Supporting information

Highly Selective Carbon Dioxide Adsorption on Exposed Magnesium Metals in A Cross-Linked Organo-Magnesium Complex

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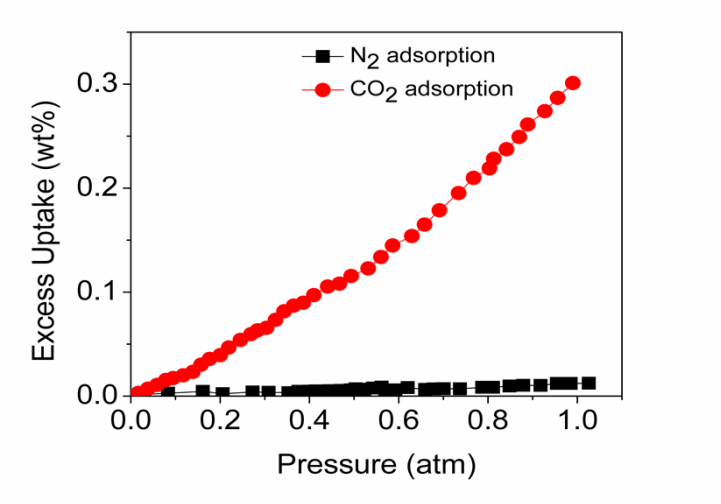

Figure S1: Adsorption isotherms of CO_2 and N_2 on MTF material without metal incorporation (SSA 300 m^2/g) at 298K and 1 atm pressure.

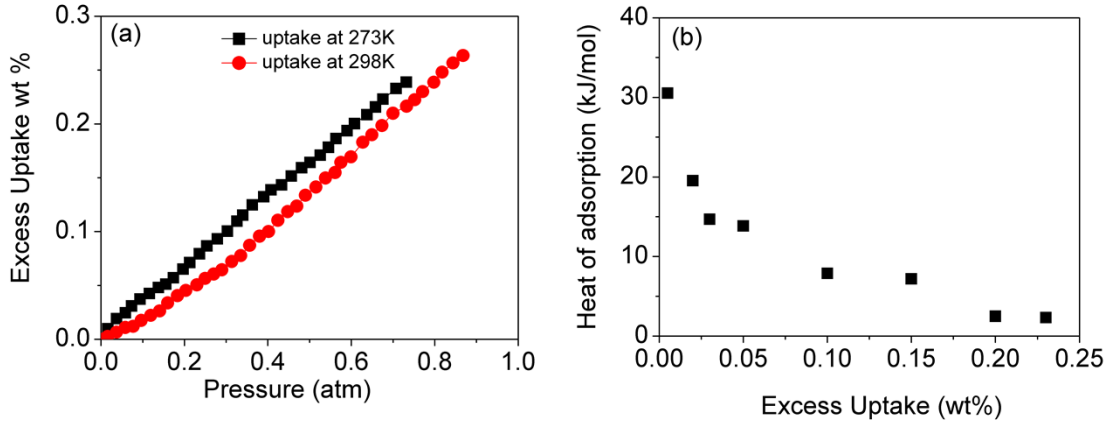

Figure S2: (a) Excess CO_2 uptake on MTF material at 298K and 273K, and (b) heat of CO_2 adsorption on MTF material calculated from Clausius-Clapeyron equation.

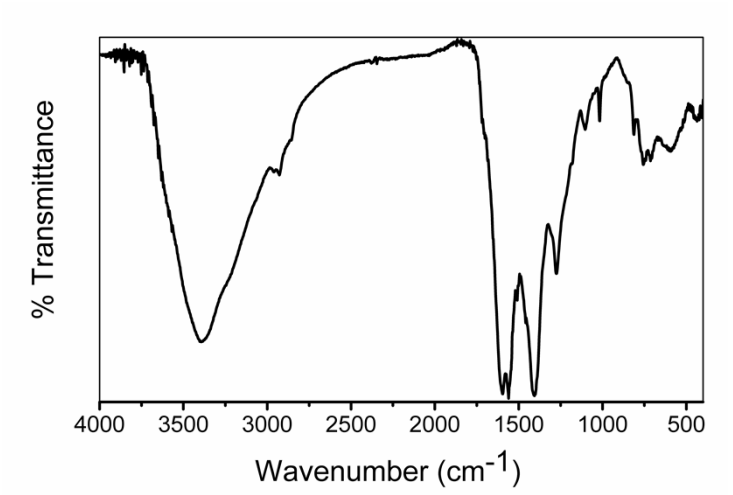

Figure S3: FTIR spectrum of the MTF-Mg complex.

The peaks at 1550 cm^{-1} and 1480 cm^{-1} correspond to the triazine rings of the MTF-Mg complex.[4] The compound shows a broad peak at 3200-3400 cm^{-1}due to the absorbed moisture during the sample preparation.

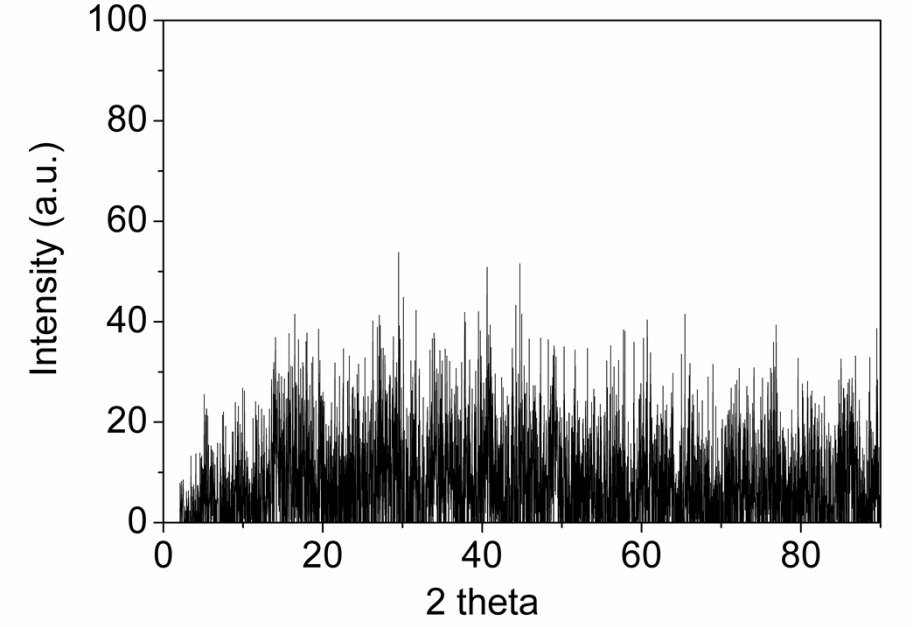

Figure S4: PXRD of MTF-Mg.

The powder X-ray diffraction profile of the MTF-Mg complex indicates that the material is amorphous with absence of a long-range order.

Gas adsorption measurement:

Gas adsorption measurements were performed following the standard US DOE guidelines to minimize the experimental errors. The instrument calibration and the experimental considerations are as follows.[1]

(1) Calibration:

- Calibration of volume, temperature sensors, pressure transducers
- Null calibration (empty sample chamber with zero uptake baseline in isothermal condition) (Fig. S5)
- Calibration of the instrument with known materials (Figs. S6 and S7)

(2) Temperature monitoring and control:

- Temperature of the sample chamber was controlled to an acceptable level by applying water bath (298K) or ice bath (273K).
- The gas reservoir is thermostatted to minimize room temperature fluctuations.

(3) Sample temperature was monitored continuously throughout the measurement.

(4) Approach to the equilibrium:

- For physisorption, the equilibrium is reached relatively fast. The pressure relaxation was measured at each step by taking the data point every minute.

(5) Sample size:

- The sample size was taken carefully to match up with the requirement on the system volume and the pressure measurement.
- Generally, sample size was taken to fill 2/3 volume of the sample chamber (3 cc).

(6) Gas purity: CO_2 (99.8) and N_2 (99.995)

(7) Sample degassing was performed under ultra-high vacuum (UHV).

(8) Sample pretreatment: 150 ^{0}C under UHV for 12 h.

(9) Leakage was tested using helium and hydrogen at the maximum measurement pressure.

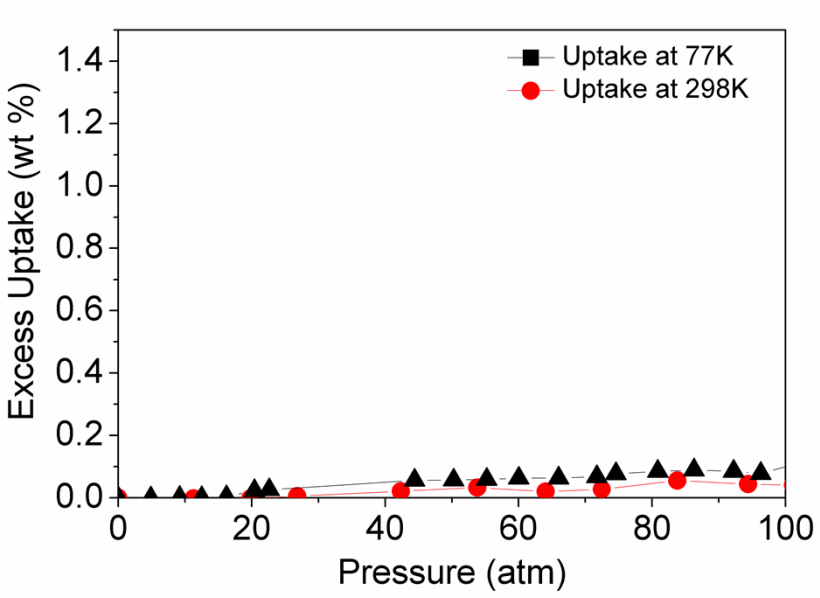

Figure S5: Empty sample holder calibration.

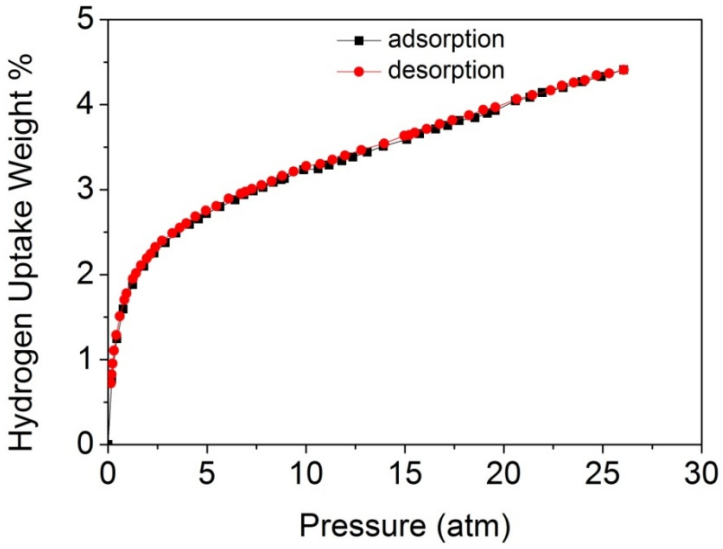

Figure S6: Hydrogen storage capacity of commercially available basolite A100 MOF obtained at 77K using the same instrument under the similar conditions to those used for the gas measurement for the MTF-Mg complex. The results are in good agreement with the reported results in Ref. [2].

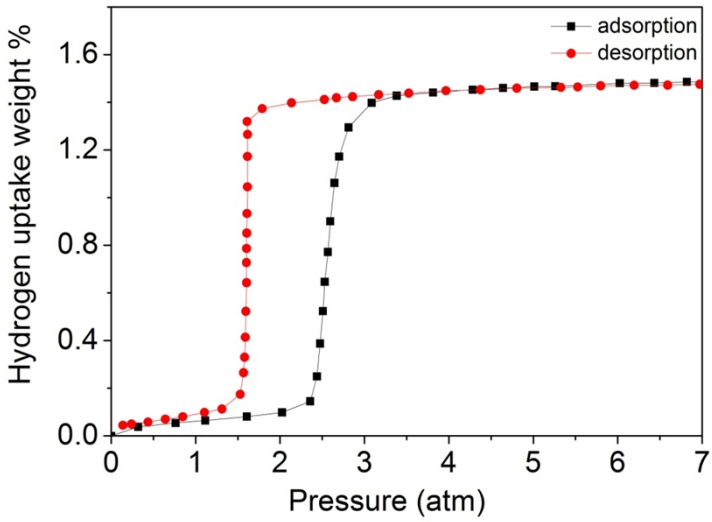

Figure S7: Hydrogen storage capacity of a commercially available LaNi5 alloy obtained at 298K using the same instrument under the similar conditions to those used for the gas measurement for the MTF-Mg complex. The results are in excellent agreement with the data shown in Ref. [3].

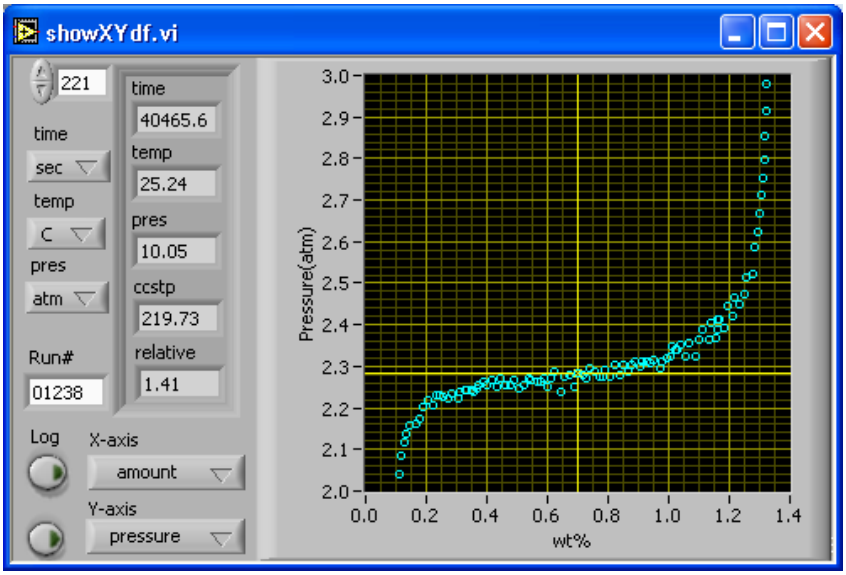

Figure S8: The pressure resolution of the instrument is 0.02 atm (LaNi5 at 298K).

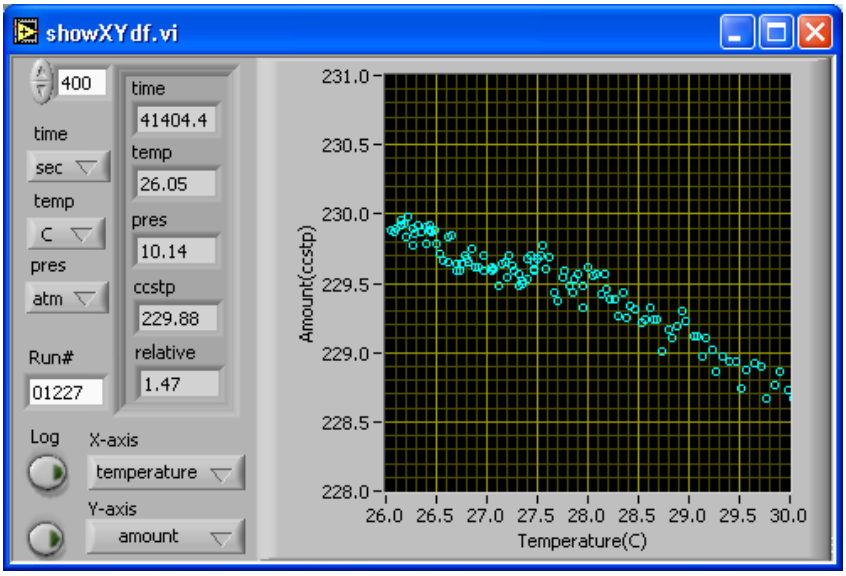

Figure S9: The gas measurement resolution with the GRC instrument 0.2 ccstp.

Estimation of CO_2 desorption temperature

Consider CO_2 desorption from an adsorbent A, which is MTF-Mg in the present case:

$$A - CO_2 \rightarrow A + CO_2$$

where CO_2 is attached to A. The Gibbs free energy can be calculated as

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

The reaction entropy is largely determined by the enthalpy of CO_2, assuming the entropies of the surface states of A and A-CO_2 are relatively small, compared to that of CO_2, and the errors can also partially cancel each other. Equation (1) then becomes

$$\Delta G \approx \Delta H - T\Delta S_{CO_2} = -RT \ln K = -RT \ln P_{CO_2} \qquad (2)$$

From Eq. (2), we have

$$\Delta H - T\Delta S_{CO_2} + RT \ln P_{CO_2} = 0 \qquad (3)$$

The entropic data of CO_2 can be obtained from the Reference 5 as a function of temperature. Assume that the CO_2 partial pressure is decreased to 0.005 bar upon desorption. From Eq. (3),

it can be determined that for a heat of adsorption of 45.2 kJ/mol, the desorption temperature is 282K, close to ambient, while for a heat of adsorption of 90kJ/mol, the desorption temperature is 500K.

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2. G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guegan, *Chem. Commun.*, 2003, **0**, 2976-2977.
3. S. Luo, J. D. Clewley, T. B. Flanagan, R. C. Bowman Jr and L. A. Wade, *J. Alloys Compd.*, 1998, **267**, 171-181.
4. G. Yang, H. Han, C. Du, Z. Luo and Y. Wang, *Polymer*, 2010, **51**, 6193-6202.
5. Yunus A. Çengel, Introduction to Thermodynamics and Heat Transfer, McGraw-Hill Higher Education, 2008, ISBN 0071287736, 9780071287739