1. Gas Sorption Experiments for PCM-4

Gas sorption experiments at low temperature were performed in a glass vacuum manifold equipped with a diffusion pump. Standard volumetric technique was used to obtain the sorption data of small gas molecules in the pressure range from 5 to 760 Torr if otherwise specified. Before gas sorption experiments, PCM-4 was slowly (1 K/min) activated by heating from room temperature to the designated temperature between 323 K and 473 K for 2h under vacuum (< 10^{-5} Torr). Otherwise specified, the evacuation temperature was 473 K. Highly pure gases were used for the sorption measurements. Desorption isotherms were obtained by decreasing the pressure after adsorption at ~760 Torr. The equilibrium time for adsorption or desorption of a probe gas was 10 min for each pressure. The BET surface area was calculated from CO_2 isotherm points within the range of 0.05-0.3 (P/P_0), assuming a CO_2 cross-sectional area of 17.0 Å/molecule. The micropore volume was determined by using the Dubinin-Radushkevich (D-R) equation:

\[ \ln w = \ln w_0 - \frac{RT}{\beta E_0} \ln^2 \left( \frac{P}{P_0} \right) \]

where \( w \) and \( w_0 \) are the adsorbed amount at a pressure \( P \) and the adsorbed amount corresponding to the micropore volume, respectively. \( P_0 \), \( \beta \) and \( E_0 \) correspond to the saturated vapor pressure, affinity coefficient and characteristic energy of adsorption, respectively. The micropore volume was calculated from the intercept of the linear region of D-R plot with the assumption that the density of the adsorbate in the pore was the same as that of the pure adsorbate in its liquid state.
2. Experimental Procedure for Temperature-Programmed Desorption (TPD)

Low temperature TPD experiments were carried out in a fixed-bed tubular reaction system equipped with a specially designed heater for control between 77K and 373K and a thermal conductivity detector. Typically, 100 mg of the sample was loaded into the glass reactor. Before TPD experiments, PCM-4 was slowly (1 K/min) activated by heating from room temperature to the designated temperature between 298K and 473K for 2 h under vacuum (<10^-5 Torr). After the gas adsorption using N2 (99.9999%), Ar (99.9999%) and O2 (99.9995%) at the designated temperature between 83 K and 93 K, the sample was evacuated to remove the physisorbed gas at the same temperature under vacuum (<10^-2 Torr). Once the baseline of the integrator was stable, the TPD run was started with flowing helium as a carrier gas at a heating rate of 10 K/min (if otherwise specified) from 93 K (83 K at N2) to 300 K. The Arrhenius desorption parameters were determined from the Ar-TPD experiments based on the heating (ramping) rate variation. Plotting ln(β/T<sub>2max</sub>) versus 1/T<sub>max</sub> yielded the kinetic desorption parameters, i.e., the activation energy (or the enthalpy) for the Ar desorption (E<sub>des</sub>) and the pre-exponential factor (A<sub>des</sub>). The enthalpy of Ar desorption (E<sub>des</sub>) was calculated with the following Arrhenius equation using the Ar-TPD profiles obtained from different ramping rate after Ar adsorption at 93 K (ref. P.A. Redhead, Vacuum, 12 (1962) 203).

\[
dT/dt = \beta, \quad dC/dt = \beta \ dC/dT \\
-dC/dT = (A/\beta) \exp(-E_{des}/RT) \ C^n
\]

At peak temperature (T<sub>max</sub>), \(-d^2C/dT^2 = 0\), and with approximation,
\[E_{des}/RT_{max}^2 = (A/\beta) \exp(-E_{des}/RT_{max}) \ C_0^{-n-1}\]
where \(C_0\) is the initial surface concentration.

For first order reaction (n=1),
\[E_{des}/RT_{max}^2 = (A/\beta) \exp(-E_{des}/RT_{max}) \quad (1)\]

T<sub>max</sub> is independent of \(C_0\) if E<sub>des</sub> is constant.

As T<sub>max</sub> goes up, so does E<sub>des</sub>.

\(E_{des}\) is obtained directly from T<sub>max</sub> by assuming \(A = 10^{13}\) S<sup>-1</sup>

\(E_{des}\) without the assumption: variation in \(\beta\)

From (1), \(\ln(\beta/T_{max}^2) = -E_{des}/RT_{max} + \ln A_{des}R/E_{des}\)

Plotting \(\ln (\beta/T_{max}^2)\) versus \(1/T_{max}\) yields \(-E_{des}/R\).

Where \(E_{des}\) : activation energy of desorption (J/mol)
\(\beta\) : heating (or ramping) rate (K/s)
R : Ideal gas constant (8.314 J/K mol)
T<sub>max</sub> : Temperature at the maximum of TPD peak (K)
A<sub>des</sub> : desorption pre-exponential factor (s<sup>-1</sup>)
C : Ar concentration (For first order reaction, C=1)
Figure S1. Solid-state $^{31}\text{P}$ NMR of PCM-4: as-synthesized sample (blue); desolvated (black).
**Figure S2.** Bulk XRPD pattern for PCM-4 as-synthesised (red) and after desolvation in vacuum (<10^{-5} Torr) at 413 K over 6 h (green) versus simulated pattern (blue) obtained from single crystal data.
Figure S3. Adsorption/desorption isotherms of CO₂ for PCM-4 degassed at 473 K under vacuum (<10⁻⁵ Torr)
**Figure S4.** Adsorption/desorption isotherms of H₂ in PCM-4 degassed at 473 K under vacuum (<10⁻⁵ Torr)
Figure S5. Adsorption /desorption isotherms of CH₄ in PCM-4 degassed at 473 K under vacuum (<10⁻⁵ Torr)
**Figure S6.** Low-temperature TPD profiles of light gases in PCM-4 (ramping rate = 10°C/min).
Figure S7. (a) Low temperature Ar-TPD profiles of PCM-4 obtained after dosing pore Ar at 90 K and 1 atm for 0.5 h using different ramping rates and (b) the Arrhenius plots obtained from the TPD profiles of (a). Experimental conditions: flow rate \( Q_{\text{He}} = 30 \text{ ml/min} \), \( W_{\text{sample}} = 0.1 \text{ g} \), ramping rate (\( \beta \)) = 10 K/min.
Figure S8. Adsorption kinetics of Ar on PCM-4 at 87 K and 500 Torr.
**Figure S9.** Sorption kinetics of Ar on PCM-4 at 87 K and 500 Torr.