Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Dissecting the Effects of Water Guest Adsorption and Framework Breathing on the $AlO_4(OH)_2$ Centers of Metal-Organic Framework MIL-53 (Al) by Solid State NMR and Structural Analysis

Alexander E. Khudozhitkov,[a] Sergei S. Arzumanov,[a] Alexander V. Toktarev,[a] Svetlana V. Cherepanova,[a] Anton A. Gabrienko,[a] Daniil I. Kolokolov,*[a] and Alexander G. Stepanov*[a]

[a] *Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences*
Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia
E-mail: kdi@catalysis.ru (D.I.K.), stepanov@catalysis.ru (A.G.S.)

1. Structural Analysis

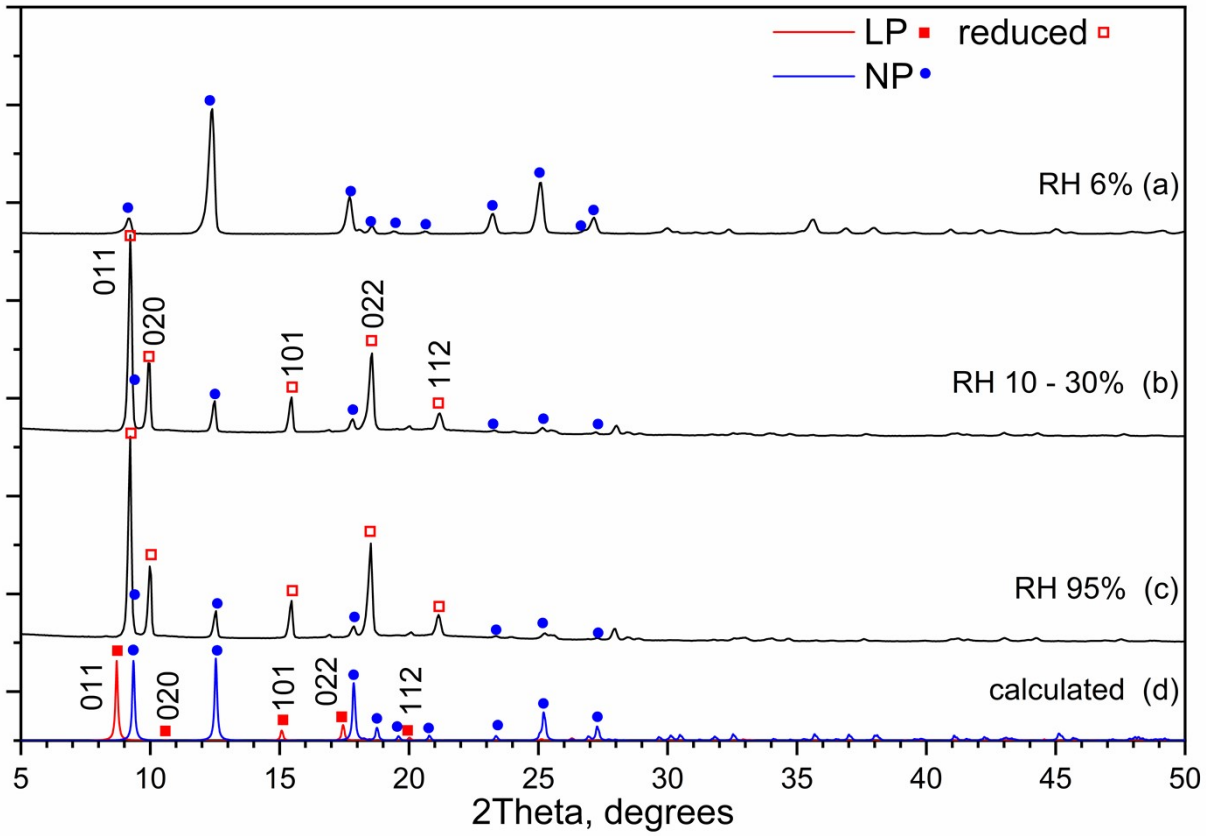

Figure S1. XRD patterns of the MIL-53 (Al) loaded with water at different relative humidity conditions: (a) 6% RH, (b) 10-30% RH, (c) 95%. The calculated patterns for pure NP and LP MIL-53 phases are given by solid lines. The empty symbols attribute peaks for the partially reduced LP phase, also denoted as the *iX* phase.

For the 5% RH sample on the NP phase peaks are observed. For samples with 10%, 30% and 95% RH there peaks characteristic for the reduced LP (*iX*) and the NP phases. The reduced phase LP (*iX*) differs from the ideal LP phase by a shift of the 011 and 101 peaks toward large angles, hence reflecting the decrease of the interplanar distances d_{011} and d_{101}. In contrast, the peak 020 is shifting towards small angles, reflecting the increase of the interplanar distance d_{020}=**b**/2. The decrease of the d_{011} with simultaneous increase of the lattice parameter **b** indicates the decrease of the lattice parameter **c**. The parameter **a** remains

constant, thus the decrease of the d_{101} also indicates the decrease of the parameter **c**. If **b** is increasing and c is decreasing, while **a** is constant, then the total unit cell volume is decreasing, i.e. the channel is contracting.

Table 1. Lattice constants and volumes of orthorhombic unit cell, weight ratio and average crystallite sizes.

Sample	LP and reduced phase				LP:NP	LP phase	NP phase
	a, Å	b, Å	c, Å	V, Å^3	Weight %	<D>, nm	<D>, nm
Guest-free phase	6.6085	16.675	12.813	1411.9			
10 or 30% RH	6.609	17.66(2)	11.32(1)	1321(1)	72:28	55	60
95% RH	6.609	17.64(2)	11.36(1)	1324(1)	77:23	60	50

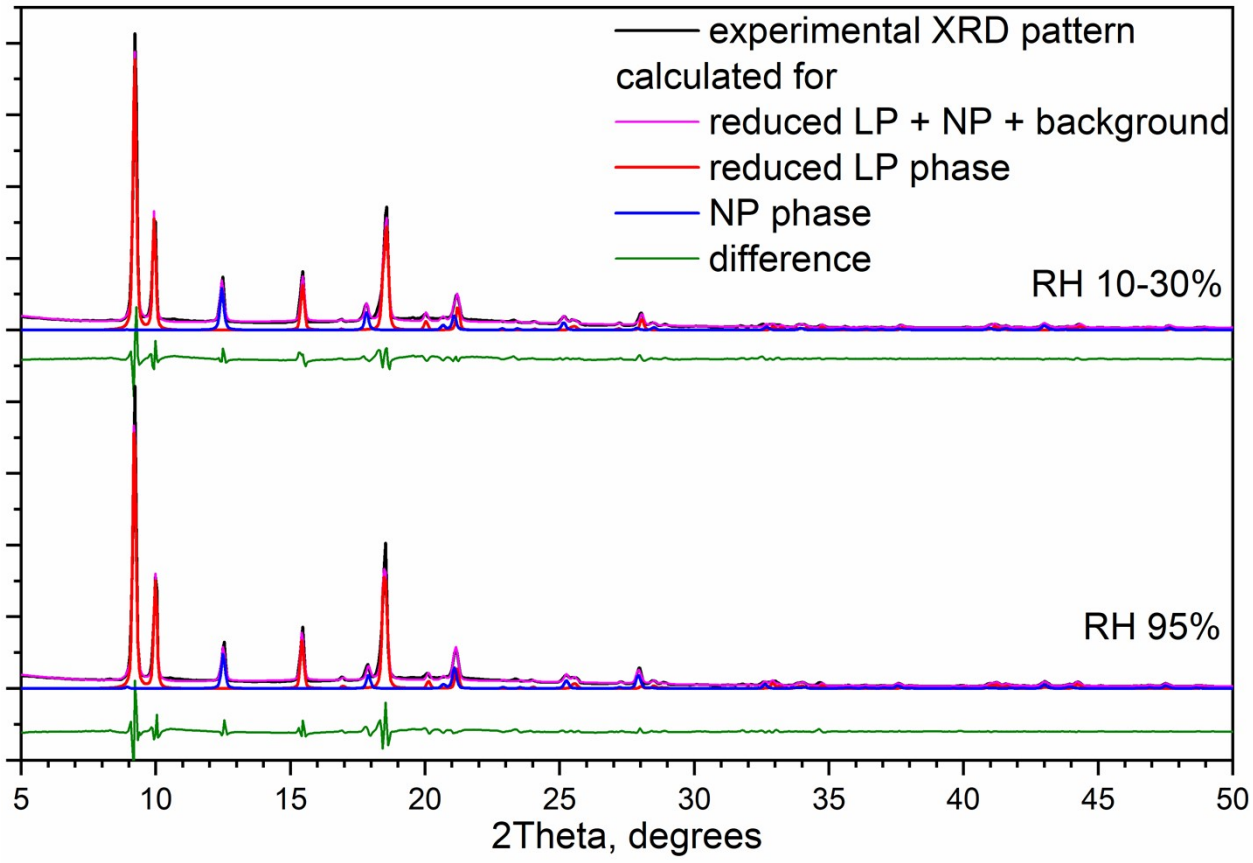

Figure S2. Rietveld analysis of the water-filled MIL-53 structures at different RH levels.

2. Experimental section

2.1 Materials

MIL-53 (Al) was synthesized via hydrothermal synthesis as reported previously.[2] The synthesized material showed BET surface area (S_{BET}) = 1250 m^2 g^{-1}. XRD pattern, ^{27}Al MAS NMR spectra and SEM image of the material used in this work are shown, Figures S3-S5.

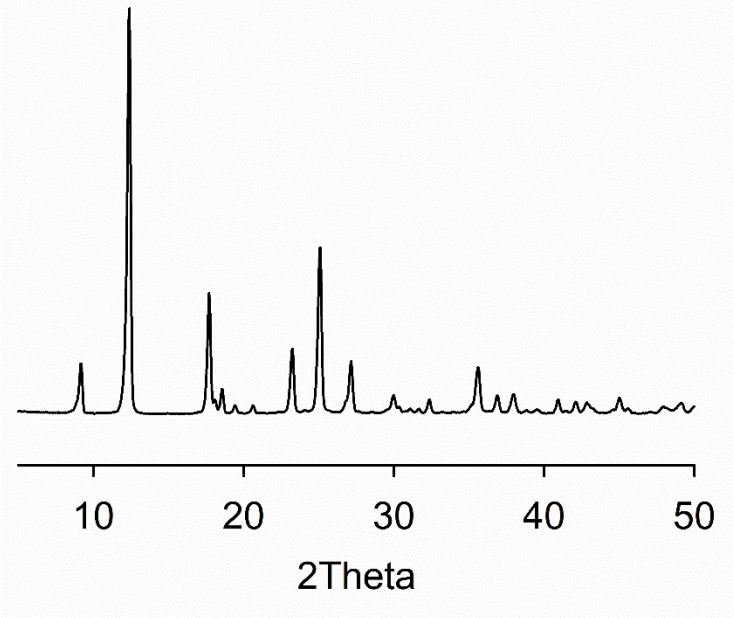

Figure S3. The structure of the as synthesized MIL-53 (Al) material was characterized by X-ray diffraction using Bruker D8 diffractometer with Cu Kα radiation. The resulting XRD pattern shows a typical MIL-53 narrow pore phase due to the adsorption of atmospheric water.

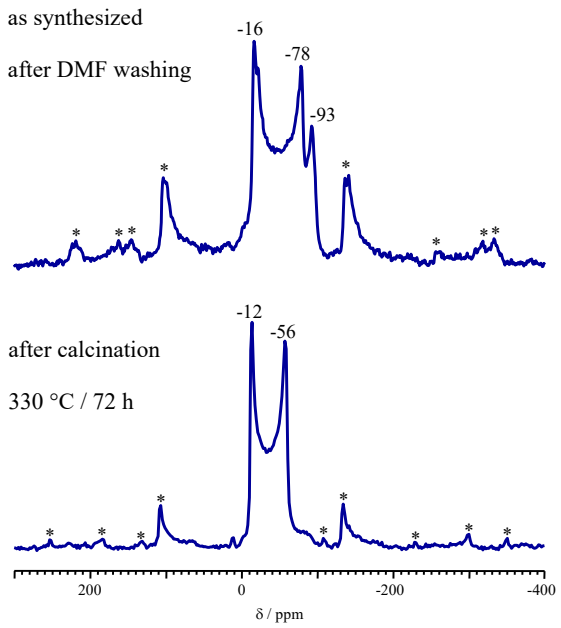

Figure S4. ^{27}Al MAS NMR characterization of as-synthesized MIL-53 (Al). The resulting pattern correlates well with previously reported results[2-3] and shows that a pure MIL-53 phase was obtained. The ^{27}Al spectra were acquired using (π/12) excitation pulse, 1000 scans, 0.5 s delay, and 15 kHz spinning rate on a Bruker Avance 400 spectrometer using 4 mm rotor.

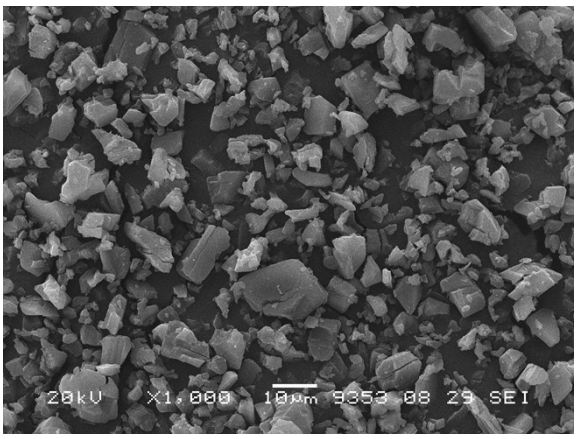

Figure S5. SEM image of the calcined MIL-53(Al) particles. The images were taken on a JEOL JSM-6700F instrument (acceleration voltage = 20 kV, current = 10 μA).