's Valence Band Spectra for two Flight (A1, A3)/Control (A2, A4) pairs.
Figure 9  Zeolite X USML-1 with Nucleation Control (2.0 TEA, Sacco Flapper, 3 Activations, Silicic Acid).
Flight – too large to be analyzed using 300 μm orifice tube.

Figure 10: PSD for Terrestrial Control showing Two separate Populations.
Figure 11 Zeolite X USML-1 with Nucleation Control (2.0 TEA, Sacco Flapper, 3 Activations, Sodium Metasilicate Anhydrous).
Figure 12 PSD's of Zeolite X USML-1 with Nucleation Control (2.0 TEA, Sacco Flapper, 3 Activations, Sodium Metasilicate Anhydrous).
Figure 13 Nitrogen Sorption at 78 K - Isotherms of Pairs Flight (X2, X4), Control (X1, X3).
Discussion

Question: What was the reason you said that the crystals would grow larger in space?
Answer: If I keep diffusion control for a week or 10 days, they get bigger. Our intention was, based on what had been shown in the literature, we knew that you could grow very large crystals. No one has ever been able to do it synthetically, but nature has done it a number of times. When you look at that data it turns out that they are in salt beds suspended, and the nutrient pool goes by them. So the idea was to suspend it in orbit and try to control the growth parameters, the nucleation parameters. We were hoping we would achieve what nature did but we were not going to wait a billion years or a half billion years, we hope.

Question: Could you just outline the advantage of larger and more perfectly grown Zeolite crystals?
Answer: Yes. Well the advantages are threefold maybe fourfold. One of the obvious advantages is for structural information. Any of you that have done any X-ray work know that is difficult to do; x-ray single crystal work on Zeolite particles of 2 microns. You can't do that. You need about a half a millimeter, or so, to get decent data and with one exception, that is one Zeolite type, I don't know of any that come up to a half a millimeter or millimeter in size. So, structural information, and in particular, in terms of the cation locations which are very important for catalyst activations as well as ion exchange, is difficult to get. A secondary reason is whenever you construct reactions with multiple reactions going on, which is what we do in a chemical process industry all the time, you need to know diffusional rates and those are all estimated for these crystals because they can't do single crystal diffusional studies. What they do is they look at packed beds with crystals that they have been palletized and put in a binder and then they back out with a series of adjustable constants because you have not only particle diffusion as well as a series of other things. People want them for diffusion studies and those are what I call the short term benefits. The other area is they are now experimenting with using them as hosts for semi-conductor materials to bridge the gap between molecular semiconductors and bulk semiconductors. That seems to be going pretty well. They are very interested in defect free crystals for obvious reasons, and in that case, special lattice defects need to be eliminated. The other things they had great hopes for and still do, is if we can grow them big enough that we could use a ceramic binder we could make semi-permeable membranes with them. Zeolites are now used as the main catalytic staple for the chemical process industry. What we are hoping could happen is if we can combine the separation train with a highly selective catalyst that means there is an enormous cost savings. Generally half the cost of production of a commodity chemical is because of the separation train. So if you can get a catalyst that doesn't give you a, b, c, d, and e but just b which is what you can do with a Zeolite membrane, and by
adjusting the diffusional distances and taking advantage of those reaction rates simultaneously, you will have a tremendous advantage.

**Question:** Can you affect activation energy by such improvements?

**Answer:** You don't really affect activation energies. What you are going to do is adjust. Certain reactions need a certain amount of time to occur by adjusting the diffusion length or diffusion path. You can selectively get certain reactions to occur and others not to occur. For example, coking in the chemical process industry occurs because the product you are interested in is in contact with an active site for a long period of time. Too long a period of time.