# Time-resolved Diffraction Crystallization Study of a porous Ti carboxylate MOF and its Water-Induced Formate structure

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Metal-organic frameworks (MOFs) are 2D or 3D porous solids combining metal cations (*M*n+) with coordinative organic linkers that have attracted tremendous attention over the last few decades due to their extraordinary chemical and structural diversity.[1] In particular, Ti-MOFs have aroused great interest for energy-related applications, such as photocatalytic water splitting,[2] formic acid dehydrogenation[3] and CO2 conversion.[4] Due to difficulty in controlling their polycondensation and crystallization processes, the latter remain relatively rare in the field.[5] In this regard, monitoring their crystallization processes and understanding the kinetics and the possible formation of intermediates (in a given set of conditions) are of great interest. To our knowledge there were no particular examples of *in-situ* diffraction studies for Ti-based MOFs reported to date. Recently, we focused our attention on crystallization kinetics and the potential intermediate(s) of MIP-177(Ti)-LT (MIP: Materials from Institute of Porous Materials of Paris; LT: low temperature) in the dried and water-containing solvent formic acid (FA).[6] The mentioned MOF comprises of a Ti12O15 oxo-cluster inorganic building unit (IBU) and a tetracarboxylate ligand (5,5’-methylenediisophtalate (mdip4-)) as organic spacer. Herein, we employed the time resolved *in-situ* synchrotron powder X-ray diffraction (SPXRD) via the monitoring of solvothermal reaction of Ti(iPrO)4 with H4mdip in FA performed in a SynRAC reactor.[7] The water-free MIP-177(Ti)-LT crystallization reaction was demonstrated to follow the Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetics with an energy barrier of 74 kJ·mol-1. In contrast, a small amount of water additive (≥2.5 vol %) results in the crystallization of other product(s), one of which contains formate anions coordinated with Ti3+ and forming Ti(HCOO)3·¾CO2·¼H2O (denoted TiF) clathrate with ReO3 net-like network in analogy to some known *M*3+-formates (*M* = Al, Mn, Fe, Ga, In).[8] The proposed crystal structure of this new phase is validated by the density-functional theory (DFT) calculations and experimental powder X-ray diffraction analysis. This makes TiF one of the first examples of pure carboxylate-based Ti-MOF, which does not contain Ti oxo-clusters in the structure. Such type of formate phases attracts great attention demonstrating remarkable selectivity for sorption-based CO2 capture owing to its hydrogen-confined pore cavity with an electropositive surface and appropriate dimensions.[9]

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