Modeling of Macroscopic/Microscopic Transport and Growth Phenomena in Zeolite Crystal Solutions under Microgravity Conditions

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Project Summary

Crystals grown from liquid solutions have important industrial applications. Zeolites, for instance, a class of crystalline aluminosilicate materials, form the backbone of the chemical process industry worldwide and are used primarily as adsorbents and catalysts. Many of the phenomena associated with crystal growth processes are not well understood due to complex microscopic and macroscopic interactions. Microgravity could help elucidate these phenomena and allow the control of defect locations, concentration as well as size of crystals. Microgravity in an orbiting spacecraft could help isolate the possible effects of natural convection (which affects defect formation) and minimize sedimentation. In addition, crystals will stay essentially suspended in the nutrient pool under a diffusion-limited growth condition. This is expected to promote larger crystals by allowing a longer residence time in a high-concentration nutrient field. Among other factors, the crystal size distribution depends on the nucleation rate and crystallization. These two are also related to the "gel" polymerization/depolymerization rate. Macroscopic bulk mass and flow transport, and especially gravity, force the crystals down to the bottom of the reactor, thus forming a sedimentation layer. In this layer, the growth rate of the crystals slows down as crystals compete for a limited amount of nutrients. The macroscopic transport phenomena, under certain conditions can, however, enhance the nutrient supply and therefore accelerate crystal growth.

Several zeolite experiments have been performed in space with mixed results. The results from our laboratory have indicated an enhancement in size of 30 to 70 percent compared to the best ground-based controls, and a reduction of lattice defects in many of the space-grown crystals. Such experiments are difficult to interpret and cannot be easily used to derive empirical or other laws since many physical parameters are simultaneously involved in the process. At the same time, however, there is increased urgency to develop such an understanding in order to more accurately quantify the process. This understanding is critical in order to develop a modeling ability in order to effectively use the space environment to control the development of defects and to grow submicron to millimeter sized crystals.

In order to better understand the results obtained from our prior space experiments and design future experiments, a detailed fluid dynamic model simulating the crystal growth mechanism is required. This will not only add to the fundamental knowledge on the crystallization of zeolites,

but also be useful in predicting the limits of size and growth of these important industrial materials.

Our objective is to develop macro/microscopic theoretical and computational models to study the effect of transport phenomena in the growth of crystals grown in solutions. Our effort has concentrated so far in the development of separate macroscopic and microscopic models. The major highlights of our accomplishments are described bellow.

Macroscopic (Fluid) Model

The macroscopic fluid model accounts for the two phases in the solution during crystal growth, i.e., the fluid phase (incompressible Newtonian fluid) and crystal particle phase, all of which are regarded as continua. The gel phase that develops from polymerization in the solution is not included in our model and the crystal growth process is modeled using an empirical exponential law. Crystals are moving under the action of gravity and drag forces. The computational domain simulates a three-dimensional cubic reactor filled with the solid and fluid phases. The derived two-phase model equations are solved numerically using a Finite Element Method and the Flux Corrected Transport technique. In the simulations, crystals grow and settle to the bottom, inducing fluid motion. Therefore, throughout the process there is continuous interaction between the two phases. Major results address the crystal settling process, induced fluid motion, and sedimentation characteristics as functions of gravity level and fluid viscosity.

Microscopic (Particle) Model

At the microscopic level, the growth and nucleation dynamics is based upon molecular theories and particle-based Monte Carlo computational methods. The theory and model are developed for a three-dimensional domain with dimensions much larger than the typical crystal size. The cell size of the grid is determined by parameters such as density, average velocity, and temperature of the nutrients. There are several concepts that are combined in a novel way in the microscopic model: (a) the presence of moving nutrients and growth sites; (b) the microscopic modeling of nucleation and crystallization; and, (c) the simulation of a large physical domain with simple macroscopic transport effects and variable gravity.

Nutrients are described using a Monte Carlo method following a prescribed distribution function. Nutrients are moving under the action of a gravity field undergoing elastic collisions. Nucleation sites are generated in random and allowed to grow to crystals of finite size through absorption collision with nutrients. Our approach is to describe the crystallization processes with a model that will be refined through successive iterations with data comparisons. As such, the crystals are considered as spherical particles that grow after their attraction and attachment of nutrients and move under the influence of gravity. Our results show the growth, motion, and size distribution of the crystals under variable gravity.

Current/Future Work

Our objective is to develop an advanced computational model based on a hybrid particle/fluid approach. The complex physical phenomena to be incorporated in our model will contribute towards improving our understanding of the fundamental physics of zeolites and crystal growth in general. Due to the complexity of these phenomena, this work will lead to significant advances in computational modeling science as well. In the course of the proposed research and model development, we will continuously validate and modify the theories using experimental data.