Understanding the preparative green MOF-74 synthesis by time-resolved ATR-IR and XRD measurements

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Metal-organic frameworks (MOFs) show great promise among nano- and micro-porous materials due to their intrinsic tunability and structural versatility, leading to their use in numerous applications such as gas separation and storage as well as catalysis.[1] While the MOF field offers a great choice of materials, one of the remaining challenges for their practical implementation is the development of reliable synthetic procedures with speed, scale, and quality matching the industry requirements. Recently, promising aqueous-based room-temperature syntheses of MOF-74/CPO-27 analogs were developed, allowing outstanding space-time yields of up to 18 720 kg m^{-3} day^{-1}.[2] However, there is still a lack of knowledge of the underlying mechanisms, which is crucial for further extension and optimization to other MOF families and the fundamental understanding of MOF formation pathways.

In this work, we studied the mechanism of formation of the MOF-74 family in aqueous solution on a preparative scale (> 0.5 g) using time-resolved Attenuated Total Reflection IR spectroscopy (ATR-IR) in a custom-made stainless steel batch reactor cell equipped with a ZnSe crystal (30°, 50x44x2 mm). An external probe loop of this cell was used for the acquisition of time-resolved (50 ms) powder X-ray diffraction (XRD) data. Multivariate curve resolution-alternating non-negatively constrained least squares (MCR-AR-NNLS)[3] of the ATR-IR data was utilized to extract the kinetic profiles of the species in the reaction mixture, while time-resolved peak profile fitting of both datasets was used to gain information on the speciation as well as nucleation and growth processes.

The MOF synthesis was found to proceed via the formation of a molecular intermediate containing a twofold deprotonated ligand molecule. The width of the growing ν(C=C) mode of the MOF along synthesis time was mirrored by changes in specific XRD peaks indicating that growth of the MOF crystals occurred along the *c* axis. Fitting the XRD data using the Gualtieri model[4] allowed to determine the nucleation and growth constansts for MOF synthesis and establish their dependence on the reaction conditions. The ATR-IR experiments also revealed that zinc salts with non-coordinating anions enhance the reaction rate and completion time by a factor of 5. The products of the synthesis in the spectroscopy cell exhibited BET areas close to the theoretical limit of 1350 m^2 g^{-1}.

The information obtained in the spectroscopic study enables us to propose optimized synthetic protocols for MOF-74 materials.

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