588a Dendritic Growth during the Early Stages of Molecular Sieve Formation from Precursor Nanoparticles

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The structure of the nanoparticles present in "clear" sols made from tetraethylorthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), and water, and their role (spectators versus participants) in nucleation and growth of silicalite-1 (siliceous ZSM-5) is a subject of considerable fundamental and practical significance.[1-4] Its fundamental importance lies in the relationship of these nanoparticles to the nuclei and growth units of silicalite-1, a system that serves as a robust model to study the self-assembly of porous inorganic materials in the presence of organic structure directing agents. The practical significance stems from the potential to control nucleation and growth of preferentially oriented thin films for catalytic and other applications, to tailor crystal size and shape, and to possibly direct the synthesis of mesoporous materials towards ordered wall structures with improved stability.

Despite the numerous ex-situ and in-situ studies of particle size/shape evolution of silicalite-1 and its nucleation at elevated temperature, to our knowledge, no report exists demonstrating silicalite-1 nucleation and growth at room temperature from nanoparticle-containing "clear" sols. It is therefore unclear if these nanoparticles, which form spontaneously at room temperature upon exceeding a certain silica solubility limit for a given pH, are thermodynamically stable aggregates requiring heating to yield silicalite-1 or transient aggregates that gradually evolve to silicalite-1. Motivated by an earlier report that indicated formation of zeolite crystals at room temperature from precipitated silica,[5] we followed the evolution of nanoparticles at room temperature over a period of 11 months by SAXS and HRTEM up to the point of silicalite-1 crystal formation. In addition to eliminating the need for high-temperature in-situ SAXS capabilities and the complications that may be associated with the interpretation of ex-situ room temperature SAXS measurements made after quenching high-temperature experiments (such complications can be easily envisioned based on the temperature dependence of silica solubility and the dynamic nature of the nanoparticles), this room temperature study led to the isolation of silicalite-1 crystals at an early stage of growth (< 5% yield). HRTEM examination revealed single crystals with cluster-like morphology providing strong evidence for an aggregation growth mechanism under these conditions.

References

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