

Supporting information

Separation of CO₂-CH₄ Mixtures in the Mesoporous MIL-100(Cr) MOF: Experimental and modelling approaches

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1. Synthesis and activation

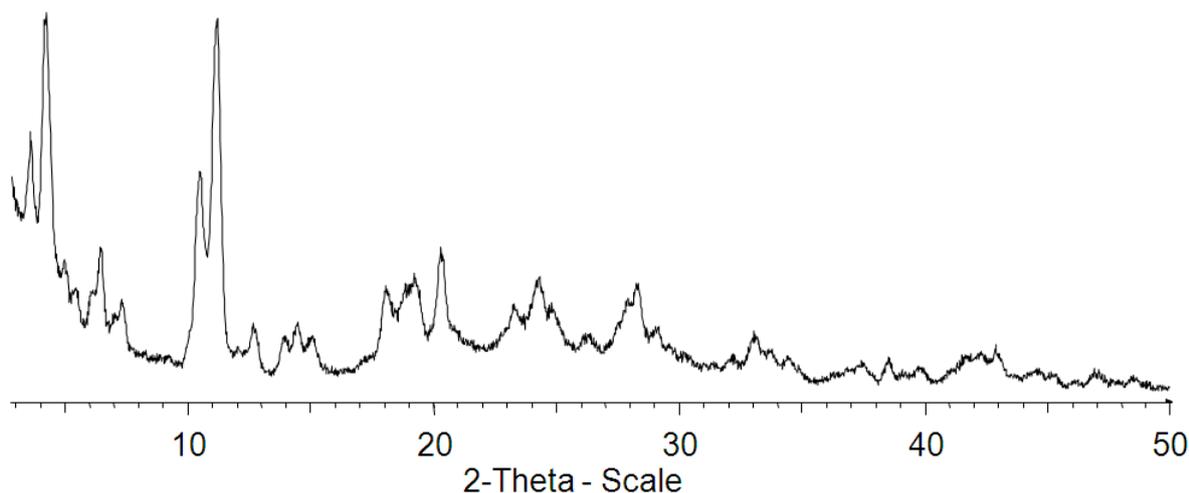


Figure S1. XRPD diagram of MIL-100(Cr).

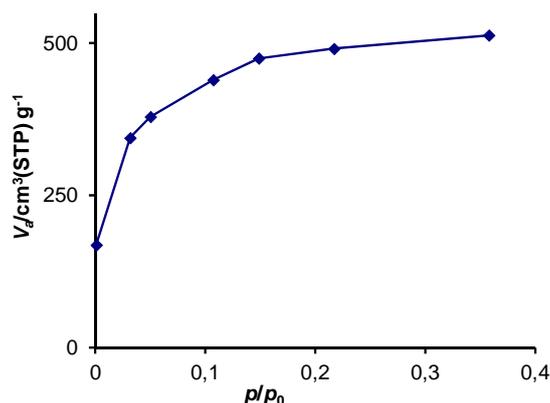


Figure S2. Nitrogen adsorption isotherm of MIL-100(Cr).

2. Volumetric apparatus

For mixture adsorption equilibrium measurements, we use an original built-in house device (Figure S3).

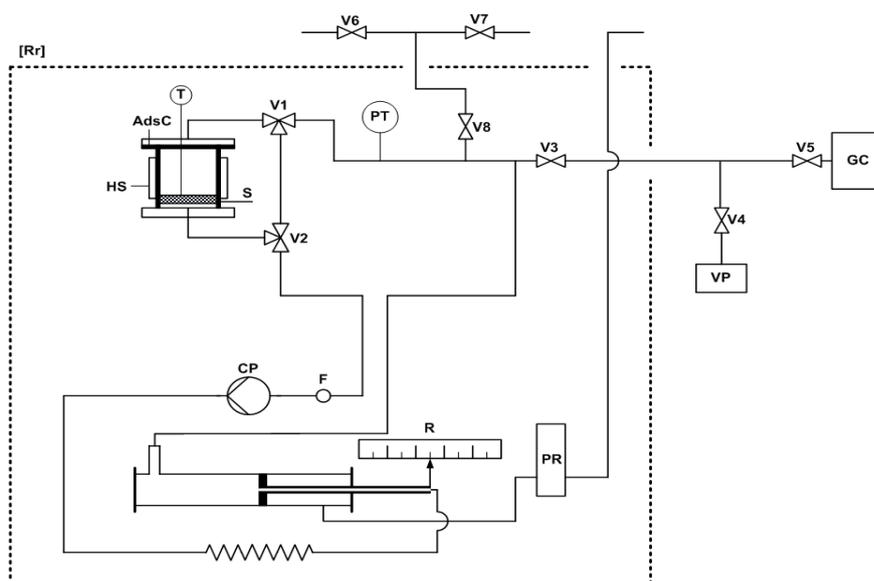


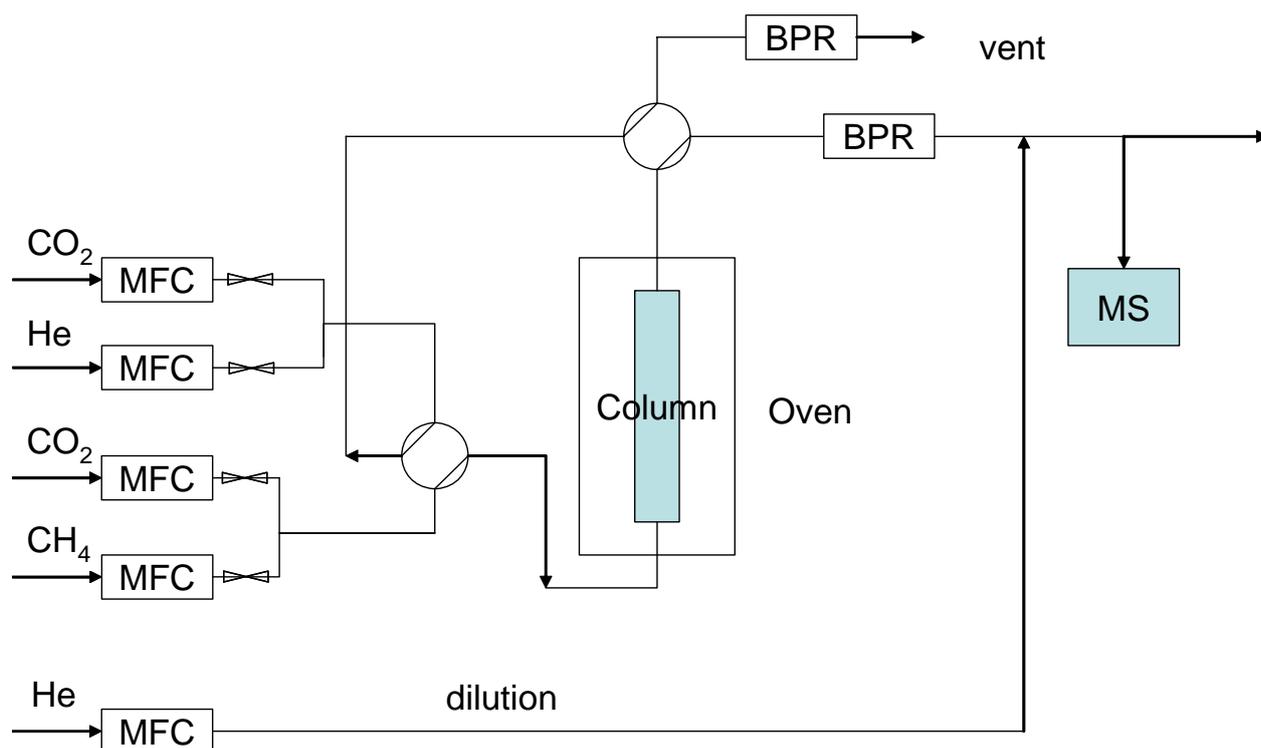
Figure S3: Mixture adsorption volumetric apparatus: (AdsC) adsorption cell; (PT) pressure transmitter; (V1 and V2) three ways manual valves; (V3 to V8) manual valves; (T) Pt 100 temperature probes; (F) filter; (HS) in-situ heating system; (VP) vacuum pump; (CP) circulation pump; (R) ruler; (PR) pressure regulator; (GC) gas chromatograph; (Rr) refrigerated room.

The principle remains identical to the pure component adsorption one. It allows the measurement of isobaric and isotherm mixture adsorption equilibria in a range of pressures from 100 kPa to 1000 kPa and for temperatures from 298 K to 353 K. In this apparatus, a cylinder piston provides a substitute of

the classic cell which enables to change the total volume in order to fix pressure on a set point value during the adsorption. A circulation pump is used to homogenize the mixture and a gas chromatograph, coupled with a thermal conductivity detector provided by Agilent (GC 6850), allows the determination of the gas mole fraction of each component in the mixture. The pressure transmitter is provided by Endress-Hauser (0 – 1 000 kPa Cerabar PMP 731) with an uncertainty of 0.1% of the full scale. Prior to each experiment, the sample was outgassed at 523 K for 8 hours under vacuum (below 10^{-3} mbar). After that, the pure gases (provided by Praxair, Belgium) are introduced one by one in the installation without going through the adsorption cell. When both equilibrium and homogenization are reached (checked by constant values of both pressure, temperature and composition obtained using a chromatography device), we determine the gas composition by at least five chromatographic analyses and the pressure, the temperature, and the volume values are recorded. With these measurements and the installation volume, we can determine the mole number of each mixture component using a mixture equation of state.¹ In the second phase, the adsorption cell is accessible via two three-ways valves. During the adsorption, the pressure is maintained on a set point value by adapting the installation volume thanks to the cylinder piston. When the equilibrium is reached (checked by constant values of both temperature and volume), we write down the pressure and temperature values and determine gas composition by at least five chromatographic analyses. Knowing the total installation volume, we can calculate the mole number of each component in the gas phase after adsorption thanks to a mixture equation of state.¹ The difference between the mole numbers in the gas phase before and after adsorption allows to determine the adsorbed amounts. The adsorbent is then outgassed allowing to start again the procedure with a new composition of initial mixture.

3. Experimental details of the breakthrough curve measurements

Figure S4 shows a scheme of the setup used for the breakthrough experiments at high pressure. Different gas mixtures can be prepared by a set of mass flow controllers. The gas mixture is either sent to the adsorption column, which is placed in an oven, or to a bypass line. A backpressure regulator is placed downstream of the column and fixes the pressure in the column and by-pass line. Downstream of the backpressure regulator, the column effluent is diluted with helium and is then analyzed by a mass spectrometer. The dilution is necessary since the response of the mass spectrometer is linear only in a concentration range of 0–15%. The dilution brings the concentrations of the eluted gases down to this range. Moreover, it keeps the total flow rate more or less constant, which is a necessary condition for obtaining correct mass balances. Mass 44 is used for analysis of CO₂ and mass 15 for the analysis of CH₄ (mass 16 is avoided because CO₂ contributes to the intensity). The signals are normalized by the intensity of mass 4 (He), in order to correct for drifts in the mass spectrometer.



MFC = Mass Flow Controller
BPR = Back Pressure Regulator
MS = Mass Spectrometer

Figure S4. Scheme of the setup used for breakthrough experiments.

4. Structural model and partial charges for framework of MIL-100(Cr)

The accessible surface area (S_{acc}) is purely based on the geometric topology of the adsorbent and calculated from a simple Monte Carlo integration technique where the center of mass of the probe molecule with hard sphere is “rolled” over the framework surface.² In this method, a nitrogen-sized (3.6 Å) probe molecule is randomly inserted around each framework atom of the adsorbent and the fraction of the probe molecules without overlapping with the other framework atoms is then used to calculate the accessible surface area. The LJ size parameters of the framework atoms were the same as those used for the calculations of the adsorption properties (DREIDING potential).

The pore volume (V_{pore}) of the MIL-100(Cr) was obtained according to the thermodynamic method proposed by Myers and Monson³, the LJ parameters for Helium ($\epsilon/k_B = 10.9$ K, $\sigma = 2.640$ Å) being taken from the work of Talu and Myers.⁴

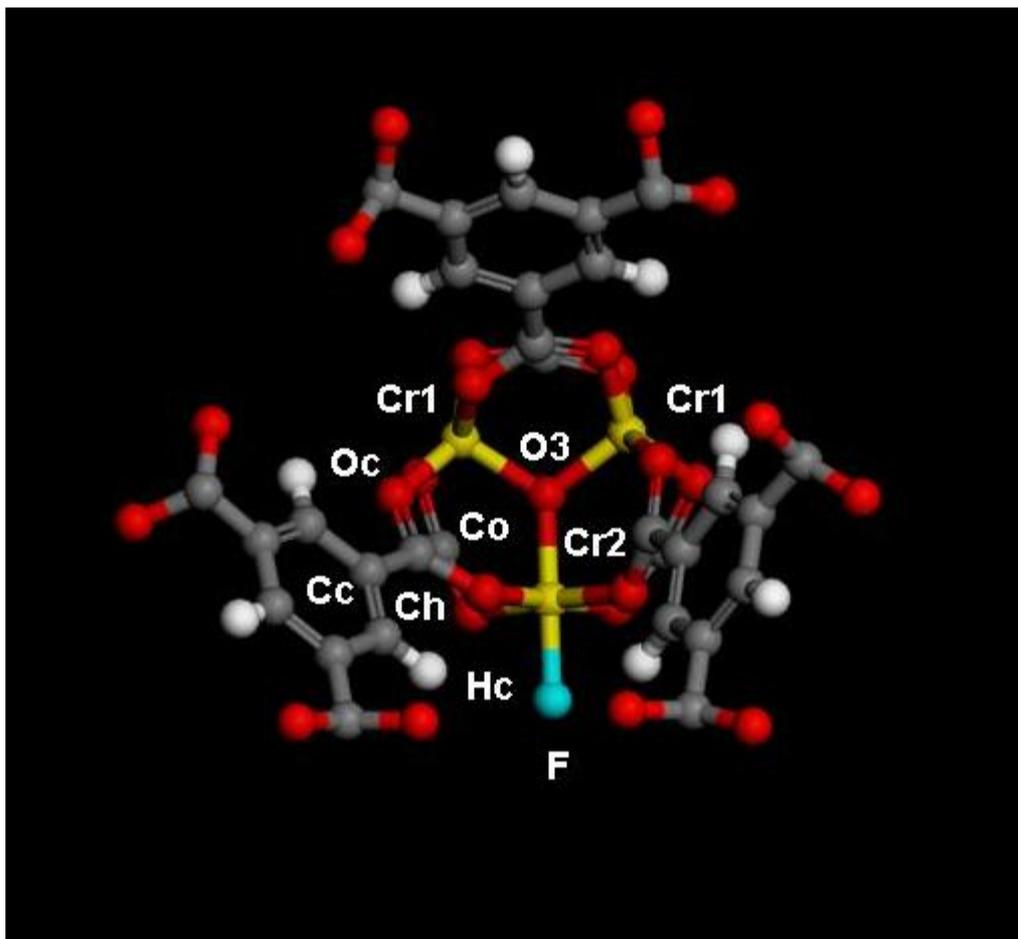


Figure S5. Labels of the atoms for the MIL-100(Cr) framework.

MIL-100(Cr)									
type	Cc	Co	Ch	Oc	O3	Cr(1)	Cr(2)	Hc	F
<i>q</i> /u.e	-0.0282	0.6008	-0.1142	-0.5062	-0.2602	1.1658	1.0310	0.1378	-0.4692

Table S1: Partial charges for all the atoms of the MIL-101(Cr) framework. The labels are described in Figure S5

7. Thermodynamic Simulations

The ideal adsorbed solution theory (IAST) was presented by Myers and Prausnitz.^{5a} In this model, the mixture adsorption equilibrium is predicted on the basis of pure component isotherms only. The basic equation for IAST has the following form:

$$p y_i = x_i p_i^0(\pi) \quad (1)$$

It describes the equilibrium between a perfect gas phase and an ideal adsorbed phase. In this equation *p* is the mixture pressure, *y_i* and *x_i* are the gas phase and the adsorbed phase molar fractions for

component i respectively and p_i^0 is the equilibrium gas phase pressure of the pure component i corresponding to mixture temperature and spreading pressure (π), i.e. in the standard state. The standard state is defined by the equality of the spreading pressure for each component to the mixture spreading pressure.

The spreading pressure of component i can be calculated by the Gibbs adsorption isotherm as follows:

$$\frac{\pi_i^0 A}{RT} = \int_0^{p_i^0} \frac{q_i^*(p_i^*)}{p_i^*} dp \quad (2)$$

q_i^* and p_i^* are related to pure component adsorption isotherms. So, in order to solve simultaneously equations (1) and (2) for determining x_i for given y_i and p , we need an expression representing the single component isotherm. Different classic expressions can be used. In this work, the multi-sites Langmuir equation is chosen.

Finally, the total numbers of adsorbed moles is determined by:

$$\frac{I}{q_t} = \sum_i^N \frac{x_i}{q_i^0(p_i^0)} \quad (3)$$

where N is the number of components in the mixture and $q_i^0(p_i^0)$ is the pure gas adsorbed quantities at pressure p_i^0 obtained from single component isotherm.

If the adsorbed phase is non ideal (Real Adsorbed Solution Theory, RAST), it is necessary to take into account the non ideality of adsorbed phase by the mean of the activity coefficients, $\gamma_i(\pi)$, which are functions of spreading pressure:

$$p y_i \phi_i = x_i p_i^0(\pi) \gamma_i(\pi) \quad (4)$$

In the equation (4), the non ideality of gas phase is also taken into account. Peng-Robinson equation of state⁶ is then used to determine fugacity coefficient ϕ_i

Moreover the total amount adsorbed includes also an excess term^{5b}

$$\frac{I}{q_t} = \sum_i^N \frac{x_i}{q_i^0(p_i^0)} + \frac{I}{q^{ex}} \quad (5)$$

All excess terms can be deduced from excess Gibbs free energy. So in order to apply RAST in a thermodynamic way, we use the following form of excess Gibbs free energy given by Siperstein and Myers^{5c} which takes account of the spreading pressure dependence of the excess terms

$$g^{ex} = (\alpha_0 + \alpha_1 T) x_1 x_2 (1 - e^{-C\psi}) \quad (6)$$

With $\psi = \frac{\pi A}{RT}$

where A is the specific surface area.

As we work with isothermal data, the α_0 and α_1 parameters are replaced by the parameter α . Thus, the

equation 6 becomes:

$$g^{ex} = \alpha x_1 x_2 \left(1 - e^{-c\psi}\right) \quad (7)$$

The binary parameters are determined using binary experimental data. With a first approximation of these parameters and the experimental values of pressure, temperature and gas composition, the partial amount adsorbed (q_i^{sim}) is determined by the resolution of RAST. Then, these quantities are compared with the experimental ones (q_i^{exp}). The binary parameters are determined by minimization of the following objective function:

$$\left(q_i^{exp} - q_i^{sim}\right)^2 \quad (8)$$

7. Pure absolute experimental isotherms of CO₂ and CH₄ on MIL-100(Cr)

Adsorption isotherm measurements were performed on a built-in house apparatus based on a high-pressure magnetic suspension balance marketed by Rubotherm. This system allows to separate the microbalance (resolution: 10 µg) from the adsorption chamber in which can stand both high pressure and temperature, and corrosive operating conditions. The magnetic system couples an electromagnet linked to the balance with a permanent magnet linked to the crucible containing the adsorbent. Moreover, it avoids subcritical gases condensation. This apparatus allows to perform experiments in a wide range of temperatures (243 – 393 K) and pressures (from vacuum to 150 bar). The related information about the apparatus and the set-up have been described in details in our previous studies.⁷

Prior to each adsorption measurement, the sample of MIL-100(Cr) was regenerated by heating under secondary vacuum (10^{-5} mbar). Like in volumetric co-adsorption measurements the sample was outgassed at 523 K for 16 hours under secondary vacuum.

The sample mass variations m_{meas} (g) at different pressures were measured when the thermodynamic equilibrium was reached. For our criterion, four of the five last mass measurements (noticed each 5 min) were included in 50 µg intervally. The buoyancy effect of the gas phase on the adsorbent volume V_{ads} was then corrected to determine the excess adsorbed amount,

$$m_{ads} = m_{meas} + \rho_{gas} V_{ads} \quad (9)$$

The gas phase density was determined using an appropriate equation of state (EOS). The adsorbent volume V_{ads} is evaluated by direct helium buoyancy effect measurement according to the fact that helium does not adsorb at high pressure (range from 10 bar to 100 bar). Helium density was calculated using a modified Benedict-Webb-Rubin EOS.⁸ The pressures were measured with two pressure transmitters (MKS Baratron up to 13.33 bar for adsorption measurement at low pressure and Endress-Hauser up to 100 bar). Maximum measurement error on adsorption isotherm measurement is evaluated to 0.5 % of adsorbed measured quantities with an interval of confidence of 95%. The EOS used for

buoyancy effect correction is of Helmholtz type.⁹

The experimental excess amounts have been converted into the absolute values, using the pore volumes measured for the sample outgassed at the corresponding temperature.

8. Langmuir multi-sites model

The isotherm parameters estimated by non-linear regression are obtained by minimizing the following objective function:

$$O.F. = (q_{sim} - q_{exp})^2 \quad (10)$$

Those parameters are found in Table 2. In order to compare the correlation results and the experimental data, the deviation parameter on the adsorbed amount is also provided in Table S2. It is calculated as follow:

$$D = \frac{100}{k} \sum_{j=1}^k \left| \frac{Q_j^{exp} - Q_j^{sim}}{Q_j^{exp}} \right| \quad (11)$$

Where k is the number of data, Q_j^{exp} are the experimental adsorbed amounts and Q_j^{sim} are the correlation adsorbed amounts.

CH ₄		CO ₂					
q _s (mmol/g)	b (1/kPa)						
8.7254	0.0289	1.8263	49.4316	1.5672	0.9976	23.3604	0.0357

Table S2. Adsorption isotherm parameters and deviation factors for CO₂ and CH₄ on MIL-100 (Cr) at 303.15 K.

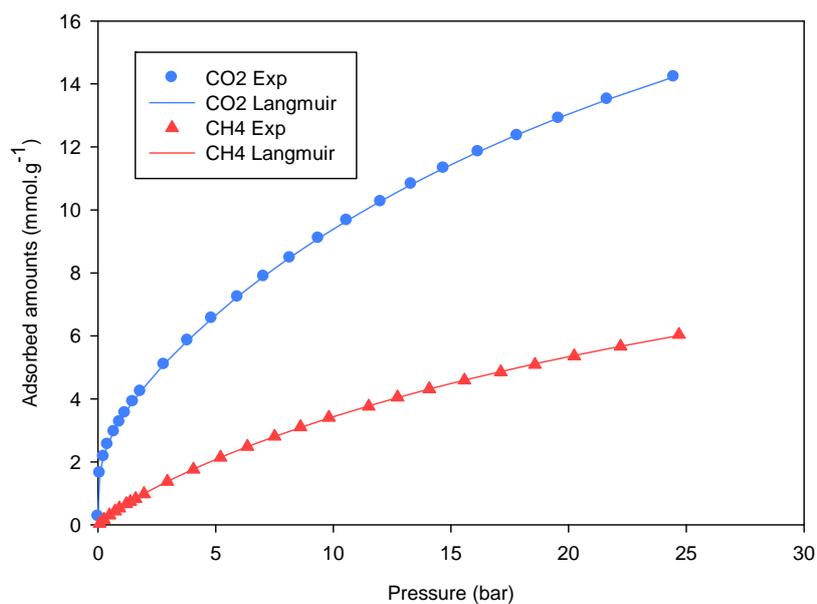


Figure S6. Experimental and Langmuir fitted isotherms on MIL-100 (Cr) at 303K.

9. Experimental differential enthalpies of adsorption of CO₂ and CH₄ in MIL-100(Cr).¹⁰

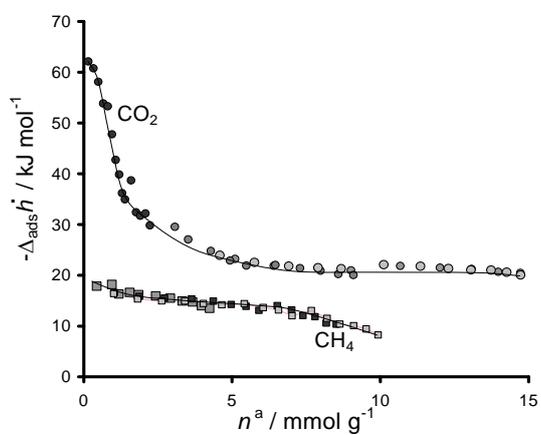


Figure S7. Differential enthalpies of adsorption of carbon dioxide and methane on MIL-100(Cr) at 303K.

10. Comparison between the GCMC simulated absolute adsorption isotherms for the pure CO₂ and CH₄ on the MIL-100(Cr) and the experimental measurements.

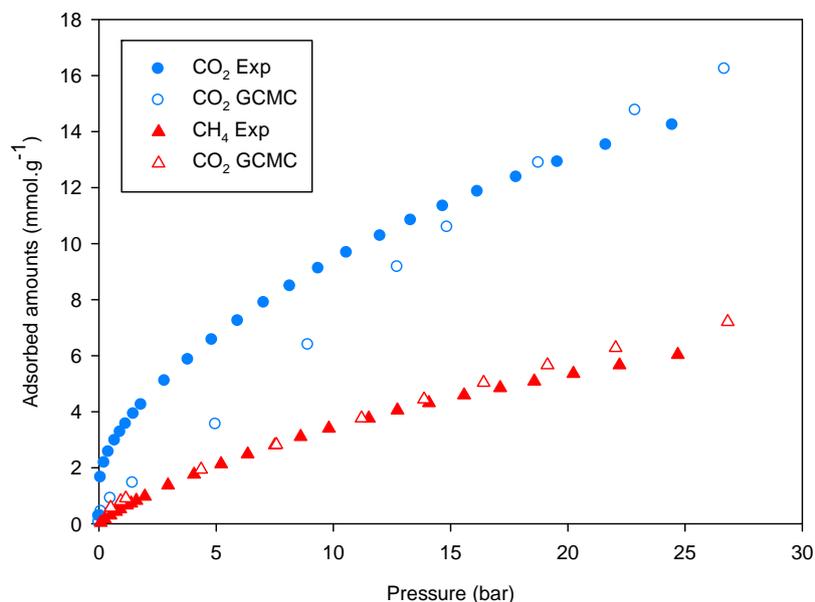


Figure S8. Experimental and GCMC simulated isotherms on MIL-100(Cr) at 303K.

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