Supplementary Material for PCCP

A Pulse Chromatographic Study of the Adsorption Properties of the Amino-MIL-53 (Al) Metal Organic Framework

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Supporting Information

Contents

1. Pulse chromatographic technique

An adsorbing component is injected in an inert carrier; the retention time of the injected component is related to the adsorption equilibrium constant (Henry constant) by the following equation:

$$\mu = \frac{L}{v_f}\left[(\varepsilon_{ext} + \varepsilon_{macr}) + (1 - \varepsilon_{ext} - \varepsilon_{macr}) RT\rho_c K'\right] \quad (1)$$

L : the column length

v_f : the average superficial gas velocity

ε_{ext} : the bed voidage, external porosity

ε_{mac} : the macroporosity

ρ_c : the crystal density

K' : the Henry constant

The average superficial velocity v_f over the column is given by Chiang *et al.*[1]:

$$v_f = \frac{v_{out} p_{out}}{\Omega} \frac{3(p_{in} + p_{out})}{2(p_{in}^2 + p_{in} p_{out} + p_{out}^2)} \frac{T}{T_{out}} \quad (2)$$

υ_{out} : outlet gas flow rate under standard conditions (m^3/s)

P_{out} : outlet pressure (Pa)

P_{in} : inlet pressure (Pa)

Ω : area of the column cross section (m^2)

T : experimental temperature (K)

T_{out} : room temperature (K)

From the temperature dependency of the Henry constants, the adsorption enthalpy at zero coverage (ΔH_0) can be derived

$$K' = K'_0 \exp\left(\frac{-\Delta H_0}{RT}\right) \quad (3)$$

K'_0 : pre-exponential factor (mol/kg/Pa)

2. Characterization of the material

Results from elemental analysis are as follows for the dried material (% wt.): C: 48.6, H: 3.5, O: 33.9, N: 4.5, Al: 8.25. The obtained N/Al atomic ratio in the MOF (0.54) fits well the expected one (0.52).

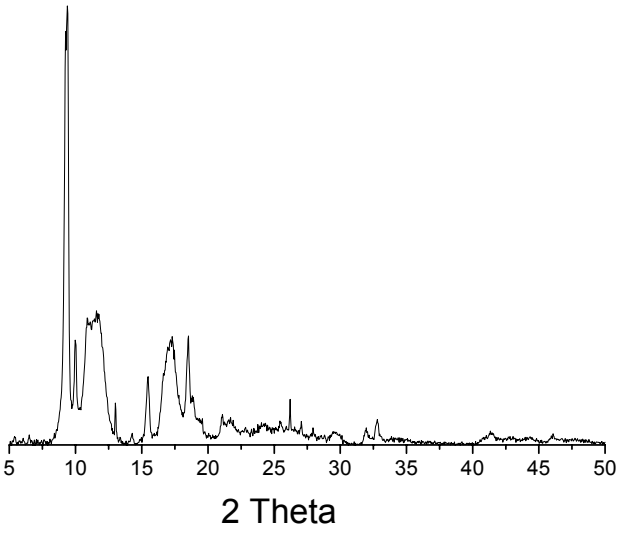

Figure S1: Experimental XRD data for the Amino MIL-53(Al) structure.

To demonstrate the absence of other Al species within the structure, ^{27}Al 30 kHz-MAS NMR spectra were collected. The spectrum indicates a unique resonance signal with a powder pattern indicative of second-order quadrupolar interaction. These findings strictly agree with

structure analysis for which only one crystallographic site is found for aluminum with an octahedral coordination[2,3].

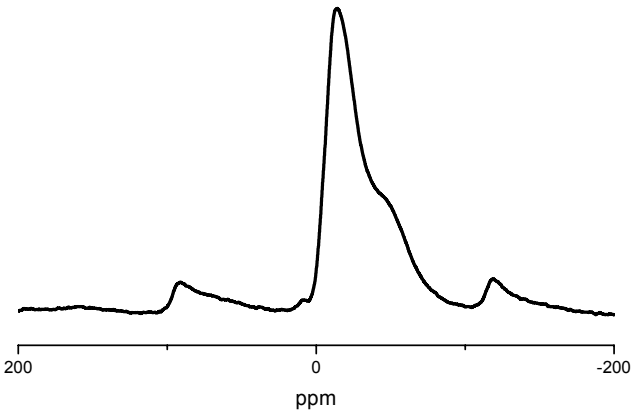

Figure S2: ^{27}Al 30 kHz-MAS NMR spectrum for the Amino MIL-53(Al) structure.

(1) Chiang , A.S.; Dixon, A.G.; Ma Y.H. *Chem. Eng. Sci.,* **1984**, *39*, 1451.

(2) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Ferey, G. *Chemistry-a European Journal,* **2004**, *10*, 1373.

(3) Ahnfeldt, T.; Gunzelmann, D.; Loiseau, T.; Hirsemann, D.; Senker, J.; Ferey, G.; Stock, N. *Inorg. Chem.*, **2009***, 48,* 3057.