Supporting Information

Exploiting Dynamic Opening of Apertures in Partially Fluorinated MOF for Enhancing H₂ Desorption Temperature and Isotope Separation

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Calibration of the mass spectrometer signal

A solid polycrystalline piece of a diluted alloy Pd95Ce5 (~0.5 g) is used for calibration. Prior to the calibration, the alloy was etched with aqua regia in order to remove the oxide layer and it was heated up to 600 K under high vacuum in order to remove hydrogen which might be absorbed during the etching procedure. Afterwards it was weighted and inserted in the sample chamber. At 350 K, it was loaded with 40 mbar pure H\textsubscript{2} or pure D\textsubscript{2} for 1.5-2.5 h. As H and D were bound preferentially to the Cerium atoms at low loading pressures in this diluted alloy, the alloy could be handled under ambient conditions for a short period of time. After loading, the alloy was cooled to RT and weighted. Afterwards it was placed back in the sample chamber and a normal TDS measurement with 0.1 K/s was performed. After the desorption, the alloy was cooled back to RT and weighted again. The weight difference between unloaded state and loaded state was equal to the mass uptake of hydrogen or deuterium, respectively.

Heat of adsorption calculation

The hydrogen heat of adsorption of FMOFCu can be determined by an integration of the Clausius-Clapeyron equation as function of the surface coverage. Carrying out the integration, the Claudius-Clapeyron relation is now commonly rearranged in the Van’t Hoff form for calculating physisorption enthalpy.

\[
\Delta H = R \cdot \left( \frac{\partial \ln(P)}{\partial \frac{1}{T}} \right)_{\theta}
\]

where \( P \) is the equilibrium gas pressure, \( \Delta H \) the reaction enthalpy and \( \theta \) is the surface coverage.

From the absolute adsorption isotherms for 100-120 K, the logarithm of the pressures values at a fixed surface coverage \( \theta \) can be plotted versus the reciprocal temperature \( 1/T \) yielding a linear correlation with a slope proportional to the enthalpy of adsorption.

\[ \textbf{Scheme S1.} \text{ 2-D view of tri-modal structured FMOFCu, showing the ac plane cut at the height of the aperture between cavity B and C. The colors indicate each Cavity region; A(yellow), B(green) and C(red). The green atoms are the three flourine forming the bottle neck.} \]
Figure S1. Crystal structure of FMOFCu, and pore network analysis with grid space of 0.1 Å for the probe sphere. Three cavities (A, B, C) can be identified and are connected depending on the probe size. Pink, red, grey and blue represent copper, oxygen, carbon, and fluorine atoms, respectively.

Figure S2. SEM image of FMOFCu framework.
Figure S3. Thermogravimetric analysis for as synthesized FMOFCu
Figure S3. PXRD pattern of FMOFCu as (a)synthesized, (b) Simulated
Figure S5. FT-IR spectra of FMOFCu (red) and CPHFP (black).
Figure S6. BET isotherm of sample FMOFCu at 1 bar and 77 K using N$_2$ (top) and 20 K using H$_2$ (bottom). Closed and open symbols represent the absorption and desorption of the sample. The calculated BET surface area is very low which is within the measurement errors, implying the inaccessible aperture for both H$_2$ at 20 K and for N$_2$ at 77 K.
Figure S7. Hydrogen adsorption and desorption isotherms of FMOFCu at various temperatures: (a) 19.5 K, (b) 25 K, (c) 40 K, (d) 60 K, (e) 77 K, (f) 100 K, and (g) 120 K. Closed and open symbols represent the absorption and desorption.

Figure S8. Deuterium adsorption and desorption isotherms of FMOFCu at various temperatures: (a) 23 K, (b) 25 K, (c) 40 K, (d) 60 K, (e) 77 K, (f) 100 K, and (g) 120 K. Closed and open symbols represent the absorption and desorption.
Figure S9. Neutron Powder Diffraction (NPD) measured at 24K under vacuum and fulling loading of D₂, showing no structural change by gas sorption.
[Details of the uncertainty of TDS]

Typically, there are three major sources of error in a thermal desorption experiment:

1. **Mass spectrometer: filament sensibility/efficiency**
   
   The efficiency of filament of the mass spectrometer may decay over several months of time. For a short-term experiment, the efficiency of filament can be seen as constant. Therefore, it can be seen as a systematic error.

2. **Sample mass: balance error**
   
   Based on the accuracy of our balance, the error associated to the sample mass is ± 0.01mg, which corresponds to an error of 0.25% of the gas uptake. For comparison of different experiments based on the same sample, this can also be assumed as a systematic error.

3. **Measurement accuracy (random error): pressure transducer, temperature control, time variation**

Thus, a reasonable assumption of the total error can be assumed to be ~5%. However, the errors arising from (1) mass spectrometer and (2) sample mass can be assumed to be systematic errors, which can be neglected when a series of systematically experiments are carried out and compared. Therefore, the error of our experiment/analysis comes from the random error, (3) measurement accuracy. Nevertheless, this error has a small impact on the reproducibility of TDS experiments. To clarify this point, for instance, we calculated the reproducibility of H2 and D2 uptake collected at 25 K. The mean H2 uptake is 0.01317 mmol/g, with standard deviation 4.2281E-4; while the mean D2 uptake is 0.14601 mmol/g, with standard deviation 0.00377. It shows the high reproducibility of the TDS experiments, and it’s therefore the reason we omitted the uncertainty for the measurements.

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**Figure S10.** The comparison H\textsubscript{2} and D\textsubscript{2} desorption spectra of 10 mbar 1:1 isotope mixture loading for a different exposure temperature: 60K, 77K, and 87K, of FMOFCu and MOF-74-Ni. Note the different unit of desorption rate.
Figure S11. Isosteric heat of adsorption of hydrogen for FMOFCu as function of the adsorption amount.
Figure S12. Kinetic effect of FMOFCu at 25 K. H₂ and D₂ desorption spectra of 50 mbar 1:1 isotope mixture loading for a different exposure time: (a) 10 min, (b) 60 min, (c) 120 min and (d) 300 min, and its corresponding (e) selectivity and (f) D₂ uptake.