

## Atomic Structure of Hierarchical Few-Unit-Cell MFI Zeolites

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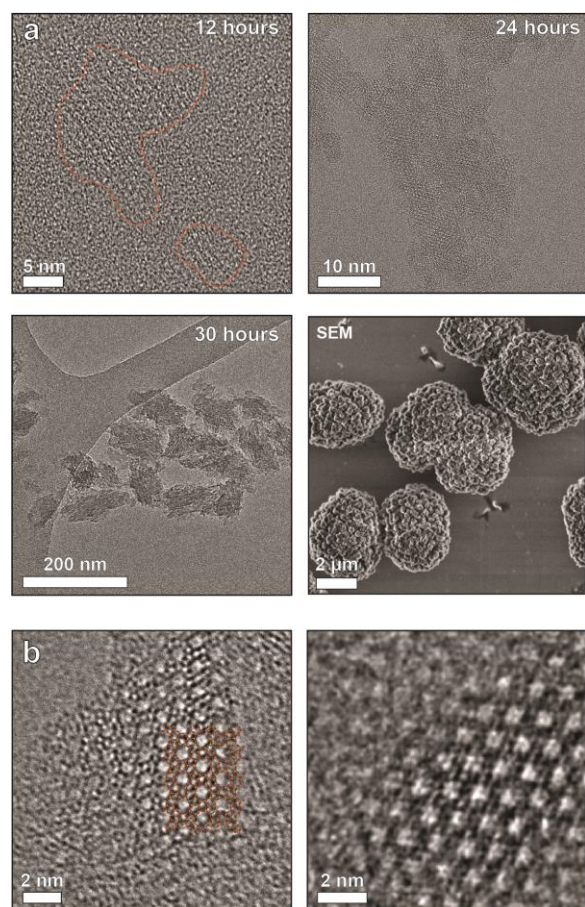
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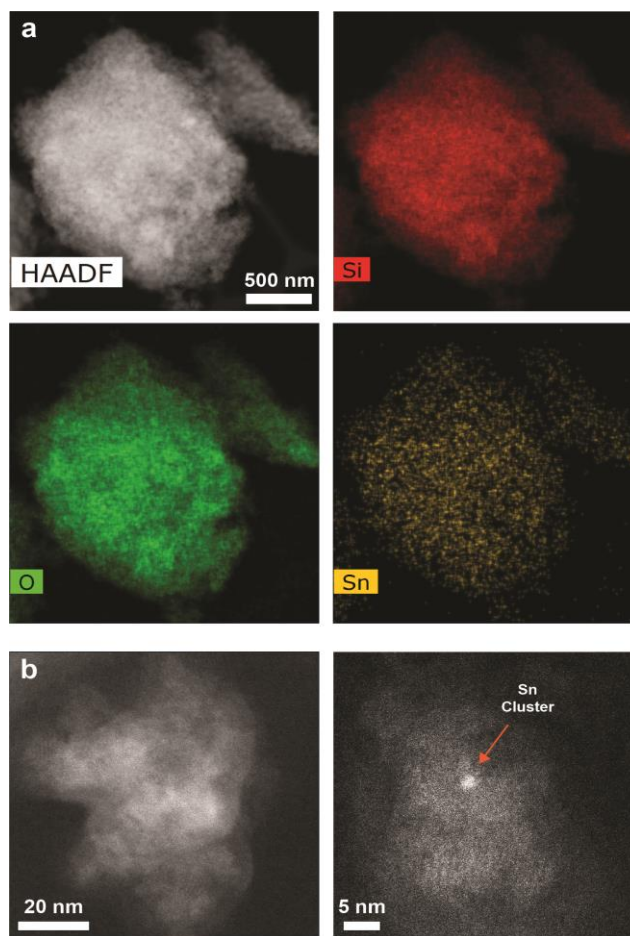
Zeolites with one to few unit cell domains are highly desirable for their superior catalytic and adsorption properties, when compared to their bulk crystalline form [1, 2]. One such desirable framework is of the MFI-type zeolite which has a distinct 10-membered pore in the framework, ideal for hosting catalytically active sites as well as allow molecular-size-based separations of isomer mixtures like ortho- and para-xylene [3, 4]. Incorporation of guest atoms such as Al and Sn in the zeolite framework is used to introduce active sites for catalyzing industrially sought-after reactions like conversion of methanol to hydrocarbons and isomerization of glucose to fructose respectively [4, 5]. The catalytic activity of these reactions can be improved by allowing faster access of the guest molecules to the active sites, which is possible through reduction in particle size.

In this work, we report the atomic structure characterization as well as the crystallization kinetics studies in the development of a new crystalline hierarchical zeolite called few-unit-cell domain pentasil (FDP) [6]. Using low dose high-resolution transmission electron microscopy (HR-TEM), the growth of the FDP crystals was monitored during the crystallization, revealing first smaller nanoparticles (c.a. 10-15 nm) form which over time nucleate together and assemble into larger hierarchical particles (Fig. 1 (a)). HRTEM from larger FDP particle show they are comprised of these smaller nanocrystalline domains, which are not aligned. Atomic resolution image from such particles confirm they are of the MFI type, which is seen from the unique pore-arrangement in the [010] direction having sizes in the range of ~ 10 nm (Fig. 1(b)). The HRTEM experiments were carried out on an FEI Tecnai G<sup>2</sup> F30 (S)TEM microscope operated at 300 keV and images were acquired under low-dose conditions using a Gatan K2 Summit camera.

To catalyze the isomerization of glucose to fructose, Sn was incorporated in the FDP framework during synthesis to introduce active “acidic” sites. For the detection of Sn in the FDP framework, analytical scanning (S)TEM experiments were carried out on an aberration-corrected FEI Titan G2 60-300 (S)TEM microscope with a Super-X energy dispersive X-ray (EDX) spectrometer operated at 200 keV with a probe current of 15 pA. Low magnification spatially resolved EDX maps showed a uniform distribution of Sn from the entire particle (Fig. 2(a)). Closer observation with high resolution high-angle annular dark-field (HAADF)-STEM showed no contrast variation in the nanoparticles, further confirming their complete incorporation into the FDP framework (Fig. 2(b)). As a result, the Sn-FDP zeolite had a catalytic performance for glucose isomerization comparable to that of another hierarchical SPP zeolite, reported to have the highest activity for this reaction [7].



**Figure 1.** (a) FDP samples collected at different crystallization times, showing growth from nanoparticles to large spherical clusters. HRTEM demonstrates the polycrystalline nature of FDP. (b) Filtered atomic-resolution images of individual nanocrystals, confirming the unique MFI-type structure along the b and a-directions respectively.



**Figure 2.** (a) STEM-EDX from Sn-FDP showing uniform distribution of Sn across a large particle. (b) High resolution HAADF-STEM images of Sn-FDP particles, showing no strong contrast variations, indicating incorporation of Sn in the FDP lattice. Only a very small number of particles demonstrated clustering of Sn atoms as indicated.

#### References:

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