

Exploring an Unidentified Phase Transformation in MIL-53(Al) Crystallization: Influence of Hydrothermal Synthesis, Calcination, and Modulation Conditions

Bella Mele, Class of 2027

Metal-organic frameworks (MOFs) are crystalline materials composed of metal nodes linked by organic ligands. Since their discovery in 1995, MOFs have become a major focus in materials science due to their porous structures, which result in low packing density and ultrahigh surface area. These characteristics make them valuable for applications in catalysis, gas storage, and drug delivery.

Within the Ortoll-Bloch lab, our MOF of interest is MIL-53(Al), which is composed of aluminum nodes coordinated by terephthalate linker molecules. MIL-53(Al) exhibits a unique “breathing” behavior, whereby its pore size and structure change based on temperature, pressure, and the availability of guest molecules that can insert themselves into MOFs through adsorption. As a result, there are three distinct known phases of MIL-53. However, in spring 2025, Victoria Jang ‘26 synthesized a batch of MIL-53 that did not match any known phase.

This summer, our objective was to investigate this unidentified phase by adjusting parameters to determine its formation mechanism. Our goal was twofold: (1) isolate the unknown phase and (2) prevent its formation during synthesis of pure MIL-53(Al). Over the first few weeks, we synthesized a range of MIL-53(Al) growths, varying both the heating temperature and duration for initial crystal growth (synthesis) along with the subsequent calcination step, where samples are heated to high temperatures to remove excess linker molecules. Samples were analyzed by X-ray diffraction (XRD), comparing observed peaks in XRD patterns to those from literature and previous samples to determine which MIL-53(Al) phases formed. Nuclear magnetic resonance (NMR) and attenuated total reflectance Fourier-transform infrared (ATR/FTIR) spectroscopies were used to further analyze linker abundance and ordering within the crystalline materials. These experiments showed that calcination temperature, rather than other growth parameters, primarily determines relative phase abundance.

To investigate the unknown phase formation mechanism, we utilized modulated crystal growth. By adding a modulator—a small molecule similar in structure to the linker—we introduced competition for coordination sites on the metal centers. Our chosen modulator, acetic acid, slows nucleation and crystal growth, yielding MIL-53(Al) products that are less prone to highly ordered defects during calcination. After conducting growths with various acetic acid concentrations, we found no unknown phase formed using a solution containing 7 M acetic acid, regardless of calcination temperature.

Because modulators primarily target defect formation, these results suggest the unknown phase arises from highly ordered defects associated with incomplete linker sublimation during calcination. Scanning electron microscopy (SEM) imaging supported this conclusion, showing distinct morphology for samples synthesized with 7 M acetic acid solution (Fig. 1) compared to unmodulated samples (Fig. 2) and those grown with 2 M acetic acid solution. By linking defect formation to calcination temperatures and modulator concentrations, our results provide a foundation for tuning MIL-53(Al) phase behavior, informing future synthesis strategies and exploration of atomic-scale structure.

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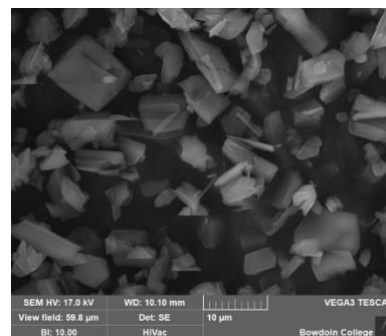


Figure 1. Block-like morphology of pure MIL-53(Al) sample

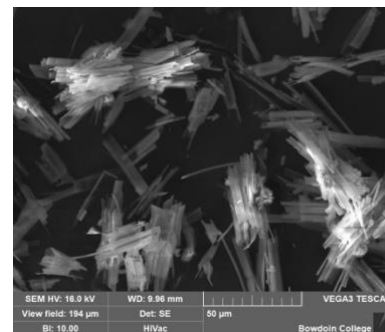


Figure 2. Needle-like morphology of heavily modulated MIL-53(Al) sample