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Use of Ultrasonic Monitoring for In situ Diagnostics of Zeolite and MOF Crystallization

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The investigation and understanding of the underlying mechanisms for the crystallization of molecular sieve materials such as metal-organic frameworks (MOFs) and zeolites have received increasing interest in recent years. This is mainly because improvements of the corresponding equipment were made that is essential for in situ diagnostics. In contrast to classical techniques, such as X-ray diffraction and neutron scattering, nuclear magnetic resonance or infrared and Raman spectroscopy, ultrasonic monitoring has not received proper attention [1]. Thereby, especially for zeolites, important insights have been gained with this technique already. In the present study, we report the successful use of ultrasonic device as a real-time, in-situ diagnostic tool for monitoring the crystallization progress of zeolite A from homogeneous, colloidal solutions with the composition 0.4 Na2O : 10 SiO2 : 1.4 Al2O3 : 16 (TMA)2O: X H2O (X: 650, 750, 850, 950, 1050). Kinetic information like reaction rate or reaction order of crystal growth can easily be calculated from the measured ultrasonic signal data. For the mathematical description of the crystallization curves, the experimental curves were fitted with different kinetic models. The crystallization proceeds in more than one step suggesting a change of the kinetics during the formation of the crystalline material. The evaluated reaction exponents for the different steps could only be described with Avrami-Erofeyev nucleation model. The results indicate that - depending on amount of water in synthesis mixture - first a three dimensional and then a one dimensional crystal growth takes place.

The understanding of metal organic framework syntheses is still a challenging task in the field of porous materials. Proposed models for the MOF formation mechanisms includes the formation of pre-nucleation building units (PNBU), which are "the minimum assembly of atoms, ions or molecules which, by condensation of the group with others (identical or different) give rise to the final solid"[2]. The nature of these PNBUs is widely discussed, but detailed insights are still rare. In this study, ZIF-8 with varying particle size and morphology is synthesized from zinc nitrate hexahydrate, 2-methylimidazole and CTAB in different solvents. In our study, we found that the ultrasonic attenuation already increases rapidly within the first minute of the ZIF-8 syntheses. Depending on the molar ratio of linker to metal, not only the final particle size, but also the course of the ultrasonic signal changes. After stopping the syntheses at different times of during the attenuation increase, it can be seen that in the synthesis with higher linker excess a second phase, namely ZIF-L is formed in the first three minutes, while in the synthesis with an antilogarithmic course of attenuation HMIM/Zn2+ = 60 only reflexes of ZIF-8 and the linker are visible.

References:

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