

Real-time Investigation of Metal-Organic-Framework Synthesis via Ultrasound Monitoring and Spectroscopy

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Understanding the complex synthesis of metal-organic frameworks (MOFs) is still a challenge in the field of porous materials. Current models suggest the formation of pre-nucleation building units (PNBUs), whose nature is still widely discussed. For ZIF-8, which is an extensively studied MOF, the formation mechanism is not yet fully understood. While Venna et al. propose a solution- and solid mediated mechanism, Cravillon et al. suggest the involvement of pre-nucleation clusters as well as nanoparticles. In situ methods, such as the ultrasound-monitoring (figure 1) allow obtaining additional insights, which are often missed by ex situ characterizations. In addition, ultrasound monitoring is a robust and simple technique, offering a non-destructive analysis with high time resolution [1].

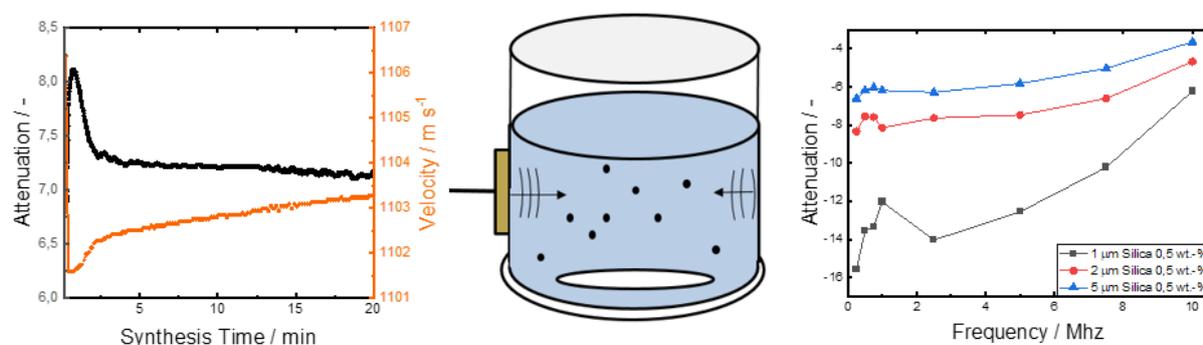


Figure 1: Setup for in situ US-monitoring (center) with exemplary US-signals over time (left) and spectroscopic measurement (right).

Using the pulse echo method, the ultrasound velocity increases continuously from the start of the ZIF-8 synthesis. Since sound propagates faster in solids than in liquids, this increase can be correlated with particle formation. The ultrasound attenuation rises sharply at the beginning of the synthesis, and then gradually decreases until a plateau is reached at the end. Notably, at the attenuation maximum, a change in the velocity trend becomes apparent. Further investigations revealed the formation of an intermediate phase in the early stages of the synthesis, which subsequently transforms into ZIF-8 as the reaction progresses. Ultrasound spectroscopy provides a valuable insight to the particle formation, since the ultrasound attenuation depends both on the particle size within the dispersion as well as on the frequency of the ultrasound wave. Figure 1 (right) shows that attenuation increases as particle size decreases.

The talk will also combine ultrasound monitoring with other in-situ and ex-situ techniques (such as DLS and IR and Raman spectroscopy) in order to unravel the mechanism of the synthesis of other MOFs such as HKUST-1 and MIL-53 [2].

References

- 1) M. Ermer, R. Reber, H. Baser, M. Fischer, W. Schwieger, M. Hartmann, *Cryst. Growth Des.*, **2023**, 23,5355-5367.
- 2) H. Embrechts, M. Kriesten, M. Ermer, W. Peukert, M. Hartmann, M. Distaso, *Cryst. Growth Des.*, **2020**, 20, 3641-3649.