

# Zeolite Crystallization Process Modeling and Comparison with Microgravity Flight Results

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The study of the transport phenomena during zeolite crystallization has indicated that at 1g, gravity-induced secondary nucleation is the only possible detrimental effect due to gravitational sedimentation. In this paper experimental results on zeolite growth from the STS-40 and STS-50 mission experiments are compared with our theory for determining the conditions where microgravity is beneficial. The theory is consistent with those experiments. Additionally, zeolites were synthesized in our laboratory using compositions similar to those of the STS-40 and STS-50 experiments to 1) examine the effect of a nucleation suppresser, triethenolamine, on gravity-induced secondary nucleation, and 2) develop a process to synthesize larger zeolites in both 1g and microgravity. At 1g limitations on the second goal are found. Furthermore, growth-in-gel zeolite crystallization in microgravity is modeled. The overall porosity of the gel portion is defined as an important space-experiment parameter, which is a counterpart of the gel-portion shrinkage at 1g. This parameter can be used for zeolite crystallization in microgravity to determine the time when nutrients should be added to grow much larger zeolites in space.

## Nomenclature

$D$	= mass diffusion coefficient for gel species (dissolved), $m^2/sec$
$\frac{d\phi_{sg}}{dt}$	= volume consumption rate of solid gel due to dissolution, $m^3/sec\ m^3$
$g$	= gravitational acceleration, $m/s^2$
$h$	= height of shrinking gel portion illustrated in Fig. 1, m
$h_0$	= initial height of gel portion (Fig. 1), m
$I_g$	= gel species (dissolved) mass transfer rate through crystal surface, $kg/sec$
$M$	= total amount of nutrients, kg
$N_{crl}$	= total number of crystals formed
$n_{crl}$	= crystal number concentration, $m^{-3}$
$n_{crl0}$	= initial crystal number concentration (total number of primary nuclei), $1/m^3$
$r$	= distance originating at the center of crystal (Fig. 11), m
$r_{\infty}(t)$	= time-dependent cavity radius illustrated in Fig. 11, m
$r_{crl}$	= crystal dimension (radius), m
$r_0$	= crystal radius illustrated in Fig. 11, m
$U_s$	= downward shrinking velocity in Fig. 1, $m/s$
$V_{crl}$	= total volume of crystals, $m^3$
$V_{gel}$	= total volume of solid gel particles, $m^3$
$V_{sln}$	= total volume of solution within gel portion, $m^3$
$\epsilon$	= porosity
$v_{sln}$	= volume of solution with shaded area (Fig. 11), $m^3$
$\Delta\rho$	= density difference between crystals and solution, $kg/m^3$
$\rho$	= mass concentration for gel species (dissolved), $kg/m^3$
$\rho_{sat}$	= saturated mass concentration for gel species (dissolved), $kg/m^3$
$\rho_{sg}$	= density of solid gel, $kg/m^3$
$\phi_{sg}$	= Volume fraction of solid gel

## Introduction

THE wide-ranging industrial applications of zeolite molecular sieves<sup>1-3</sup> have motivated researchers to seek a new approach to

growing large and perfect zeolite crystals. Orbiting spacecraft seem to offer an attractive environment, since on earth gravity causes crystals to settle out of a nutrient pool. To reach this goal, there have been a number of attempts to grow zeolite crystals in space. Stewart and his colleagues<sup>4</sup> conducted their zeolite experiment aboard the Shuttle Atlantis in 1990. However, the result was not conclusive. Sano et al.<sup>5,6</sup> carried out ZSM-5 zeolite crystallization under microgravity using a Soviet re-entry system (CASIMIR) in 1990. The hydrothermal synthesis mixture for their space experiment was a clear aqueous solution. They concluded that, in space, the degree of concentration varies spatially within the reaction mixture as the crystallization time elapses, because one has a pure diffusion field without convective flow. They also found that crystals in space grew to about  $10\ \mu m$  in size and they aggregated to a fractal pattern, which might indicate the existence of Brownian motion for crystals. However, microgravity did not help to grow larger ZSM-5 zeolite crystals. Sacco et al.<sup>7</sup> proposed to synthesize zeolite crystals in space as early as in the mid 1980s. The justification for growing large zeolites in space was initially based on experimental evidence that adding triethenolamine (TEA) to the reaction mixture resulted in larger zeolite-A crystals. The TEA was then claimed to be a viscous suspending agent that prevented crystals from settling,<sup>8</sup> but it was later found that TEA and some other tertiary alkanolamines in fact serve as nucleation suppressers.<sup>9,10</sup> Fewer nuclei can be formed in a system with TEA, so that the sizes of the zeolites increase.

Sacco et al.<sup>11</sup> conducted two consecutive space-flight experiments on zeolite growth. The experiments were STS-40 (SLS-1 mission) in June of 1991 and STS-50 (USML-1 mission) in June of 1992 and were aimed at growing large zeolites. For the USML-1 mission, the reaction mixtures were made in space, and three different types of zeolites—type A, type X, and mordenite—were synthesized and then compared with their on-earth counterparts. The reason for the selection of these types of zeolites was that they require relatively low temperatures ( $<100^\circ C$ ) for hydrothermal growth in autoclaves (the temperature is usually from  $70$  to  $350^\circ C$ ) and therefore meet safety requirements for space shuttles. From the experiments, it was found that only those samples where the nucleation event was controlled by the additive TEA gave larger crystals than the terrestrially processed samples. Otherwise, crystals grown in space were identical to those grown on earth. For the SLS-1 mission, the chemical additive TEA was also used to control the initial nucleation. But the reaction mixture of zeolite-A for the space experiment was subjected to a 120-day delay prior to the experiment activation (heating to  $95^\circ C$ ). Again, the crystals grown in space were found to be identical to those on earth. Therefore, Sacco et al.<sup>11</sup> concluded that 1) zeolite crystals will grow larger in orbit than on earth if the nu-

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cleation rate is controlled, and 2) on-orbit mixing is important for growing larger zeolites in space.

Zhang et al.<sup>12,13</sup> studied transport phenomena in zeolite growth and found that, among all the gravitational effects claimed to be detrimental by Sacco et al.,<sup>8</sup> gravity-induced secondary nucleation (GSN) is the only one without which crystals would possibly have grown larger. It was believed that after initially formed crystals settle down under gravity, secondary nucleation will occur within the reaction mixture except for the bottom part. The secondary nuclei will grow and then settle down. Such a process can repeat again and again until the nutrients are depleted. The total number of crystals formed increases in such a fashion that the sizes of the crystals will decrease, which is in fact the detrimental effect of GSN. Based on our analyses of the mass transfer during the process of growth-in-gel crystallization, a nondimensional parameter was derived to determine under what conditions GSN occurs.<sup>14</sup> Also, the gravity-dependent structure and the behavior of the gel portion were investigated,<sup>15</sup> and a correlation for the shrinkage, i.e., the rate of height decrease (RHD), of the gel portion under normal gravity was derived, which agrees well with experimental observations. By the RHD correlation, the stages of nucleation and growth as well as the onset of growth can be easily identified.

In this paper we will compare our previous theory and experiments with the conclusions reached by Sacco et al.<sup>11</sup> from their space-flight experiments. The agreement will be demonstrated in detail. Our ground-based zeolite syntheses using the additive TEA (nucleation suppresser) will be examined carefully in order to explain why some synthesis recipes lead to larger zeolites in space and some do not. The aging effect on the reaction mixture with TEA is also examined. It is proposed to add nutrients at an appropriate time to increase the size of zeolite crystals grown from a reaction composition with the additive TEA. This method can, in principle, be applied to zeolite growth in space so that much larger zeolites can be obtained. To show this possibility, growth-in-gel zeolite crystallization under microgravity will be modeled in this paper. The overall porosity will be defined as a parameter to distinguish the different crystallization stages, corresponding to the RHD at 1 g; with its help, the moment to add nutrients in microgravity can be determined.

### Comments on Zeolite Growth Experiments Aboard Shuttles STS-40 and STS-50

Zeolite crystals commonly grow from a molecularly inhomogeneous dispersion system termed a gel. In addition to the solution-phase-only species, weakly soluble amorphous solid gel particles of colloidal size serve as a source of species also needed by growing crystals. Namely, the solid gels continuously dissolve into the solution upon the consumption of the dissolved gel near crystal surfaces. Therefore, when the zeolite crystals formed settle down under normal gravity, the top portion remains supersaturated as far as the gel species is concerned, and secondary nucleation may occur. From our previous work<sup>15</sup> it is known that, under normal gravity, there is a downward-shrinking boundary that separates an upper clear portion from a lower gel portion (opaque white), as shown schematically in Fig. 1. We also have shown that GSN can occur at most within the lower gel portion.

The shrinkage of the gel portion is directly related to the consumption of gel particles, which are flocculated to form a porous network (the gel portion) because of interparticle forces. For the above reasons, if the velocity of the boundary,  $U_s$ , is less than that of growing crystals that settle through the gel portion, GSN will occur. Upon detailed hydrodynamic analyses,<sup>12,14</sup> the criterion for the occurrence of GSN is given as

$$\frac{h_0 n_{\text{crl}0}}{1 - \varepsilon} \left( \frac{\mu D}{\Delta \rho g} \right)^{2/3} \lesssim 10^{-1} \quad (1)$$

Instead of giving an exact number, the right side of Eq. (1) gives an order of magnitude because some estimated typical values were used in the calculation. As can be seen, in addition to other physical properties, this nondimensional parameter is most strongly dependent upon  $h_0$  and  $n_{\text{crl}0}$ . The height of the gel portion for a laboratory

Table 1 Length of nucleation vs crystal size

TEA/Al <sub>2</sub> O <sub>3</sub>	Aging, h	Length of nucleation, h	Crystal size, <sup>a</sup> $\mu\text{m}$
0	36	1.6	1
0	12	2.4	2
0	0	4.0	3
2.12	0	8.0	8
4.24	0	36.0	25
6.36	0	110.0	43

<sup>a</sup>  $\pm 20\%$ .

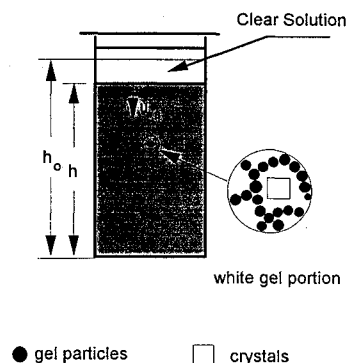


Fig. 1 Shrinkage of gel portion within a reaction vessel.

scale is more or less fixed (a few centimeters); however, the total number of primary nuclei formed can be changed dramatically (decreased by a factor of  $10^{-3}$ ), for example, by using the nucleation suppresser TEA.

Let us first explain the experimental results of STS-50 (USML-1 mission) and then STS-40 (SLS-1 mission) by Sacco et al.<sup>11</sup> according to the nondimensional parameter on the left side of Eq. (1). Basically, the above-mentioned criterion indicates that, for a given synthesis system with a smaller number of primary nuclei, it is more likely to have GSN at 1g. This system will yield relatively larger zeolites in space because GSN will be eliminated under microgravity. GSN is detrimental in the sense that it yields a larger number of crystals; hence, the average crystal size decreases. From our experiments (see Table 1 in the Results and Discussion Section), we know that a system using an additive TEA with a molar ratio TEA/Al<sub>2</sub>O<sub>3</sub> = 6.36 yields zeolites more than 10 times as large as without TEA. From a simple analysis showing that  $r_{\text{crl}}^3 \sim M/N_{\text{crl}}$ , we know that  $N_{\text{crl}}$  in the above-mentioned system with TEA is of order less than one-thousandth of its value in the system without TEA. Therefore, the system with nucleation control (i.e., with TEA) may yield larger zeolite crystals in space than its duplicate on earth. On the other hand, for a system without a nucleation control (i.e., without TEA), microgravity should make no difference.

Now let us examine the space-flight results. Experiments on glovebox-zeolite crystal growth (GBX-ZCG) and zeolite crystal growth (ZCG) were designed for USML-1. Three different types of zeolites—type A, type X, and mordenite—were synthesized in space. By comparison, it was found that all the samples where the nucleation rate was controlled (with TEA) gave larger zeolite crystals than those identically processed on earth, whereas the samples in space without a nucleation control were identical to those on the ground.

For STS-40 the chemical additive TEA was used to control the nucleation. But the reaction mixture was loaded about 120 days before launch, i.e., there was a 120-day delay prior to experiment activation. The flight and terrestrial samples were found virtually identical. From our previous work it is known that aging has the effect of increasing the nucleation rate (i.e., increasing the number of nuclei) for the system without TEA, and it will be shown in this paper that it has the same effect on the system with TEA (cf. Fig. 4 in the Results and Discussion Section). Since the system with a large number of nuclei does not have GSN on earth [cf. Eq. (1)], the system in space must have the same crystal size as that on earth.

## Experiment

In order to study the special features of a zeolite synthesis system with nucleation control, which has been thought important for space processing, a composition similar to that of USML-1, in which the nucleation rate was controlled, was used in our laboratory to grow zeolites. The composition is  $\text{Al}_2\text{O}_3\text{-}0.84\text{SiO}_2\text{-}1.94\text{Na}_2\text{O-}194\text{H}_2\text{O-}x\text{TEA}$ , where the amount of TEA, denoted by  $x$  (moles), can be varied in a systematic fashion to study the role of TEA. The raw materials are: aluminum wire, Aldrich (99%); sodium hydroxide, Mallinckrodt (98.4%); fumed silica, Cab-O-Sil M5, Degussa Corp.; and TEA, Aldrich (98%). The procedure for preparing the reaction mixture was as follows: 1) sodium hydroxide pellets were dissolved in deionized water to obtain NaOH solution of a certain concentration; 2) sodium aluminate ( $\text{NaAlO}_2$ ) solutions were then made by dissolving the aluminum wire in the aqueous sodium hydroxide; 3) Cab-O-Sil M5 was added to deionized water to obtain a silica water slurry (for a recipe with the organic amine TEA, the latter was first dissolved in the water); and 4) the reaction mixture (aluminosilicate gel) was finally made by mixing the sodium aluminate solution with the slurry. The description of the sequence of chemical events involved in the formation of the gel and the subsequent crystallization is beyond the scope of this paper. Interested readers should refer to Ref. 16.

To observe the gel-portion shrinkage, the reaction mixtures were transferred to 12-ml vials (sealed), which then stayed in an oven with a temperature of about  $95^\circ\text{C}$  (the same temperature range as that in STS-40 and STS-50). A camera and a timer were set to take pictures of the vials intermittently through the fabricated Plexiglas oven door. A scanning electron microscope was employed to take photomicrographs of crystal specimens. The magnification was adjusted to insure that each photomicrograph contains more than 50 crystal particles so that the average crystal size could be measured.

## Results and Discussion

For the composition  $\text{Al}_2\text{O}_3\text{-}0.84\text{SiO}_2\text{-}1.94\text{Na}_2\text{O-}194\text{H}_2\text{O-}x\text{TEA}$ , we selected  $x = 0, 2.12, 4.24, 6.36$  (moles) to prepare the reaction mixtures. For the case of  $x = 0$  we also aged the reaction mixtures at ambient temperature for 12 and 36 h before they were activated (heated to about  $95^\circ\text{C}$ ). Figure 2 shows the shrinkage curves for the reaction mixtures with and without the nucleation suppresser TEA. Data are shown for mixtures without TEA after 0, 12, and 36 h of aging. From the shrinkage curves, the onset of growth after a shorter or longer nucleation period is indicated by a sudden change in height (a change from concave upward to downward).<sup>15</sup> As seen from the figure, aging shortens the nucleation period, which is consistent with our previous work. For 0-, 12-, and 36-h aging the nucleation periods are about 4, 2.4, and 1.6 h, respectively. It is noted that for this reaction composition, the reaction mixtures with 12- and 36-h aging have smaller initial heights than the one with no aging. In other words, the reaction mixtures shrink at room temperature during the aging. From the figure, we also see that adding TEA hinders the nucleation. The nucleation period for  $x = 2.12$  is approximately 8 h.

Figure 3 shows that the length of the nucleation period increases further as more TEA is added. For  $x = 4.24$  it is approximately

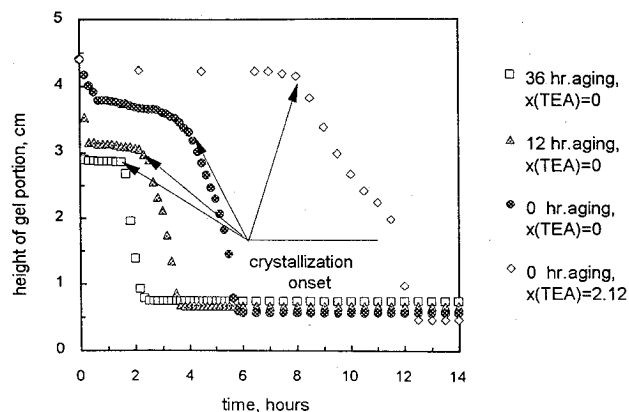


Fig. 2 Gel shrinkage curves with and without TEA.

36 h, and for  $x = 6.36$  it is approximately 110 h. It turns out that the behavior of these shrinkage curves is consistent with crystallization curves determined by x-ray powder diffraction.<sup>9,10</sup> Table 1 shows the crystal size vs the length of the nucleation period. The numbers shown in the table only represent the data for this particular reaction batch. These data may vary (perhaps  $\pm 20\%$ ) from one batch to another on account of history-dependent factors, for example, stirring and the order of mixing. However, the trend is obvious: larger crystals were obtained from the synthesis with a longer nucleation period, in which there is a lower nucleation rate. The crystal size for  $x = 6.36$  is more than 10 times as large as that without TEA added. It has been reported<sup>10</sup> that the maximum amount of TEA added for this composition is about 10; otherwise, zeolite-X will be formed.

The question remaining to be answered is the effect of aging on a reaction mixture that contains the nucleation suppresser. This is the actual condition of the STS-40 zeolite growth experiment. In our experiment, we compared the result of synthesis ( $x = 6.36$ ) with 30 days of aging to that without aging. Figure 4 indicates that aging up to 30 days decreases the length of the nucleation period for the reaction mixture with  $x = 6.36$ . Figure 5 shows a photomicrograph of crystals grown from the reaction mixture with 30 days of aging. By a comparison between Fig. 5 and Fig. 10b (for crystals grown from the same reaction mixture), it can be seen the crystal size decreases by about 10%. In fact, in the STS-40 experiment the reaction mixture aged up to 120 days. As mentioned earlier, a shorter nucleation period results in a larger number of nuclei (the crystal size decreases), and GSN does not occur on earth. This is believed to be the reason why the space-processed zeolites from STS-40 (SLS-1 mission), which have much smaller sizes than those from STS-50, were identical to those processed on earth.

As described in our previous work,<sup>15</sup> the zeolite crystal size can be increased by adding nutrients after the onset of growth.

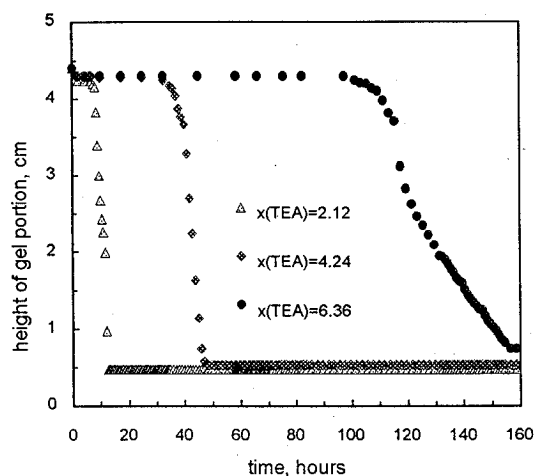


Fig. 3 Shrinkage curves with different amounts of TEA (no aging).

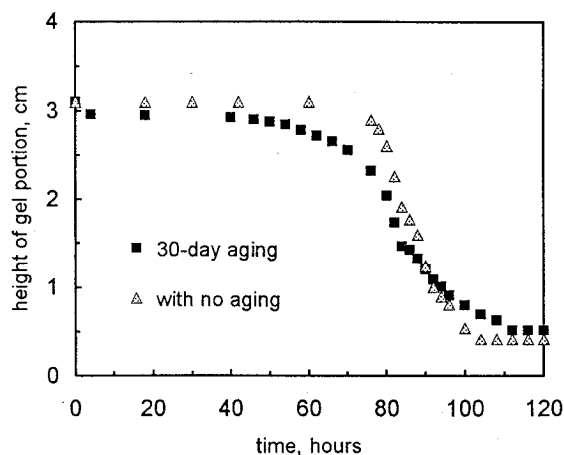


Fig. 4 Comparison of 30 days of aging with no aging ( $x = 6.36$ ).

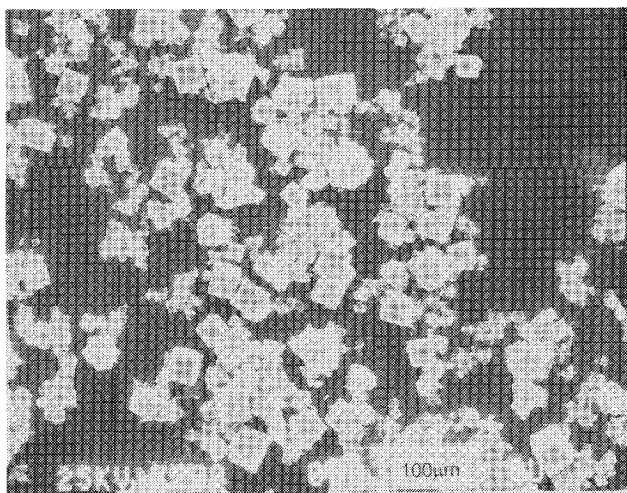
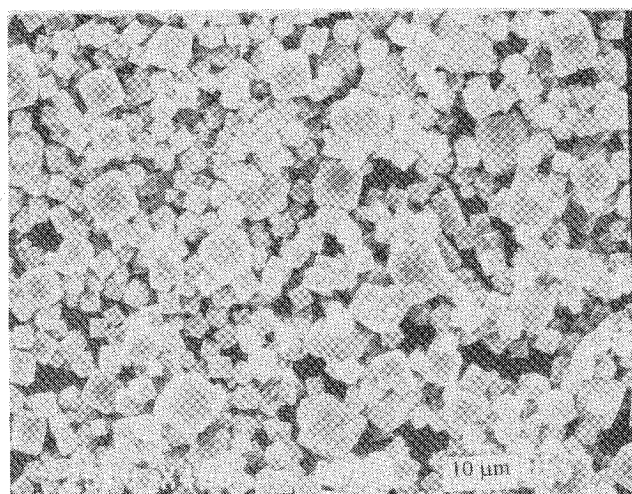
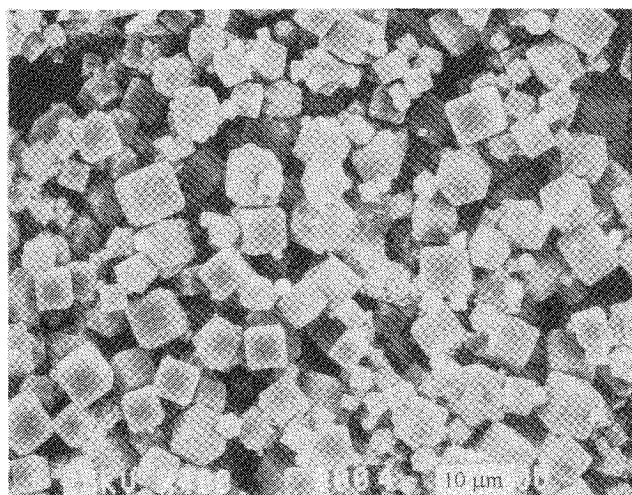


Fig. 5 Photomicrograph after 30 days of aging ( $x = 6.36$ ).



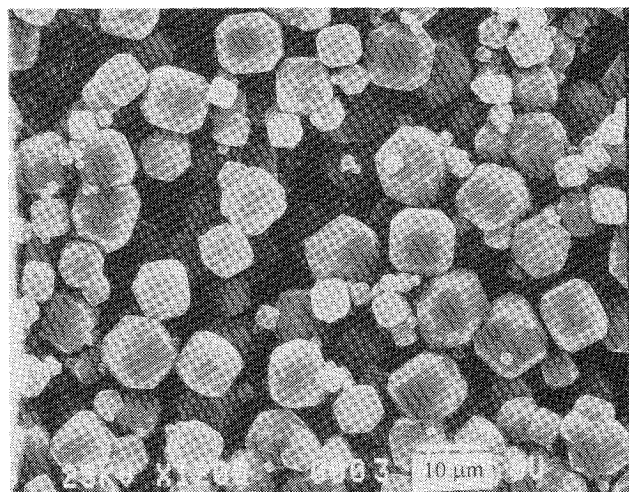
a) With addition of nutrients



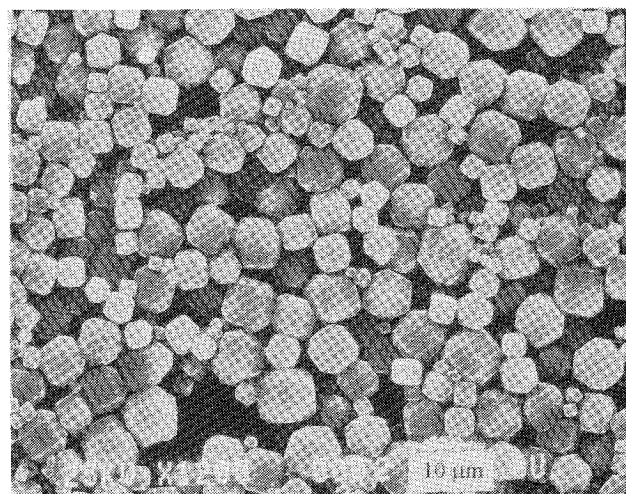
b) Without addition of nutrients

Fig. 6 Photomicrographs for  $x = 2.12$ .

(The nutrients have exactly the same composition as aluminosilicate gels made for zeolite crystallization.) For the composition without TEA ( $\text{Al}_2\text{O}_3\text{-}1.04\text{SiO}_2\text{-}2.04\text{Na}_2\text{O-}169\text{H}_2\text{O}$ ), the crystal size increased from  $7\text{ }\mu\text{m}$  to about  $10\text{ }\mu\text{m}$ . However, compositions for zeolite growth aboard shuttles have a nucleation suppresser, TEA; therefore, it is more interesting to see if a similar method can be applied to the synthesis system with TEA, so that the crystal size may be further increased in space. Again, the method was applied



a) With addition of nutrients



b) Without addition of nutrients

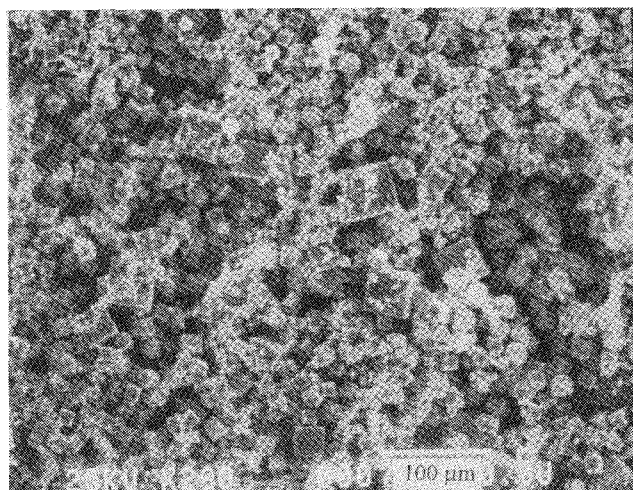
Fig. 7 Photomicrographs for  $x = 4.24$ .

in systems with different amounts of TEA ( $x = 2.12, 4.24$ , and  $6.36$ ). Figure 6 gives two photomicrographs for the zeolite samples obtained with and without adding nutrients for the case of  $x = 2.12$ . The crystal size was found to be increased by about 30–50%. Figures 7 and 8 show the cases for  $x = 4.24$  and  $x = 6.36$ , respectively. From these two figures, we see that with an increasing amount of TEA the crystal size increases. However, adding nutrients does not increase the crystal size, but merely introduces additional smaller crystals. To understand why this has occurred, the shrinkage was again observed after nutrients were added and mixed.

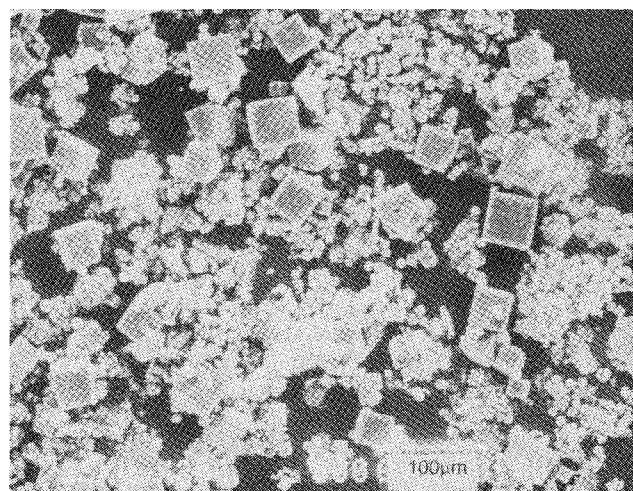
Figure 9a shows the case for  $x = 2.12$ . The primary shrinkage curve and the shrinkage curve after nutrient addition are presented. Again, for the primary curve the sudden change in height indicates the growth onset, which is preceded by the nucleation period and is followed by the growth period. It is seen that, after nutrients are added and mixed at about the 8th hour, the curve after nutrient addition has almost the same slope as the growth period in the primary curve, which means growth continues. In this case, we have seen from Fig. 6 that the method of adding nutrients works very well. This implies that all crystals are uniformly mixed within the added nutrients and that the crystal number concentration remains large enough although the volume is doubled as a result of adding nutrients. Thus, all the neighboring gels can be depleted in a short period of time, so that no additional nuclei will be formed.

Figure 9b shows the case for  $x = 4.24$ . It is seen that, after nutrients are added and mixed at about the 30th hour, the new mixture first undergoes about 9 h of nucleation (the curve is concave upward), followed by the growth period after the sudden change in height.





a) With addition of nutrients



b) Without addition of nutrients

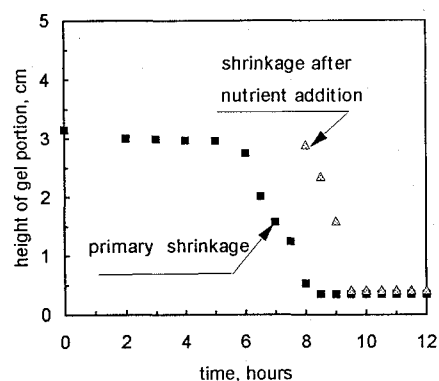
Fig. 8 Photomicrographs for  $x = 6.36$ .

For the case of  $x = 6.36$ , similar behavior was observed, which is not presented here.

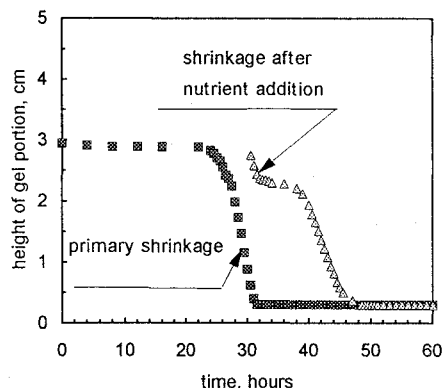
Figures 7 and 8 indicate that for  $x = 4.24$  and  $x = 6.36$ , adding nutrient does not increase the crystal size, but nurtures some extra smaller crystals. Therefore, it seems that the initially formed crystals are so large (for example,  $25 \mu\text{m}$  for  $x = 4.24$  and  $43 \mu\text{m}$  for  $x = 6.36$ ) that they settle down after nutrients are added and mixed, leaving some "precursors" of crystals within the new mixture. These precursors nucleate and then become those smaller crystals. It must be noted that adding nutrients not only reduces the crystal number concentration by half, but also dilutes the gel portion to make it less compact, thus enhancing the crystal settling. Nevertheless, based on the above discussions, an alternative method of adding nutrients by partly decanting the clear portion was tried in order to increase the crystal size further for the system with the larger amount of TEA. Figure 10 presents two photomicrographs for the samples with and without using this alternative method. The crystal size increases by about 20–30% for the system with  $x = 6.36$ , but the crystal intergrowth problem becomes more serious.

### Modeling of Microgravity Growth

The microgravity environment may help grow larger zeolites in a system that has the problem of GSN on earth. As mentioned earlier, GSN occurs only when the number of primary nuclei is reduced greatly by means of a nucleation control. Recently, Morris et al.<sup>10</sup> have used some tertiary alkanolamines as additives to obtain more effective control of the nucleation rate, which may be advantageous to zeolite space processing in the sense that the number of primary



a)



b)

Fig. 9 Shrinkage curves after nutrients are added:  $x =$  a) 2.12 and b) 4.24.

nuclei can be decreased further. Moreover, it is unquestionable that the method of adding nutrients can also be applied to zeolite growth in microgravity, so that much larger zeolites will be obtained in space. However, nutrients must be added following the onset of growth. Under normal gravity this time can be determined by RHD; however, in microgravity there is no appropriate parameter to determine the time for adding nutrients. Therefore, in this section we model the growth-in-gel process in microgravity, and subsequently we derive the necessary parameter.

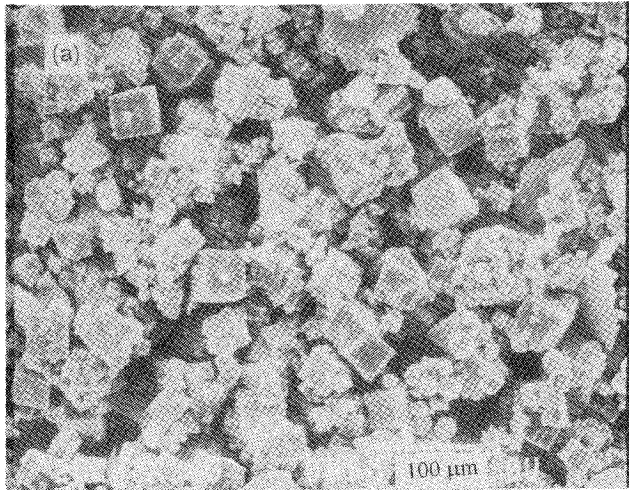
A number of assumptions for growth in microgravity are made: 1) there is no disturbance, such as a  $g$ -jitter effect; hence, there is no crystal or fluid motion; 2) the crystals have a spherical shape and are uniformly distributed throughout the gel portion; and 3) the dissolved gel species is a vital species for growing surfaces, while the solution-phase-only species is redundant<sup>14</sup>; in other words, growth is dependent merely on the gel-species transfer.

Figure 11 sketches the growth-in-gel process, based on the above assumptions. The inner circle represents a crystal surface, and the outer circle a cavity within the porous gel network, which is indicated by the shaded area in the figure. It is also assumed that any voids within the shaded area are much smaller than the cavity within which the crystal grows. As growth proceeds, the cavity becomes enlarged because of the continuous dissolution for gel particles at the edge of the cavity. Unless neighboring cavities finally become interconnected, the problem is one-dimensional because of spherical symmetry. The mass conservation equation in terms of the dissolved gel species within the solution between the crystal surface and the cavity edge [ $r_0 < r < r_\infty(t)$ ] is given by

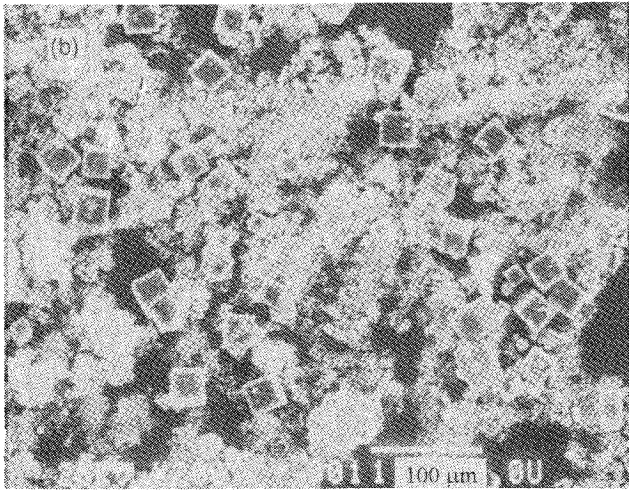
$$\frac{\partial \rho}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial \rho}{\partial r} \right) \quad (2)$$

In this model the initial time  $t = 0$  is the moment right after the onset of growth. The initial condition, hence, is given by

$$\rho(r, t = 0) = \rho_{\text{sat}}, \quad r_\infty(t = 0) = r_{\infty 0} \quad (3)$$



a) With nutrient addition



b) Without nutrient addition

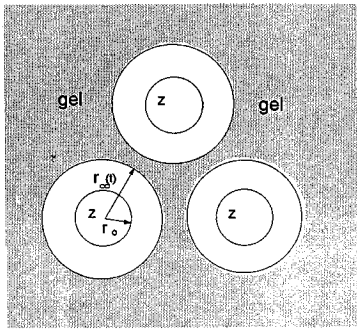
Fig. 10 Comparison of sizes for an alternative method ( $\alpha = 6.36$ ).

Fig. 11 Illustration of grow-in-gel in microgravity.

The boundary conditions are specified as follows:

$$\rho = 0 \quad \text{for } r = r_0 \quad (4)$$

$$\rho = \rho_{\text{sat}} \quad \text{for } r = r_\infty(t) \quad (5)$$

For the boundary condition at the crystal surface,  $r = r_0$ , we assume the Damkohler number<sup>17</sup>  $Da = (\text{reaction rate})/(\text{diffusion rate}) \gg 1$ . Also, the crystal size  $r_0$  is assumed constant as a first approximation. From our previous experiment<sup>12</sup> it is known that for a given system the crystal size does not increase much after the onset of growth. For the boundary condition at the edge of the cavity, we assume a

saturated concentration exists there. However, this edge moves as the cavity is enlarged, because of the dissolution of gel particles.

Obviously, one more equation is required to determine the radius change for the cavity. Based on mass conservation for the gel species, we have the equation<sup>15</sup>

$$n_{\text{crl}} I_g = -\rho_{\text{sg}} \frac{d\phi_{\text{sg}}}{dt} \quad (6)$$

The left side stands for the mass consumed at crystal surfaces, and the right side is related to the dissolution rate of solid gels. Next, it is known that the cavity is enlarged while amorphous solid gels are consumed near the edge of the cavity. Hence, we obtain the following equation:

$$-\frac{d\phi_{\text{sg}}}{dt} = n_{\text{crl}}(1 - \varepsilon') \frac{d\left(\frac{4}{3}\pi r_\infty^3(t)\right)}{dt} \quad (7)$$

where  $\varepsilon' = v_{\text{sln}}/(V_g + v_{\text{sln}})$  is the porosity of the shaded area in Fig. 11. By virtue of Eq. (6) and the fact that  $I_g = 4\pi r_0^2 \mathcal{D}(\partial\rho/\partial r)_{r=r_0}$  we have

$$\frac{dr_\infty}{dt} = \frac{r_0^2 \mathcal{D}}{r_\infty^2(t) \rho_{\text{sg}}(1 - \varepsilon')} \left( \frac{\partial\rho}{\partial r} \right)_{r=r_0} \quad (8)$$

Equation (8) gives the radius change for the cavity, which should be incorporated into Eq. (5). Therefore, Eq. (2), together with the initial condition Eq. (3) and the boundary conditions (4), (5), and (8), describes the zeolite growth process under microgravity. Note that this problem involves a moving boundary [Eq. (5)], and the rate of boundary motion [Eq. (8)] depends on the density change  $(\partial\rho/\partial r)_{r=r_0}$ , which appears in Eq. (2). Hence, the equation can only be solved numerically. This will be done in the future for a meaningful range of parameters to be determined by experiments. The cavity radius  $r_\infty(t)$ , which can be found from Eq. (8), increases as the time elapses. Therefore, the appropriate parameter to distinguish crystallization stages, in comparison with the RHD under normal gravity, is the variation of overall porosity  $\varepsilon = (V_{\text{sln}} + V_{\text{crl}})/V < 1$ , where  $V = V_{\text{gel}} + V_{\text{sln}} + V_{\text{crl}}$ .

Under microgravity conditions, the gel portion has an initial porosity that is smaller than one. As the growth process proceeds,  $\varepsilon$  will increase and finally reach unity, which means the reaction mixture becomes clearer and clearer. However,  $\varepsilon = 1$  does not mean that the liquid is completely clear, because numerous crystals are still suspended within it. Therefore, a measurement of the porosity can well represent the growth process. By differentiating  $\varepsilon = \frac{4}{3}\pi r_\infty^3(t) N_{\text{crl}}/V$  with respect to time and using Eq. (8) we have

$$\frac{d\varepsilon}{dt} = \frac{4\pi n_{\text{crl}} r_0^2 \mathcal{D}}{\rho_{\text{sg}}(1 - \varepsilon')} \left( \frac{\partial\rho}{\partial r} \right)_{r=r_0} \quad (9)$$

From the above equation it is interesting to note that the rate of change for the overall porosity represents the mass transfer rate  $(\partial\rho/\partial r)_{r=r_0}$  at the growing crystal surface. The rate of change in porosity is expected to decrease significantly at the final stage, because the distance  $r_\infty(t) - r_0$  will become so large that the mass transfer rate will decrease.

Although a direct measurement of the overall porosity is difficult, the reaction mixture, as the porosity changes, will have the different absorption for a light beam that goes through it. From this information, it can be determined when the nutrients should be added, so that much larger zeolites can be grown in space, over and above the size increment brought about by reduced gravity.

## Conclusions

It has been demonstrated that zeolite crystals would grow larger on earth in the absence of gravity-induced secondary nucleation (GSN). A previously derived nondimensional parameter, which serves as a criterion for the occurrence of GSN, is presented. The benefit of microgravity regarding the increment of the crystal size is discussed in terms of whether or not GSN (which is detrimental) occurs on earth (because microgravity would eliminate GSN). In order to grow

larger crystals in space than on earth, two important requirements must be met: 1) the synthetic system must have sufficient nucleation control; and 2) mixing of solutions must take place in orbit, because, according to our experiments, a delay (aging) for a reaction mixture to be activated causes a higher nucleation rate once the mixture is heated up. In fact, the essence of the above requirements is to keep the number of primary nuclei to a minimum, so that the system is more likely to have GSN on earth, as can be seen from the nondimensional parameter derived. Our theory was found to be consistent with the results of the STS-40 (SLS-1 mission) and STS-50 (USML-1 mission) experiments, the systematic space experimental studies performed by Sacco et al.<sup>11</sup>

It is convenient to use shrinkage curves to determine the length of the nucleation period as well as the growth period, which is commonly done by x-ray powder diffraction (XRD). Addition of a nucleation suppresser, TEA, decreases the nucleation rate and prolongs the nucleation period, thereby increasing the crystal size. For a system with or without TEA, aging (a delay in the activation of the reaction mixture) increases the nucleation rate and thus shortens the nucleation period; hence, the crystal size decreases. However, why aging increases the nucleation rate needs to be further investigated.

The method of adding nutrients can be used for a growth system with TEA to synthesize larger zeolites. Under normal gravity, however, a restriction has been found. With more TEA, much larger zeolite crystals are obtained, and adding nutrients merely introduces some additional crystals in smaller sizes. Our experimental evidence suggests that the large crystals settle down after being mixed with nutrients. Therefore, it suggests that space can provide an ideal environment to increase the crystal size by applying the method of adding nutrients, in addition to the size increment due to the elimination of GSN at microgravity.

Growth-in-gel zeolite crystallization in microgravity has been modeled. In principle, the method of adding nutrients can be applied to zeolite crystal growth in space. In fact, the same step can be repeated a number of times for a system in space, so that much larger zeolites can be obtained. In order to determine the time for adding nutrient, a parameter, the overall porosity or the change of the overall porosity, was derived, which is equivalent to the gel shrinkage under normal gravity.

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