Supporting information available for

Activation of the Metal-Organic Framework MIL-47 for Selective Adsorption of Xylenes and other Difunctionalized Aromatics

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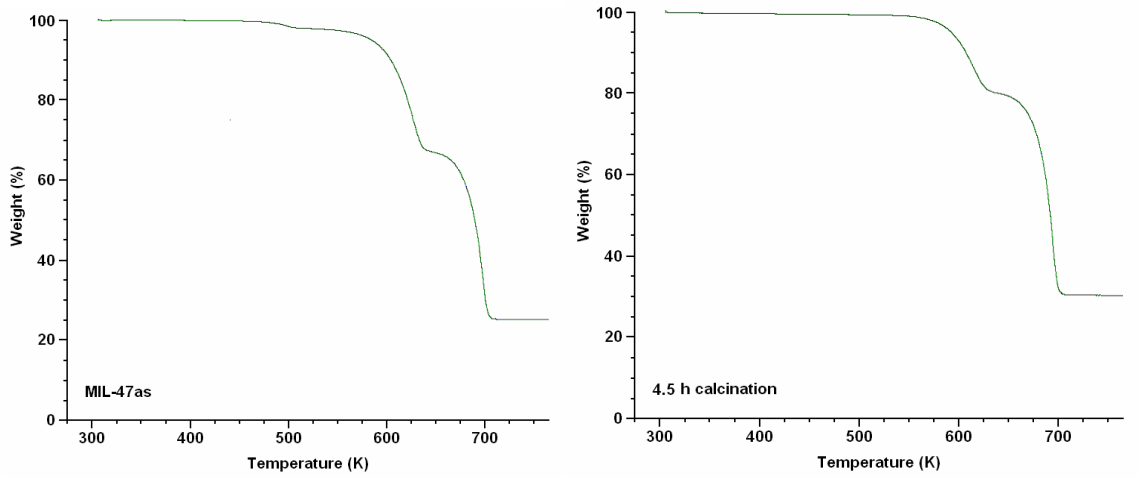
Thermogravimetric analyses on MIL-47.

TGA curves have been recorded for MIL-47 samples calcined during different time intervals and are shown in Figure S1.



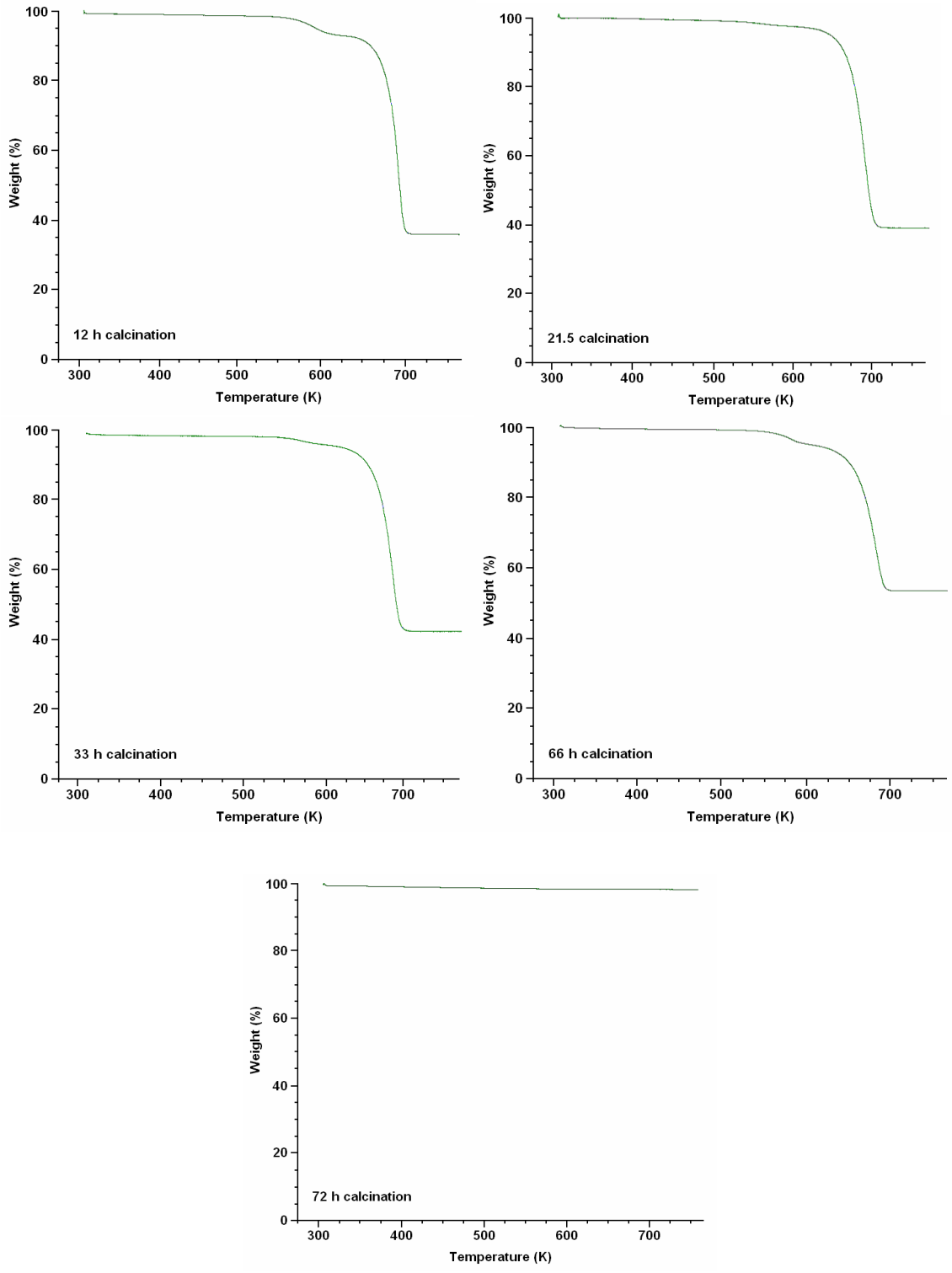


Figure S1: Weight loss as a function of temperature for MIL-47 samples calcined during different time intervals at 573 K with calcination bed thickness of 0.016 g cm^{-2} (heating rate of 5 K min^{-1} under O_2).

All curves in Figure S1 except for the curve of MIL-47 calcined for 72 h show the typical weight losses of MIL-47as or MIL-47. Even for ambient-exposed samples, no significant weight loss is observed below 473 K, pointing to the hydrophobic nature of the MIL-47 channels. In the TGA curve of MIL-47as a small weight loss is observed at ca. 500 K, which can be attributed to the presence of a small amount of extraporous terephthalic acid recrystallized from the synthesis mixture. This small step is not observed in the calcined samples, as the non-occluded terephthalic acid is evaporated more easily than the uncoordinated terephthalic acid occluded in the MIL-47 pores. The departure of the latter can be observed between 550 K and 640 K. The step between 640 K and 700 K corresponds to the destruction of the metal-organic structure of MIL-47. The weight loss in this second step can serve as a measure for the true amount of MIL-47 present in a sample. The curve of MIL-47 calcined for 72 h does not show any significant weight loss as the sample contains almost only V_2O_5 (see main text).

Figure S2 schematically shows the gradual changes in the height of the characteristic weight losses during calcination of a MIL-47as sample.

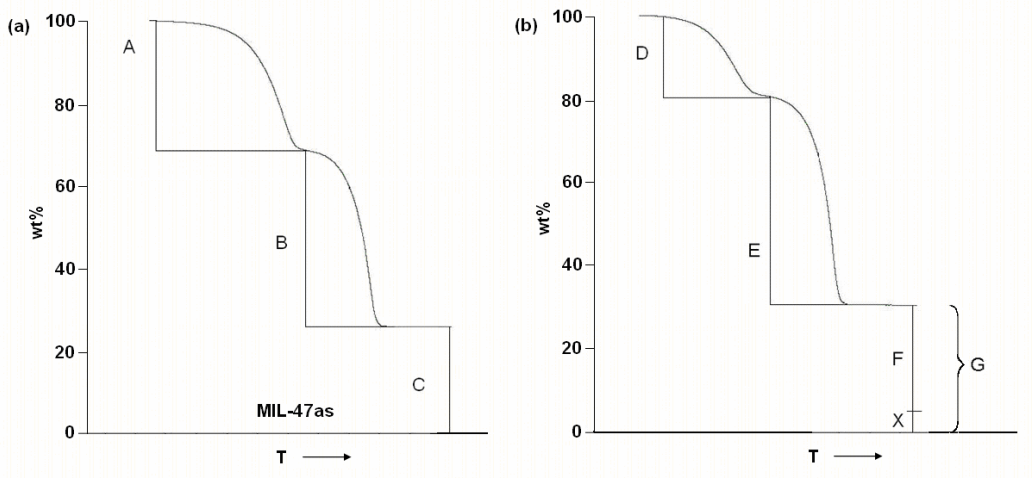


Figure S2: Schematic representation of the evolution of a TGA curve of MIL-47 in function of calcination time: (a) typical TGA curve of MIL-47as; (b) TGA curve after calcination. Capitals refer to specific weight losses that will be used in the calculations below.

Scrolling through Figure S1, the first typical weight loss between 550 K and 640 K gradually decreases and eventually disappears as a function of calcination time. Considering this particular weight loss in the curve of MIL-47as as the maximal possible amount of terephthalic acid that can be present in the MIL-47 pores, the amount of residual uncoordinated terephthalic acid can be calculated as in Equation 1:

$$\text{residual terephthalic acid} = \frac{D}{E} \times \frac{B}{A} \times 100\% \quad (1)$$

with *A*, *B*, *C* and *D* corresponding to the weight loss steps indicated in Figure S2. The relative amount of residual terephthalic acid in function of calcination time is shown in Figure 6a in the main text.

The succession of TGA curves displayed in Figure S1 also shows that from a calcination time of 21.5 h on, the residue *G* relatively increases due to the increasing amount of V_2O_5 in the calcined samples. The residue *G* thus must contain an amount *F* of V_2O_5, formed by degradation of MIL-47 during the TGA analysis, and an amount *X* of V_2O_5 already formed during calcination (Equation 2):

$$G = F + X \quad (2)$$

with *F*, *G* and *X* as indicated in Figure S2. In the TGA curve of MIL-47as (Figure S1), the residue *C* corresponds to ~ 40 % of the sum B + C; this is exactly what is expected based on the stoichiometry of the transformation of (V=O)terephthalate to V_2O_5. Taking the second weight loss *E* as a reference for the amount of intact MIL-47 in a particular sample, the residue *F* provening from intact MIL-47 in this sample can be calculated using the reference ratio between *C* and *B*:

$$\frac{F}{E} = \frac{C}{B} \quad (3)$$

with B, C, E and F as indicated in Figure S2. The value of X can then be calculated by combining Equations 2 and 3:

$$X = G - \frac{E \times C}{B} \tag{4}$$

Figure 6b in the main text shows the relative amount of V_2O_5 formed as a function of calcination time.