Investigating an Unknown Phase in MIL-53(Al) Synthesis

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Metal-organic frameworks, also known as MOFs, are crystalline materials composed of metal ions or clusters coordinated to multiple organic linker molecules. What sets MOFs apart from other materials is their porosity, large surface area, and structural flexibility. As a result of these phenomenal properties, MOFs have numerous applications and are used in areas such as gas storage and separation, drug delivery, water purification, and energy storage.

The MOF of interest in the Ortoll-Bloch lab is MIL-53(Al), which has an essentially octahedral structure consisting of aluminum ions coordinated to terephthalate linker molecules. What separates MIL-53(Al) from other MOFs is that it is a breathing MOF, meaning it can reversibly transition between different phases in response to external factors. In the case of MIL-53(Al), its three distinct known phases arise because of variation in the size of the MOFs' pores due to the presence or absence of guest molecules. Previous work in the Ortoll-Bloch lab identified an unknown phase of MIL-53(Al) using x-ray diffraction (XRD), which measures how x-rays scatter when they interact with a crystal lattice to give information about a sample's crystallinity and structure, thereby laying the foundation for this summer's research.

This summer, the goal was to 1) identify the composition and structure of the unknown phase, and 2) rationalize its formation. To these ends, MIL-53(Al) growths were carried out along with XRD to confirm the relative amounts of the unknown phase under different calcination temperatures. Energy-dispersive spectroscopy (EDS) and proton nuclear magnetic resonance (NMR) were conducted to further analyze these samples. EDS gave their elemental composition, allowing for the detection of impurities and foreign guest molecules inside the pores of the MOF, either of which was hypothesized to have been the cause for the unknown phase. On the other hand, calculations using NMR yielded their linker weight percentage, a metric of how much of the total mass of a sample is due to linker molecules. Comparing these linker weight percentages with theoretical values gave insight into whether all the excess, uncoordinated linker molecules had sublimed at different calcination temperatures.

EDS data showed that the elements in unknown phase samples were aluminum, oxygen, and carbon, which are expected to be present in MIL-53(Al). So, it ruled out impurities as being the cause for the unknown phase. On the other hand, NMR results showed that samples that underwent calcination at temperatures between 300°C and 350°C had linker weight percentages greater than that of samples containing only the narrow-pore phase, implying the presence of excess linker molecules. The decrease in the relative amount of linker present in these samples given an increase in calcination temperature within this range could be explained by the fact that given more thermal energy, excess linker molecules are better able to overcome the secondary forces holding them in place inside the pores. Importantly, the XRD patterns of the samples containing the highest degree of the unknown phase, which were those calcined between 325°C and 350°C, showed only the diffraction peaks corresponding to the unknown phase and narrow-pore phase, the latter of which involves the adsorption of only atmospheric water molecules. So, our results suggest that the unknown phase arises as a result of the incomplete sublimation of linker molecules from the pores of MIL-53(Al) due to calcination temperatures being too low.

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