Supporting information for:

Coupling External and Internal Pressure for the Structural Transition of MIL-53(Cr)

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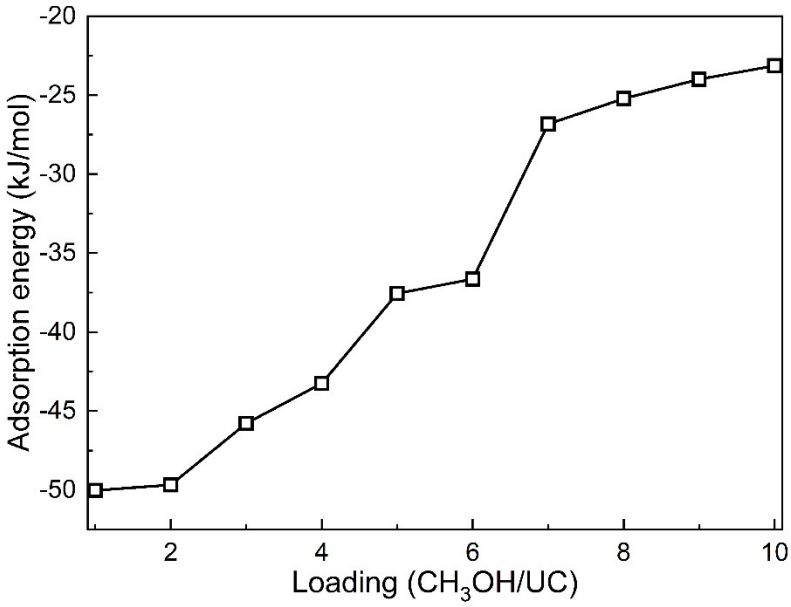


Figure S1. The computed adsorption energies as a function of the number of methanol molecules within MIL-53.

The computed virial pressures for MIL-53(Cr) with different loading of methanol shows the same variation trend as the actual pressure (Figure S2). In order to clarify the contribution of the configuration, the virial pressures (no thermal contribution), instead of actual pressure, were employed to analyze the host-guest interactions later. The virial pressures for MIL-53(Cr)-guest system is consisting of three parts: $P_{\text{MIL-53}}$, P_{methanol} and $P_{\text{interface}}$ in equation S1.

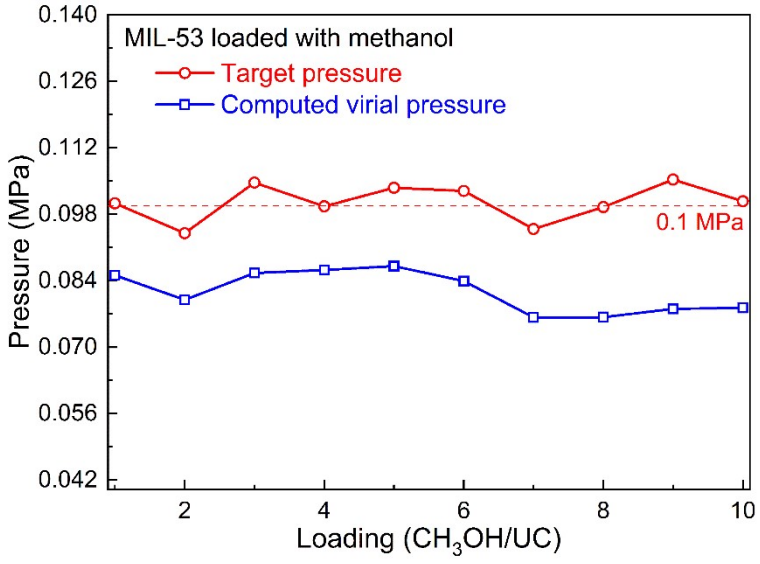


Fig. S2 The target pressure and the computed virial pressures for MIL-53(Cr) with different loading of methanol. The external pressure was fixed at 1 bar.

$$P_{\text{interface}} = P_{\text{total}} - P_{\text{MIL-53}} - P_{\text{methanol}} \quad \text{(S1)}$$

Where $P_{\text{interface}}$ denotes the virial pressure of the interface between MIL-53 and methanol phase;

P_{total} is the total virial pressure of the host-guest system; $P_{MIL\text{-}53}$ and $P_{methanol}$ are the contributions to the virial pressure from pure MIL-53 and methanol phase respectively. It should be noted that

For every frame of the equilibrium MIL-53-methanol structures, the virial pressure of the pure host, guest and the host-guest phases were computed and the equation S1 was employed to obtain the virial pressure of the interface between MIL-53 and methanol phase. The average of the computed virial pressures across all frames for different concentration of methanol guests were plotted in Figure S3. It can be seen that the virial pressure of methanol phase in the low loading range (1-2 CH_3OH/UC) is zero. The MIL-53 NP structure under the loading of 2 CH_3OH/UC can be attributed to the methanol adsorption, instead of the methanol-methanol interaction. The severe crowding (the most negative virial pressure) of methanol molecules was achieved at the loading of 4 CH_3OH/UC, where more guest molecules located inside narrow porous (MIL-53 NP structure). With the increasing of the methanol loading, the LP structure was gradually recovered to accommodate more guest molecules. Still, the guest molecule crowding (negative virial pressure of methanol phase) existed in the high loading range. The expansion trend of the methanol phase can be balanced by both of the external pressure (1 bar in Figure S3) and the MIL-53 framework structure (the positive pressure in Figure S3).

The virial pressure of the interface between MIL-53 and methanol phase is positive and shows the variation trend as the indicators of MIL-53 LP-to-NP transition (Figure S3). Large positive virial pressure indicates the tendency for the structure contraction to form MIL-53 NP phase. Thus, we employed the variation of the positive virial pressure of the host-guest interface to analyze the structure contraction (LP-to-NP transition of MIL-53).

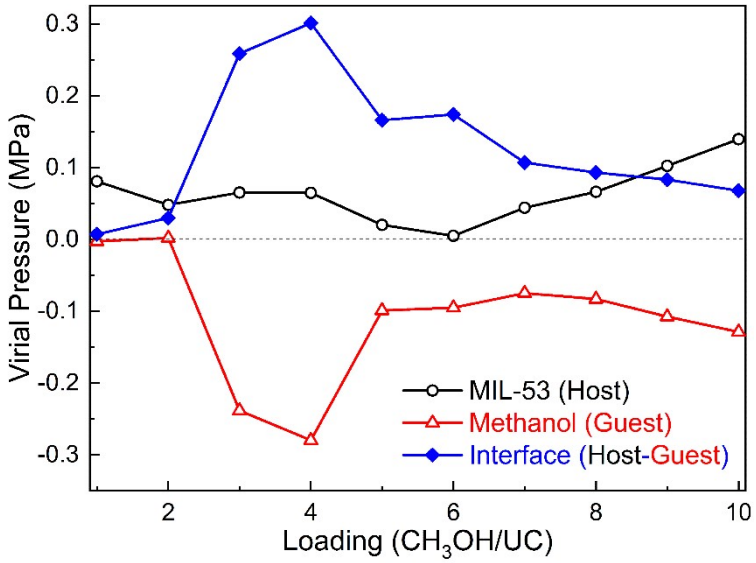
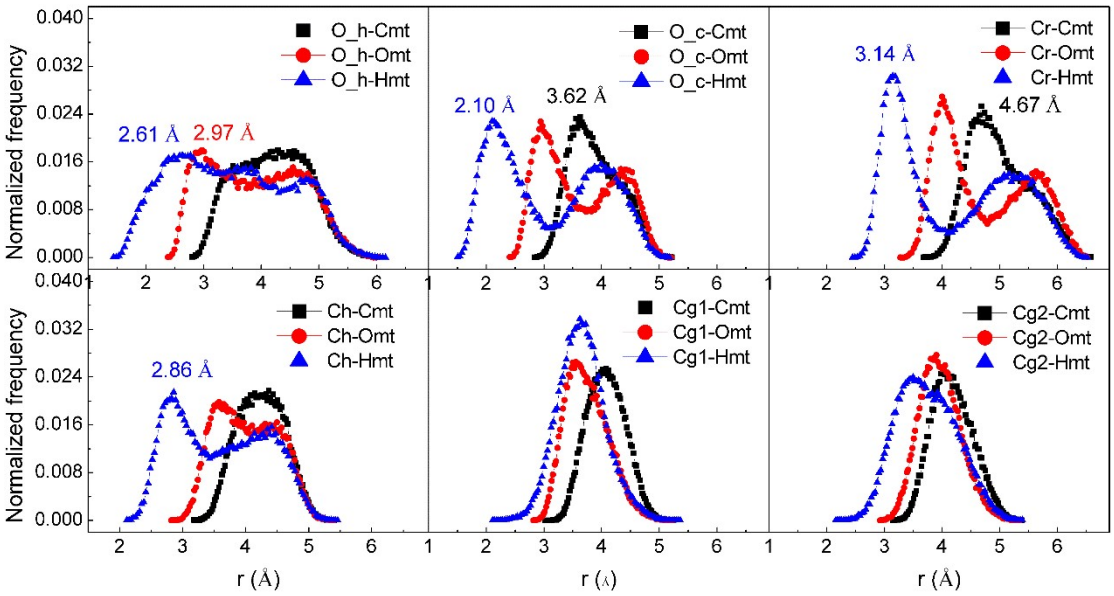


Fig. S3 The computed virial pressures for methanol (guest), MIL-53(Cr) (host) and the host-guest interface, as a function of the methanol loading. The external pressure was fixed at 1 bar.

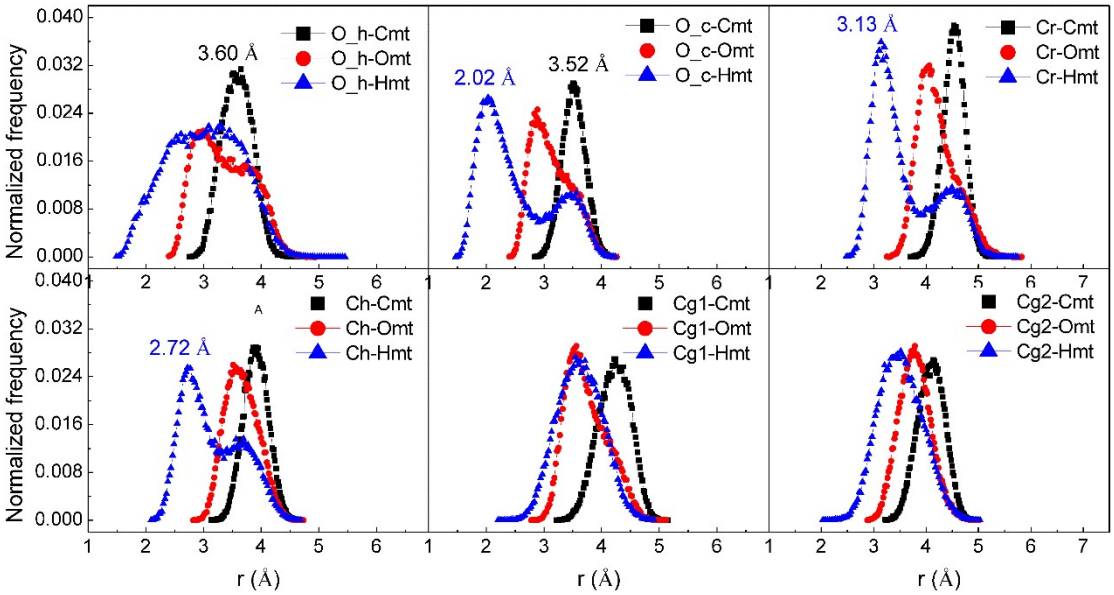
$$Distribution = P\{g_i[min(g_i \cdots h_j), j = 1,n], i = 1,m\} \quad \text{(S2)}$$

Where g_i denotes the atoms of all guest molecules, h_j denotes atoms of the host framework (MIL-53 here), m and n is the number of atoms constituting guests and host respectively, $g_i \cdots h_j$ denotes the distance between atom g_i and h_j, P and min denote the probability and the minimize function

respectively.

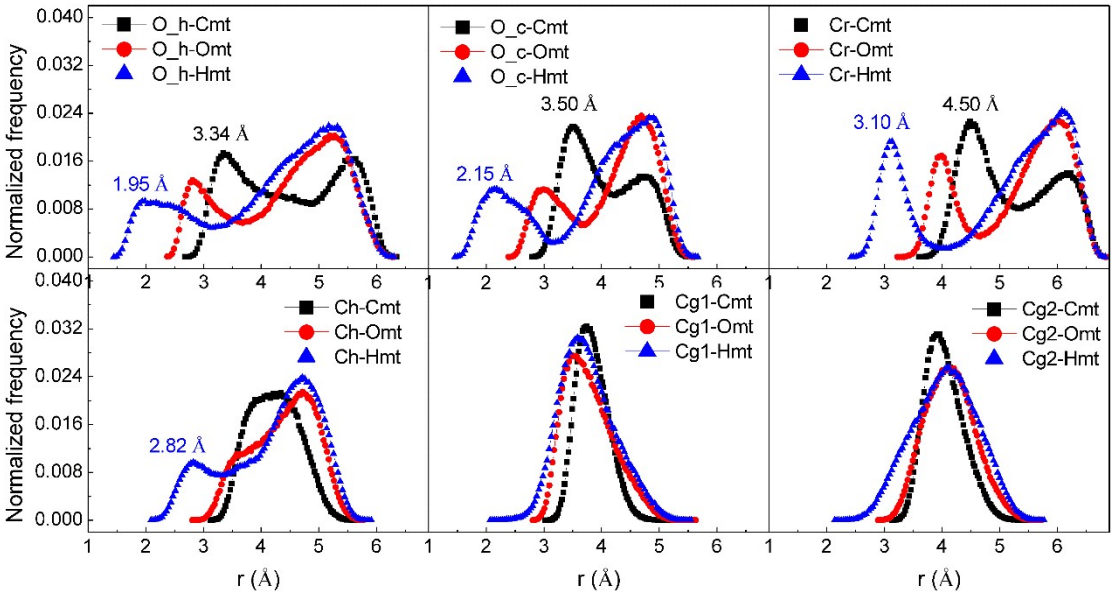


(a) 5 MPa

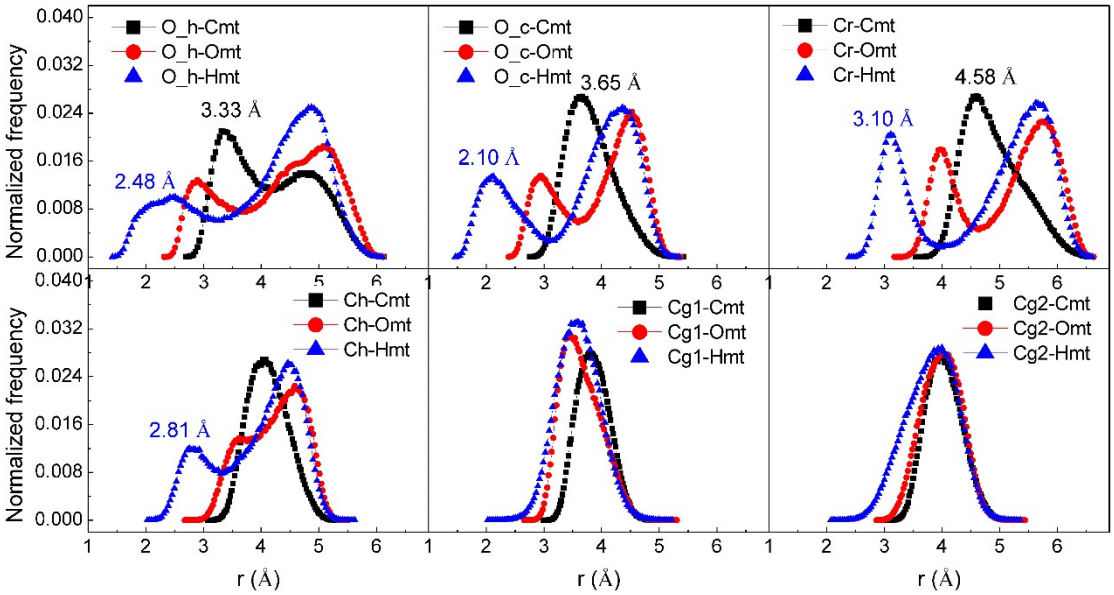


(b) 9 MPa

Figure S4. Distribution of the nearest distance between guest and host atoms. MIL-53(Cr) with a loading of 1 CH_3OH/UC under external pressure of (a) 5 MPa and (b) 9 MPa.



(a) 90 MPa



(b) 110 MPa

Figure S5. Distribution of the nearest distance between guest and host atoms. MIL-53(Cr) with a loading of 7 CH_3OH/UC under external pressure of (a) 90 MPa and (b) 110 MPa.