174c Determination of Zeolite Nanoparticle Morphology Evolution Mechanism from Simulations and Saxs/Tem Measurements

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The morphology of zeolite nanoparticles plays a critical role in the functionality of devices that utilize zeolite films. Incomplete understanding of the mechanistic steps involved in the growth of templated crystalline zeolite nanoparticles limits the ability to optimize synthesis conditions for the growth of continuous mesoporous zeolite films. Although experimental and simulation studies have been performed to characterize the formation of zeolite nanoparticles[1-6] the mechanistic details have not been completely described. In this study, a process is developed to elucidate the mechanistic details in the aging and coalescence of zeolite nanoparticles through a combined experimental and simulation approach. The experimental and simulation methodology developed here can readily be applied to numerous zeolite systems, as well as other nanoparticle systems.

TPA-silicalite-1 nanoparticles are formed from clear solutions comprised of TPAOH, TEOS, and H2O. The nanoparticles are aged for various times and at various temperatures to study the kinetics of particle growth and morphology evolution. TEM and SAXS are used to analyze the particle size and shape. TEM provides images of the particles and has a resolution on the order of nanometers, which makes it possible to observe the morphology of the nanoparticles. SAXS analysis produces a scattering curve and pair distance distribution function (PDDF) that provide information about the distribution of the size and shape of the nanoparticles.

Although the experimental analysis performed gives excellent insight into the evolution of the particle size and shape, it does not provide as much insight into the mechanistic details involved in the morphology evolution. Simulation models make it possible to observe the size and morphology evolution simultaneously. Here, population balance modeling is used to simulate the particle size distribution as a function of time. One weakness of only using population balance modeling is that it provides no information about the morphology evolution of the particles in the population. In order to compute the PDDF for a distribution of particles, the morphology of the particles must be known or assumed.

A novel simulation methodology has been developed to compute pair distance distribution functions (PDDF) from a particle population. The utility of the multiscale analysis method extends beyond the application presented here. The particle population size distribution is computed as a function of time with the use of a Kinetic Monte Carlo (KMC) population balance model.[7] The KMC population balance method is used because it offers the flexibility to simulate complex interactions between particles, as well as particle aging, without having to solve complex population balance equations. Moreover, it is relatively straightforward to change the aging and coalescence mechanism simulated with the KMC technique. The KMC model is used to simultaneously simulate an aging mechanism, where particles are transformed from fresh particles to nucleated particles, and a coalescence mechanism, where DLVO interactions amongst the particles are simulated.

The morphology of the particles is simulated with an Eden model.[8] The Eden model provides a means to propose morphologies of different sized particles and has been used to simulate particle morphology evolution in numerous systems.8 In the Eden model, morphology evolution is performed on a structured lattice; here the evolution is performed on a 3D cubic lattice. A single molecule is placed in the center of the simulation domain and subsequent molecules are added at random to the nearest neighbor positions of existing molecules. The molecular addition process without possibility of the rejection of the placement of a particle is analogous to diffusion-limited aggregation, which is what is occurring in this

system. In the composite model, the KMC model passes the population size distribution for a given time to the Eden model, which computes possible configurations for each cluster.

The cluster configurations produced by the Eden model are composed of numerous molecules, which are composed of numerous electrons. In SAXS, the x-rays pass through the sample and are deflected by the electrons in the sample. In the simulation model, the configurations that are produced by the Eden model are populated with points, which are analogous to electrons. Once the configurations are populated with points, the PDDF for that configuration can be computed. The composite PDDF for the population of configurations is computed by adding the PDDF for the individual configurations.

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