Supplementary Information for

Modeling and Simulation of Crystallization of Metal-Organic Frameworks

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S1 Supersaturation depletion

The supersaturation depletion as a function of time for the cases described in Figure 2 and Figure 3 of the main article is shown in Figure S1 and Figure S2, respectively.

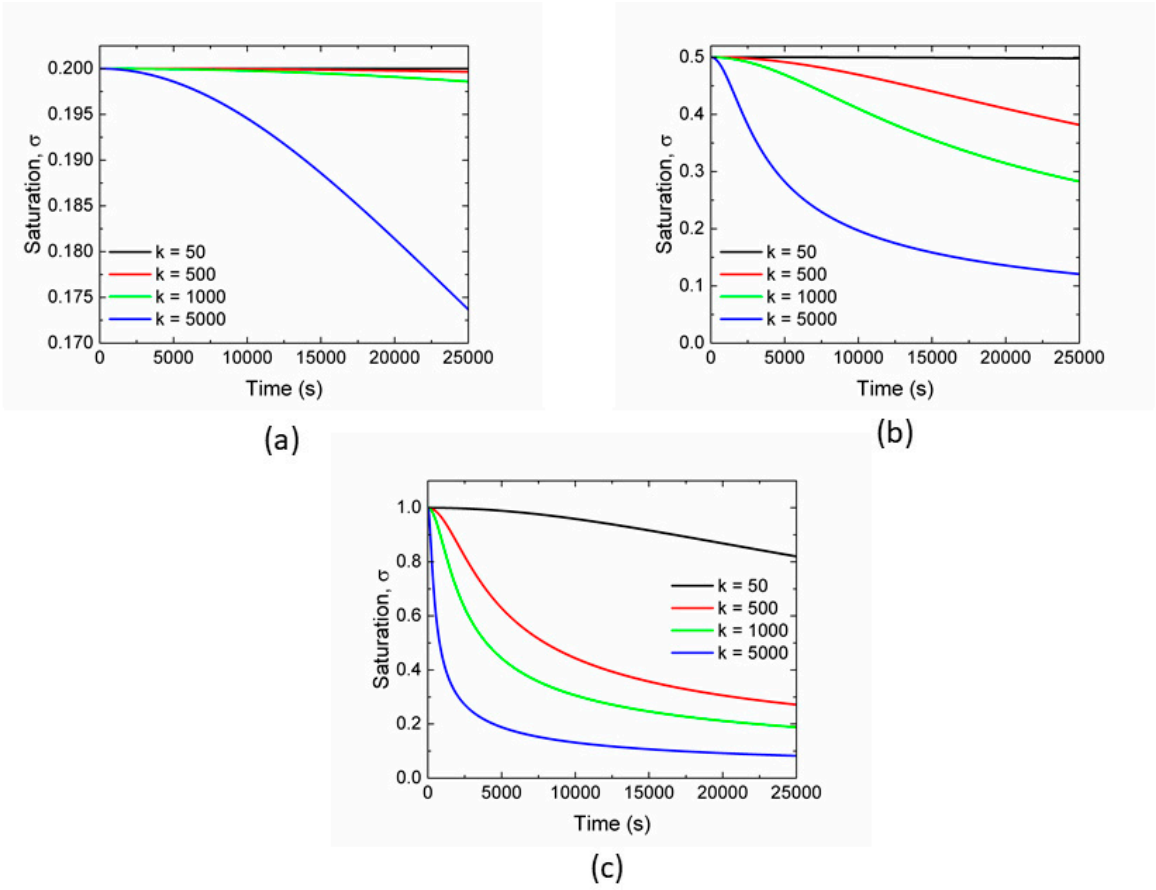

Figure S1. Supersaturation depletion as a function of time due to the growth of SBU oligomers in absence of BTC crystallization for different rate constants and initial saturation ratios (a) 0.2, (b) 0.5 and (c) 1. These results correspond to figure 2 of the main article.

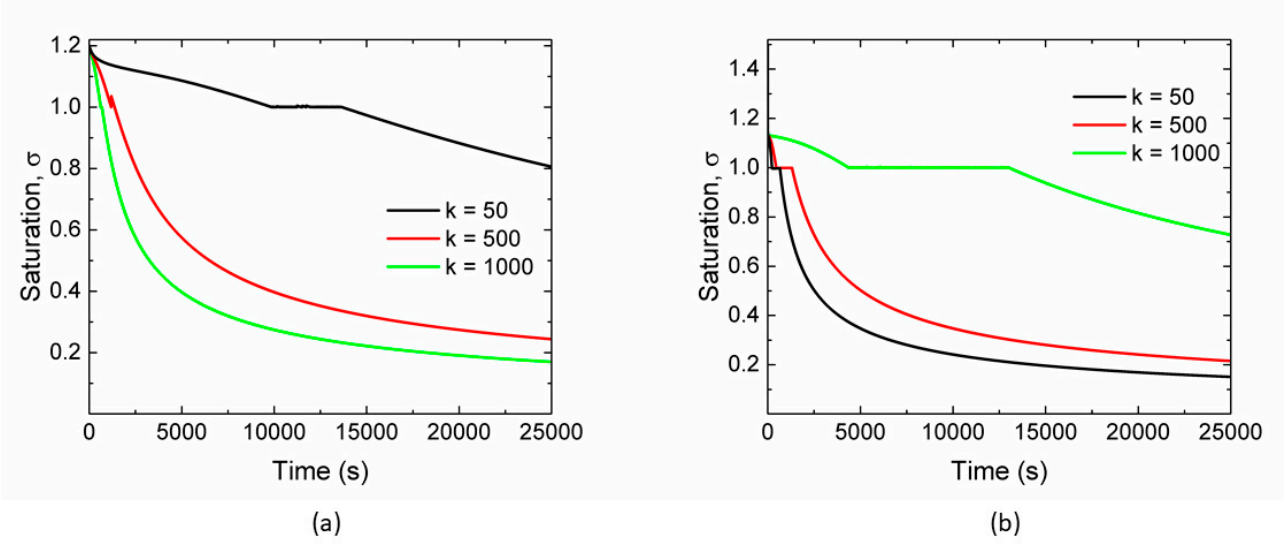

Figure S2. Supersaturation depletion as a function of time due to the growth of SBU oligomers in the presence of BTC crystallization for different rate constants and initial saturation ratios (a) 1.2 and (b) 1.5. These results correspond to figure 3 of the main article.

S2 Morphology of needle-like BTC crystals

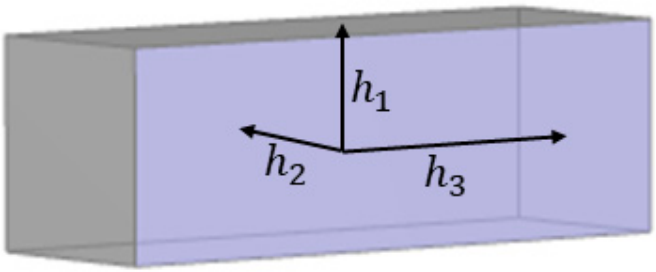

Figure S3. Needle-like (parallelopiped) morphology of BTC crystals showing h_1, h_2, and h_3 as the perpendicular distances of flat faces from the center.

S3 General Model Considering Simultaneous Oligomerization, Crystallization of linkers, and Aggregation of Oligomers

S3.1 Formation of SBU Oligomers

This section provides a framework to generalize the reaction-aggregation model for a constant-volume crystallizer described in the main article.

Let L be the organic linker, M be the metal-ligand and P_i denotes the SBU oligomer with i number of repeating units. The general reaction scheme is then,

$$L + mM + lL \xrightarrow{k_1} P_1$$

$$P_1 + mM + lL \xrightarrow{k_2} P_2 \qquad \text{(S1)}$$

$$P_{n-1} + mM + lL \xrightarrow{k_n} P_n$$

where m is the stoichiometric coefficient of metal-ligand M, l is the stoichiometric coefficient or organic linker L required for the formation of higher-order oligomers. k_i is the rate constant of the reaction for the formation of P_i.

The system of differential equations corresponding to the reaction system described in equation (S1) is then,

$$\frac{d}{dt}\begin{bmatrix}[P_1]\\ [P_2]\\ .\\ .\\ [P_n]\\ [M]\\ [L]\end{bmatrix} = -[M]^m[L]^l \begin{bmatrix} k_2 & 0 & 0 & . & . & 0 & -k_1 \\ -k_2 & k_3 & 0 & . & 0 & 0 & 0 \\ 0 & . & . & & & . & . \\ . & & . & k_n & & . & . \\ 0 & & & -k_n & 0 & . & . \\ k_1 & k_2 & . & . & k_n & 0 & 0 \\ k_1 & k_2 & . & . & k_n & 0 & 0 \end{bmatrix} \begin{bmatrix}[P_1]\\ [P_2]\\ .\\ .\\ [P_n]\\ [M]\\ [L]\end{bmatrix} \qquad \text{(S2)}$$

where square brackets denote the concentration [units: $mol\ L^{-1}$] of a component.

S3.2 Aggregation of SBU Oligomers

Aggregation can occur as soon as SBU oligomers are formed. Consider discretization of continuous variable x in population balance equation (Eq. 12 in the main article) into M bins containing $N_1, N_2, \ldots, N_M$ concentrations [units: mol L^{-1}] of MOFs, such that N_1 contains all the SBU oligomers $N_1 = \sum_{i=1}^{n} [P_i]$.

The evolution of N_1 and the higher-order clusters N_i [$i = 2,3,....$] can be written in terms of population balance equations, solved by fixed pivot method as in [1]. The discrete set of ordinary differential equations are as follows.

$$\begin{aligned} \frac{dN_1}{dt} &= k_1 [M]^m [L]^{l+1} - N_1 \sum_{j=1}^{M} N_j Q_{i,j} \\ \frac{dN_i}{dt} &= \frac{1}{2} \sum_{j=1}^{i-1} N_j N_{i-j} Q_{j,i-1} - N_i \sum_{j=1}^{M} N_j Q_{i,j}, \quad i = 2,3,...,M \end{aligned} \tag{S3}$$

where, $Q_{i,j-1}$ is the frequency of attachment of clusters of size i to form the clusters of size $j-1$.

For $i = 1$, the term denoting the formation of N_1 is obtained from equation S2.

S3.3 Crystallization of Metal Salt and Organic Linker

The crystallization of organic linker and metal-ligand can be written as 1-dimensional population balance equations,

$$\frac{\partial n_i}{\partial t} + \frac{\partial (G_i n_i)}{\partial h_i} = 0$$

$$n_i(h_i, 0) = 0 \tag{1)(S4}$$

$$n_i(0,t) = \frac{\dot{N}_i(0,t)}{G_i(t)}$$

where, $i = L, M$ and $i = L$ refers to the organic linker and $i = M$ refers to metal-ligand. All the other definitions of variables are given in the main article. The solution is given by method of characteristics as,

$$n_i(G_i t, t) = \frac{\dot{N}_i(t)}{G_i(t)} \tag{2) (3)(S5}$$

S3.4 Differential equation for the mass balance of organic linker and metal-ligand

The rate of change of depletion of concentration of metal-ligand and organic linker in a complete sense is then given as,

$$\frac{d[L]}{dt} = -[L]^l [M]^m \sum_{i=1}^{n} k_i P_i + \frac{\rho_L}{m_{w,L}} \int_0^{h_L} \frac{\partial \left(n_L(h_L', t) V_L(h_L, t) \right)}{\partial t} \partial h_L' \tag{S6}$$

$$\frac{d[M]}{dt} = -[L]^l [M]^m \sum_{i=1}^{n} k_i P_i + \frac{\rho_M}{m_{w,\mathrm{M}}} \int_0^{h_M} \frac{\partial \left(n_M(h_M', t) V_M(h_M, t) \right)}{\partial t} \partial h_M' \tag{S7}$$

ρ is the density, m_w is the molecular weight. Subscript L refers to the organic linker and M refers to metal-ligand.

References:

1. Kumar, S.; Ramkrishna, D. On the solution of population balance equations by discretization—I. A fixed pivot technique. *Chem. Eng. Sci.* **1996**, *51*, 1311–1332.