Detailed step-by-step reactions towards the synthesis of a MOF

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Based on density functional theory calculations and molecular simulation, a detailed mechanism on the formation of the secondary building unit of MIL-101 is presented. MIL-101, a chromium terephthalate metal-organic framework, is one of the most porous materials known, with high gas storage capacities. A thorough and precise knowledge of MOF synthesis is currently beyond our understanding due to the complexity of the electronic states of the metal centers, metal-anion-solvent interactions and the high number of competing simultaneous events that occur during MOF formation. The secondary building unit (SBU) in MIL-101 consists of three octahedrally coordinated chromium centers linked by a central oxygen, and the adjoining terephthalate linkers. Formed SBUs are key for nucleation, the rate-limiting step in the synthesis of most MOFs. We propose a series of reactions that lead to the formation of the MIL-101 SBU. Initial reactions that form the metal center have the highest energy barrier, and are followed by multiple competing linker addition reactions. Based on transition state theory for individual reactions and the Arrhenius equation, a simple kinetic model for overall SBU formation was built, showing SBU formation rates similar to known nucleation rates.