

Supporting Information

Dynamics of Isobutane is a Sensitive Probe for Framework Breathing in MIL-53 (Al) MOF

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1. MIL-53 (Al) material characterization

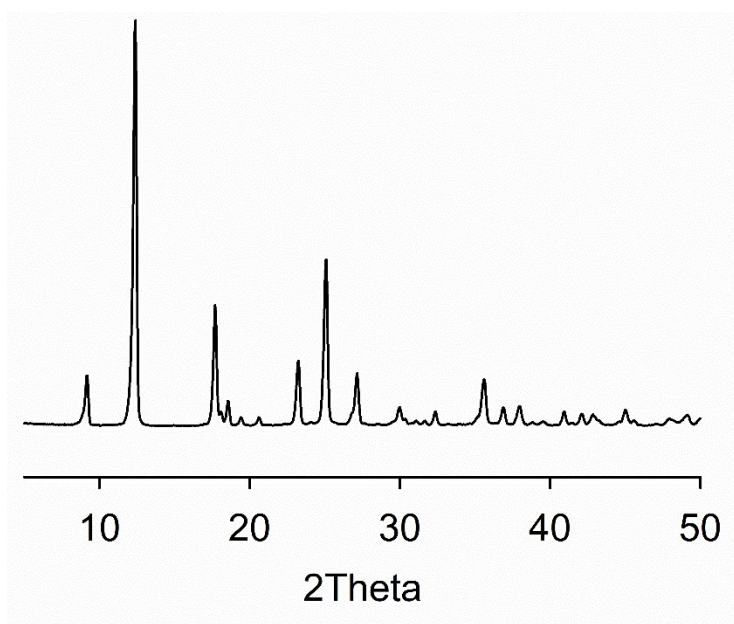


Figure S1. The structure of the as synthesized MIL-53 (Al) material was characterized by X-ray diffraction using Bruker D8 diffractometer with Cu K α radiation. The resulting XRD pattern shows a typical MIL-53 narrow pore phase due to the adsorption of atmospheric water.

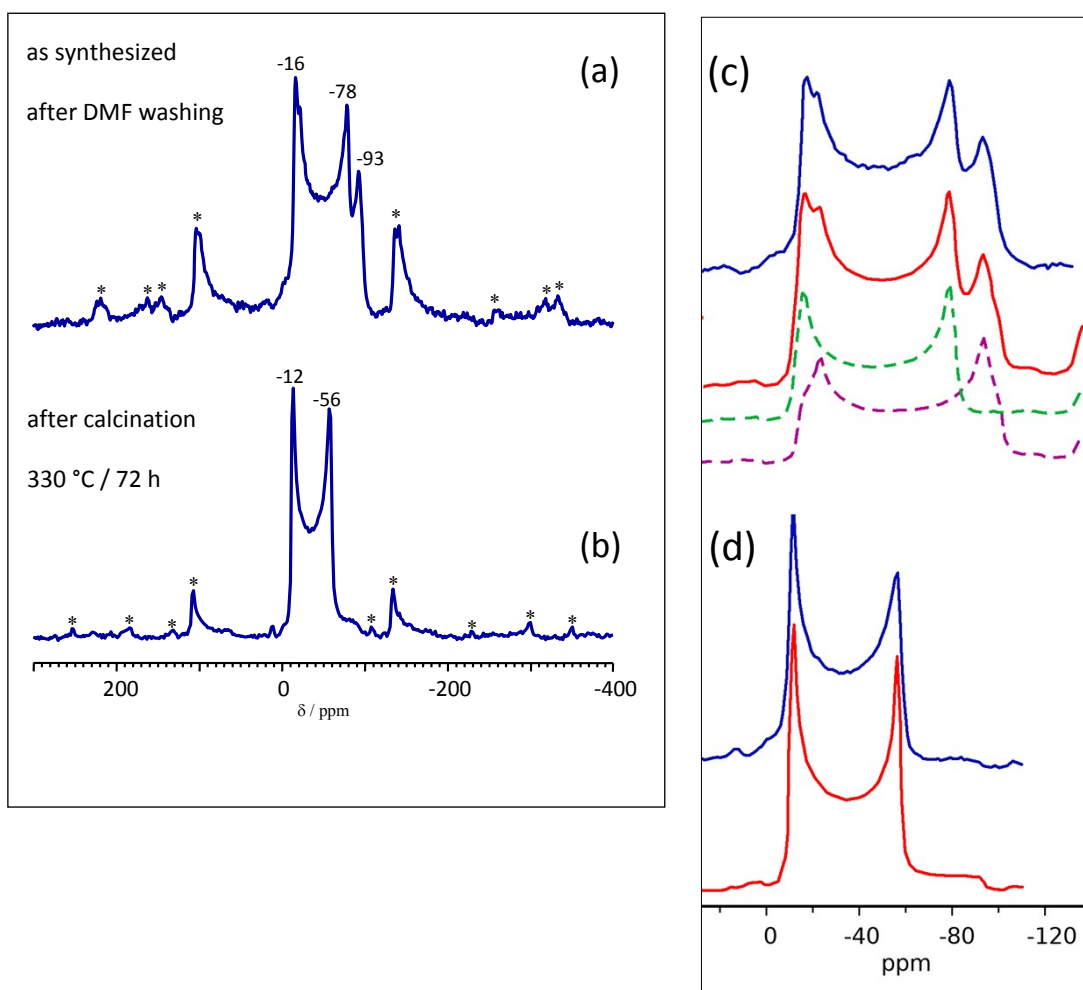


Figure S2. ^{27}Al MAS NMR characterization of the as-synthesised MIL-53 (Al). (a,c) As synthesized after DMF washing. The spectrum represent a superposition of two signals (c) with parameters: (1) $Q_0^{\text{Al}} = 10.9$ MHz, $\eta = 0.1$, $\delta = +6$ ppm; (2) $Q_0^{\text{Al}} = 10.0$ MHz, $\eta = 0.05$, $\delta = +6.3$ ppm. Experimental spectrum (a,c) is shown in blue. Simulation of experimental spectrum (c) is shown in red. The signals 1 and 2 in (c) are shown in purple and green. (b) After calcination at 330 °C for 72 h. $Q_0^{\text{Al}} = 8.4$ MHz, $\eta = 0.03$, $\delta = +3.5$ ppm. Experimental spectrum (b) is shown in blue and simulation is in red (d). The resulting pattern (b) correlates well with previously reported results^{1, 2} and shows that a pure MIL-53 phase is obtained. The ^{27}Al MAS NMR spectra were acquired using $(\pi/12)$ excitation pulse of 0.6 μs , 1000 scans, 0.5 s delay, and 12.5 kHz spinning rate on a Bruker Avance 400 spectrometer using 4mm rotor.

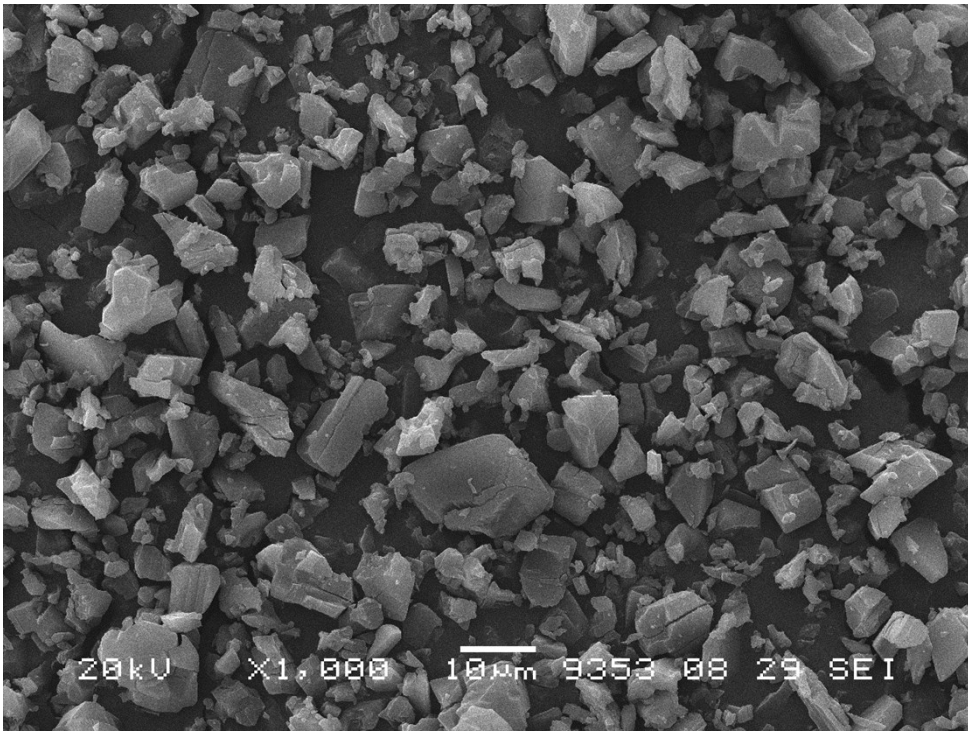


Figure S3. SEM image of the calcined MIL-53(Al) particles. The images were taken on a JEOL JSM-6700F instrument (acceleration voltage = 20 kV, current = 10 μ A).

2. The effect of temperature on isobutane librational angles in MIL-53 (Al)

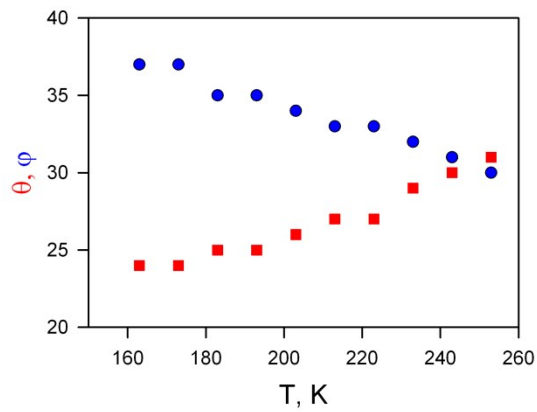


Figure S4. Temperature dependence of jump angle θ (●) and cone angle φ (■).

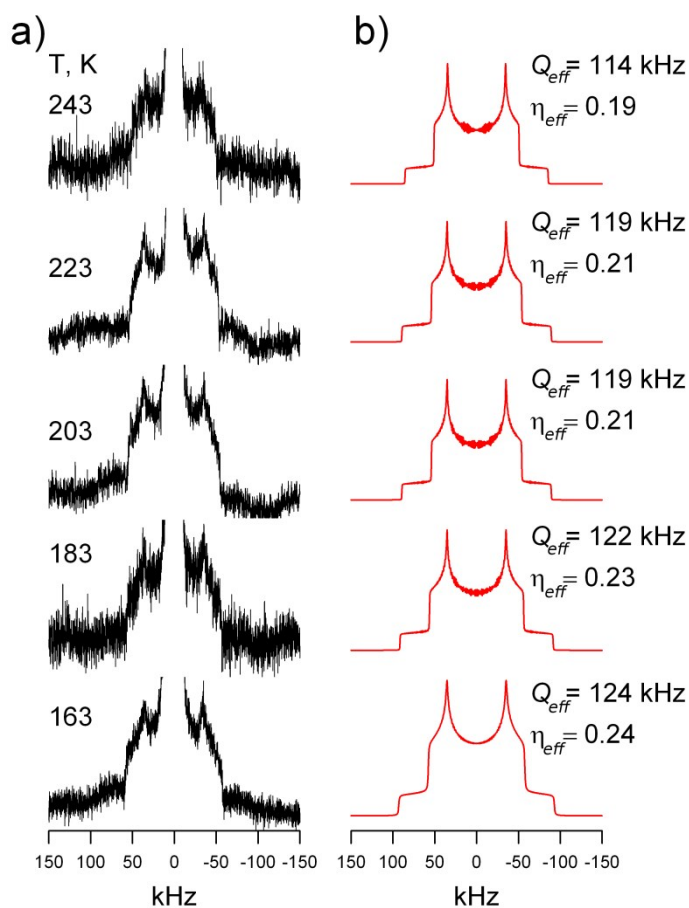


Figure S5. Evolution with temperature of ^2H NMR spectral parameters for isobutane- d_{10} C-D group: (a) experimental line shape; b) simulated line shape with effective values of Q_0 , Q_{eff} , and η_{eff} , shown near each spectrum.

3. DFT Calculations

After the relaxation of the cluster structure a molecule of isobutane was introduced in 3 possible initial positions: in the center of the channel, in the vicinity of channel corners. After the geometry optimization the configuration of isobutane in the vicinity of OH-group shown in Figure S6 had the lowest energy value. The closest distances between the guest molecule and the framework are the distances between OH-group of the framework and CH- and methyl group of isobutane ($r_{\text{CH}_3 - \text{OH}} = 2.04 \text{ \AA}$, $r_{\text{CH} - \text{OH}} = 2.318 \text{ \AA}$) and the distance between phenyl ring of the framework and methyl group of isobutane ($r_{\text{CH}_3 - \text{phenyl}} = 2.503 \text{ \AA}$). Such configuration implies that indeed at 0 K the preferred position of isobutane is in vicinity of the channel walls.

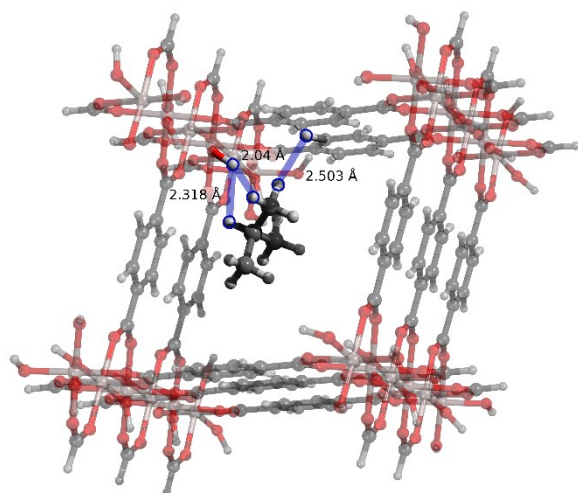


Figure S6. The configuration of isobutane in MIL-53 (Al) channel with the lowest energy value. The closest distances between the guest molecule and the framework are shown with blue lines.

4. Evolution of ^{27}Al MAS NMR pattern of MIL-53 (Al) with temperature

Table S1. Parameters of ^{27}Al quadrupole coupling derived from fitting ^{27}Al MAS NMR spectra of MIL-53 (Al) with adsorbed isobutane- d_{10} by Bruker TopSpin software.

T, K	Q_0^{Al} , kHz	η	δ , ppm
203	8060	0.09	2.5
243	8145	0.095	2.5
253	8214	0.5	2.8
263	8211	0.03	3.3
293	8200	0.05	3.1

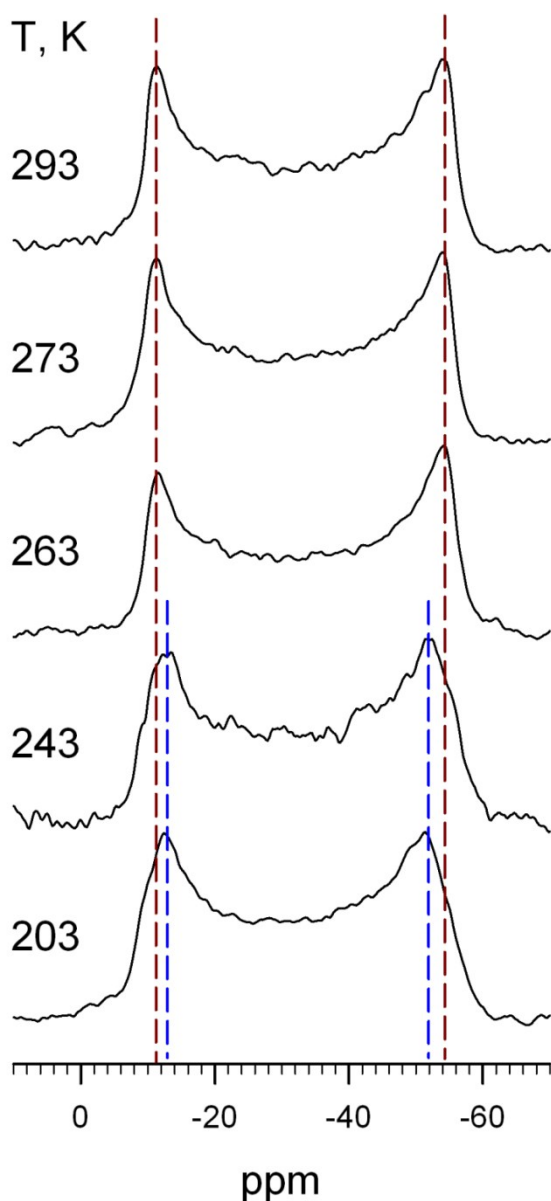


Figure S7. ^{27}Al MAS NMR spectra of MIL-53 (Al) with adsorbed isobutane- d_{10} at 203-293 K.

5. Modeling of isobutane spin relaxation

First, the relaxation of each population has been performed according to the standard approach proposed by Abragam³ and developed in details by Spiess⁴ and others.⁵⁻⁸

Spin relaxation time T_1 is generally anisotropic and depends on the observation angles θ and φ in the powder pattern. It is given by the formula:⁴

$$\frac{1}{T_1} = \frac{3}{4} \pi^2 Q_0^2 (J_1(\omega_0) + 4J_2(2\omega_0)) \quad (1)$$

where the spectral density function $J_m(\omega)$ for the chosen model of the molecule motion is defined by the expression:

$$J_m(\omega) = 2 \sum_{a,b=-2}^2 D_{a,q}(\Omega_L)^* D_{b,q}(\Omega_L) \otimes G_{0,a|0,b}(\omega), \quad (3)$$

where

$$G_{c,a|d,b}(\omega) = \sum_{l,k,n=1}^N D_{c,a}^l(\Omega_l)^* D_{d,b}^k(\Omega_k) p_{eq}(l) V_{l,n} \left(\frac{-\lambda_n}{\lambda_n^2 + \omega^2} \right) V_{n,k}^{-1} \quad (4)$$

Here Ω_L are the observation angles θ and φ , which connect the molecular frame with the laboratory frame; Ω_k are the Euler angles which connect the molecular frame with the k -th distinct position of the $C-D$ bond within the assumed geometry of the jump model; $V_{l,n}$ is a matrix composed by Eigen vectors of kinetic matrix K and λ_n are its Eigen values; N is the number of distinct jump-sites.

If one or multiple isotropic motions are present the corresponding correlation function is no longer dependent from the polar angles and the resulting function is simply a tensor multiplication of correlation functions for distinct motional modes.

Once the individual motional models have been defined, the exchange between two states has been regarded as a standard chemical exchange. The resulted relaxation rate has been derived from the Bloch's equation:

$$\frac{d}{dt} \begin{pmatrix} M_Z^I \\ M_Z^{II} \end{pmatrix} = \begin{pmatrix} -\frac{1}{T_1^I} - K_{eq}k_{ex} & K_{eq}k_{ex} \\ k_{ex} & -\frac{1}{T_1^{II}} - k_{ex} \end{pmatrix} \begin{pmatrix} M_Z^I \\ M_Z^{II} \end{pmatrix}$$

where M_Z^I and M_Z^{II} are longitudinal magnetizations of state I and II correspondingly, $K_{eq} = p_{II}/p_I$ is the equilibrium constant between these two states and k_{ex} is the exchange rate. The net longitudinal magnetization decays in biexponential manner with rates equal to eigenvalues of the matrix. Both eigenvalues are negative. One eigenvalue has large magnitude and equal to the $\lambda_{max} = -k_{ex}(K_{eq} + 1)$ in the fast exchange limit. The other eigenvalue λ_{min} has low magnitude and contains information about the molecular mobility even in the fast limit. Since $e^{-\lambda_{max}t}$ decays too fast to be observed in the experiment, the final relaxation rate is chosen as the λ_{min} .

References

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