Supplementary Materials

Understanding the Pathway of Gas Hydrate Formation with Porous Materials for Enhanced Gas Separation

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METHOD
CMK-3 was synthesized according to previous reports [27,28]. The N₂ isotherm curves were collected at 77 K by ASIQ purchased from Quanta-chrome USA. Surface areas were calculated by BET method. Pore size distributions were obtained by DFT method. The transmission electron microscopy (TEM) images were collected by FEI Tecnai G2 F20. Water vapor sorption experiments were conducted by the same equipment for determining water loading amount. Powder XRD pattern was record on MiniFlex600 Rigaku. CO₂ (purity 99.998%) purchased from Oxygen Air Liquid Singapore was used in all experiments. Static and dynamic adsorption experiments were measured by high pressure adsorption equipment purchased from AMC USA. The breakthrough experiment was carried out on home-designed facility. The sample corresponding to the dry sample weight of 2 g was compacted in the steel fixed bed with 25 cm length and 1 cm inner diameter. The environment temperature was controlled by thermostatic water bath. The feed gas flow rate was controlled by mass flow controller with precision of 0.1 mL/min purchased from Bronkhorst High Tech. The outlet gas components were detected by mass spectrometer RGA 200 purchased from SRS, USA. During the breakthrough experiment, the mole ratio of mixture gas C₂H₆/CH₄ is 1:1. The flow rate of feed gas was 100 mL/min (STP). During the regeneration, N₂ was used as purging gas with
flow rate of 100 mL/min.

Wet samples were prepared by dropping deionized water slowly into massed dry samples with continuously stirring until the added water weight meets the requirement. 0.25g dry sample was used in thermodynamic test and wet sample preparation. 0.25g water was used in CO₂ sorption experiments at 273K.

ENTHALPY CALCULATION
The phase change pressure could be obtained from isotherm curves at different temperatures. The enthalpy change of the state transition can be determined using the following Clausius–Clapeyron equation, where \( f \) is the fugacity, \( T \) is the temperature (K), and \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

\[
\Delta H = -R \left[ \frac{d \ln f}{d(1/T)} \right]
\]

THERMODYNAMIC CALCULATION AND DFT STUDY
To get thermodynamic behavior of water-CO₂ system under two-dimensional confined space, we built a 3 x 3 super cell of graphene with 1, 1.5, 2, 3 and 4 nm vacuum space to simulate the real pore of activated carbon and CMK-3. The interaction energies were computed using GGA pseudo potential method [29,30] with PBE density functional theory and dispersion correction (DFT-D3BJ) [31-33]. TNP basis set was selected during all simulations. More than one orientation of water molecule was considered. To lighten the calculation task, only one-layer graphite was built to mimic the inner wall, which is enough for us to discuss the experiment results. In all the simulations, the graphite atoms are fixed at their respective initial positions and represent an inert wall of carbon materials. The kinetic energy cut off was set to 400 eV. The maximum atom force was set as 0.05 eV for convergence criterion toward the structure optimization.

The purpose of calculation was to build a diagram that presents the relationship of pressure, temperature and pore size to Gibbs free energy. The process of water replacement can be described as follows:

\[
\text{CO}_2 + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O} + \text{CO}_{2\text{ads}}
\]

Using free gaseous CO₂, H₂O and empty surface of carbon as references, the Gibbs free energy changes of interest can finally be represented as:

\[
\Delta G(T, p) = G_{\text{H}_2\text{O}} - G_{\text{CO}_{2\text{ads}}} - \mu_{\text{CO}_2}(T, p) + \mu_{\text{H}_2\text{O}_{\text{ads}}}(T, p)
\]
\[ \mu_i = H_o(T) - TSo(T) + k_B T \ln \frac{p}{p_0} \]

where \( H_o \) is enthalpy, \( S \) is entropy, \( p \) is pressure, \( k_B \) is Boltzmann constant, \( T \) is temperature and \( \mu \) is chemical potential.

The Gibbs free energies for relevant species were calculated with the expression:

\[ \Delta G(T, p) = E_{\text{DFT}} + E_{\text{ZPE}} + E_{\text{DF}} + \int CpdT - TS \]

where \( E_{\text{DFT}} \) is the DFT calculated electronic energy in CASTEP, \( E_{\text{ZPE}} \) is the zero-point vibrational energy, \( E_{\text{DF}} \) is correction of dispersion force, and \( \int CpdT - TS \) is the correction of entropy contribution. Harmonic approximation was selected to treat the adsorbate, and \( PV \) contributions were neglected.

The entropy \( S \) can be given by:

\[ S = N k \ln q + N k T \left( \frac{\partial \ln q}{\partial T} \right)_V \]

\[ q_t = N k \left\{ \ln \left[ \left( \frac{2 \pi m k T}{\hbar^2} \right)^{3/2} \frac{V}{N} \right] + \frac{5}{2} \right\} \]

\[ q_r = \frac{8 \rho^2 I k T}{\hbar^2 \sigma} \]

\[ q_v = \prod_{i=1}^{N} \frac{e^{\frac{h \nu_i}{k T}}}{e^{\frac{h \nu_i}{k T}} - e^{-\frac{h \nu_i}{k T}}} \]

where \( q \) is partition function that consists of translation \( (q_t) \), rotation \( (q_r) \), and vibration \( (q_v) \). \( m \) is molecular weight, \( I \) is the moment of inertia about, \( \sigma \) is symmetry number, and \( \nu \) is vibration frequency. The vibration mode and frequency of free molecules (\( \text{H}_2\text{O} \) and \( \text{CO}_2 \)) and adsorbed molecules are shown in Figures S13 and S15 and listed in Table S2.
Figure S1: N₂ adsorption/desorption isotherms on (a) CMK-3 and (b) AC at 77K. Insets are DFT pore size distributions.

Figure S2: Water vapor adsorption/desorption isotherms on dry samples of (a) CMK-3 and (b) AC at 293K.

Table S1: Physical parameters of samples.

| Sample | Surface area, m²/g | Pore volume, cm³/g | Mean pore size, nm | Maximum water vapor uptake, cm³/g |
|--------|-------------------|--------------------|--------------------|----------------------------------|
| AC     | 3170              | 1.58               | 1-3                | 1.6                              |
| CMK-3  | 998               | 1.08               | 3.8                | 1.0                              |
Figure S3: CO$_2$ adsorption/desorption isotherms in bulk water at 273 K.

Figure S4: Comparison of CO$_2$ adsorption/desorption isotherms on CMK-3 at 273 K. The red blank squares represent the desorption branch after deducting an estimated gas hydrate formation value (6.83 mmol/g) from the real desorption branch.
**Figure S5:** Comparison of CO$_2$ adsorption/desorption isotherms on AC with different Rw at 273 K.

**Figure S6:** Blank experiment of CO$_2$ adsorptive kinetic temperature curve.
**Figure S7:** CO$_2$ adsorptive isotherms on CMK-3 at different temperatures when $R_w = 0$.

**Figure S8:** CO$_2$ adsorptive isotherms on CMK-3 at different temperatures when $R_w = 0.96$. 
Figure S9: CO$_2$ adsorptive isotherms on CMK-3 at different temperatures when $R_W = 2$.

Figure S10: CO$_2$ adsorptive isotherms on AC at different temperatures when $R_W = 0$. 
Figure S11: CO$_2$ adsorptive isotherms on AC at different temperatures when $R_w = 1.58$.

Figure S12: CO$_2$ adsorptive isotherms on AC at different temperatures when $R_w = 3.1$. 
**Table S2:** Vibration frequency of free molecules and adsorbed molecules.

| species                  | Stretching vibration cm\(^{-1}\) | Bending vibration cm\(^{-1}\) | Rotation cm\(^{-1}\) |
|--------------------------|----------------------------------|-------------------------------|----------------------|
|                          | symmetric | asymmetric | Out of plane | In plane | Out of plane | In plane |
| CO\(_2\)                 | 1315      | 2348.8     | 657          | 657      | 16.89       | 16.89    |
| Adsorbed CO\(_2\) in 5\(^{12}\) cage | 1316      | 2342       | 636          | 639      | 61          | 90.03    |
| CO\(_2\) in 5\(^{12}\)\(^{6}\) cage | 982       | 2106\(^{5}\) | 622\(^{5}\) | 630\(^{5}\) | 97          | 103      |
|                          |          |            | 2193\(^{6}\) | 635\(^{6}\) | 640\(^{6}\) |          |
| H\(_2\)O                 | 3710      | 3816       | 1601         |          | 134         | 91       | 53       |
| Adsorbed H\(_2\)O       | 3674      | 3762       | 1653         |          | 392         | 397      | 444      |
| H\(_2\)O of gas hydrate | 3780      | 3850-3900  | 1666         |          | -           | 406      | -        |

S: vibration of CO\(_2\) in 5\(^{12}\) cage; L: vibration of CO\(_2\) in 5\(^{12}\)\(^{6}\) cage.

**Figure S13:** Vibration modes of adsorbed water molecule and CO\(_2\) on graphene.
**Figure S14:** Optimized structures of CO$_2$ hydrate crystals based on calculations. Red represents oxygen atoms in CO$_2$, grey represents carbon atom, and blue and light green represent oxygen and hydrogen in water, respectively.

**Figure S15:** C$_2$H$_6$ adsorption/desorption isotherms on AC at 273K with different $R_w$ values. The filled symbols represent adsorptive branch, and the blank symbols represent desorption branch.
Figure S16: C$_2$H$_6$ adsorption/desorption isotherms on AC at different temperatures when $R_w = 1.5$.

Figure S17: CH$_4$ adsorption/desorption isotherms on AC at 273K with different $R_w$ values. The filled symbols represent adsorptive branch, and the blank symbols represent desorption branch.
**Figure S18:** CH$_4$ and C$_2$H$_6$ adsorption/desorption isotherms on dry AC at 273 K.