

# Adsorption of Hydrogen, Methane, CO<sub>2</sub> and their Binary Mixtures in Silicalite-1: Role of Pore Characteristics Revealed by Molecular Simulations

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## SUPPLEMENTARY INFORMATION

### Force-Field parameters

As stated in the main article this work used ClayFF [SR1] force-field to represent the adsorbent models and different force-fields to represent the hydrogen, methane and CO<sub>2</sub> molecules [SR2, SR3, SR4]. The simulations used the following expression for the interaction energy.

$$U_{ij} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (\text{S1})$$

where  $\varepsilon_{ij}$  is the depth of the potential well,  $\sigma_{ij}$  is the distance at which the intermolecular potential between the atoms  $i$  and  $j$  becomes zero, the van der Waals radius, and  $r_{ij}$  is the distance between atoms  $i$ , and  $j$ ,  $q_i$  and  $q_j$  are the charges of the  $i$  and  $j$  atoms. The parameters  $\varepsilon_{ii}$  and  $\sigma_{ii}$  and  $q_i$  for the like pairs ( $i=j$ ) of different atoms and different force-fields are provided in Tables S1 and S2. The parameters for unlike pairs ( $i \neq j$ ) are obtained using the following mixing rules.

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} * \varepsilon_{jj}} \quad (S2); \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (S3)$$

Table S1. Force-field parameters of adsorbent atoms in ClayFF and TraPPE-UA formalism

| Atom           | $\varepsilon_{ii}$ (kJ/mol) | $\sigma_{ii}$ (Å) | $q_i$ (q/e) |
|----------------|-----------------------------|-------------------|-------------|
| Si             | 0.000008                    | 3.301             | +2.10       |
| O              | 0.650198                    | 3.166             | -1.05       |
| M <sup>a</sup> | 1.231000                    | 3.730             | 0           |

<sup>a</sup> Atom M is the pseudo-atom representing the immobile methane molecule that is used to block the pores oxygen belonging to the hydroxyl group that it forms with the H atom.

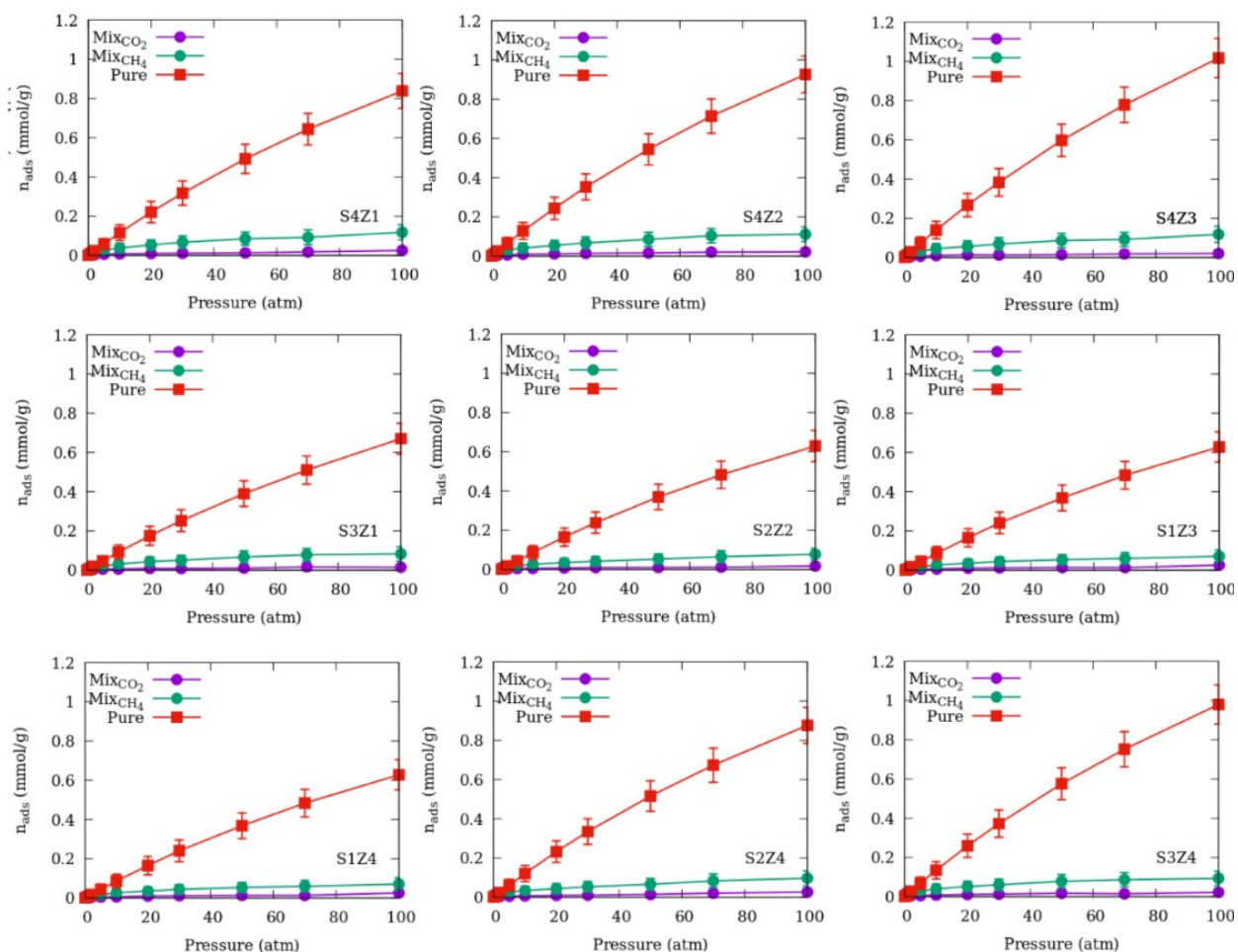
Table S2. Force-field parameters of the adsorbate in different force-fields

| Molecule        | Atom/Pseudo-atom | $\varepsilon_{ii}$ (kJ/mol) | $\sigma_{ii}$ (Å) | $q_i$ (q/e) |
|-----------------|------------------|-----------------------------|-------------------|-------------|
| Hydrogen        | H <sub>2</sub>   | 0.28435                     | 2.96              | 0           |
| Methane         | CH <sub>4</sub>  | 1.23100                     | 3.73              | 0           |
| CO <sub>2</sub> | C                | 0.22400                     | 2.80              | 0.7         |
|                 | O                | 0.65700                     | 3.05              | -0.35       |

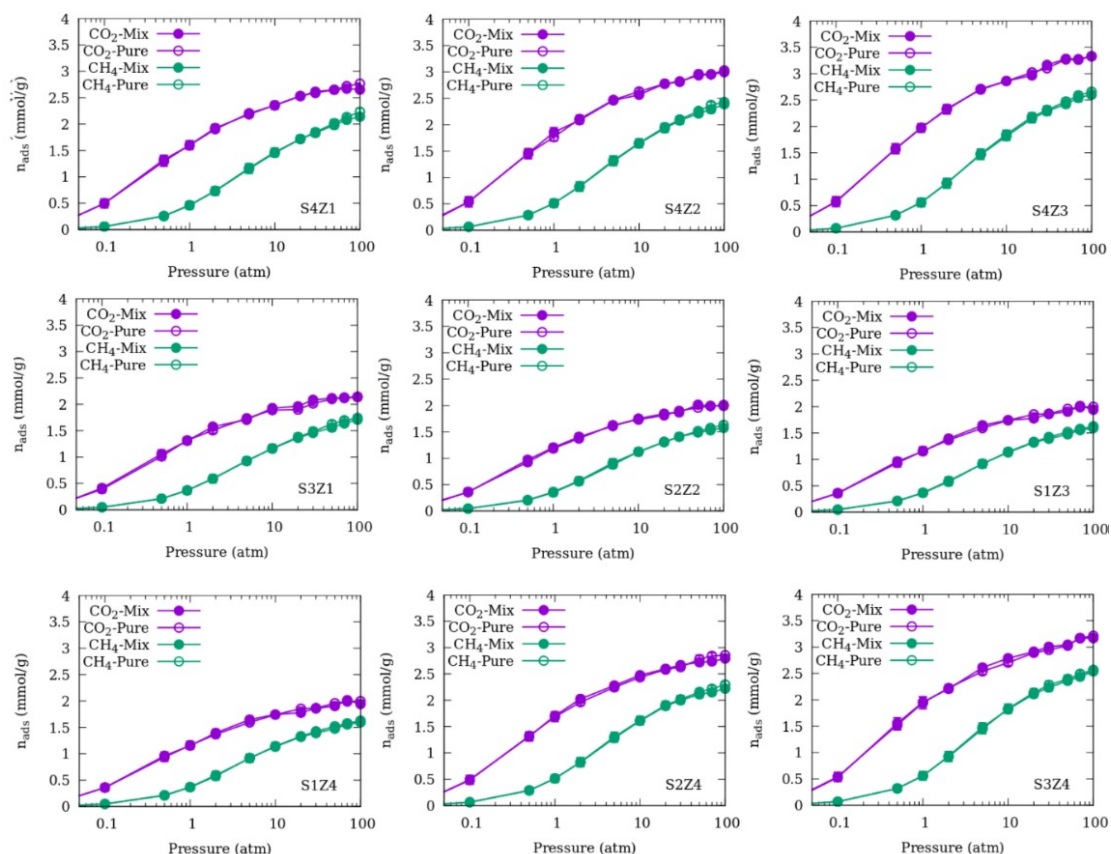
To see if incorporating the linear structure and the quadrupole moment of hydrogen molecule affects the adsorption of hydrogen in presence of the carbon fluids, a small subset of the mixture adsorption simulations in unmodified silicalite was carried out with hydrogen modeled using the force-field proposed by Darkrim and Levesque [SR5]. Hydrogen modeled in this formalism consists of three colinear sites – two extremities (H<sub>e</sub>) at a distance of 0.74 Å from each other and a central site (H<sub>m</sub>) placed at the center. Masses of H<sub>e</sub> and H<sub>m</sub> are 1 amu and 0 respectively. Partial charges of +0.468 e are attached to each of the extremities (H<sub>e</sub>) while H<sub>m</sub> has a partial charge of -0.936. The van der Waal interactions of this molecule is concentrated at H<sub>m</sub> with Lennard-Jones parameters  $\varepsilon = 0.30514$  kJ/mol and  $\sigma = 2.958$  Å.

## Adsorption isotherms and effects of pore characteristics

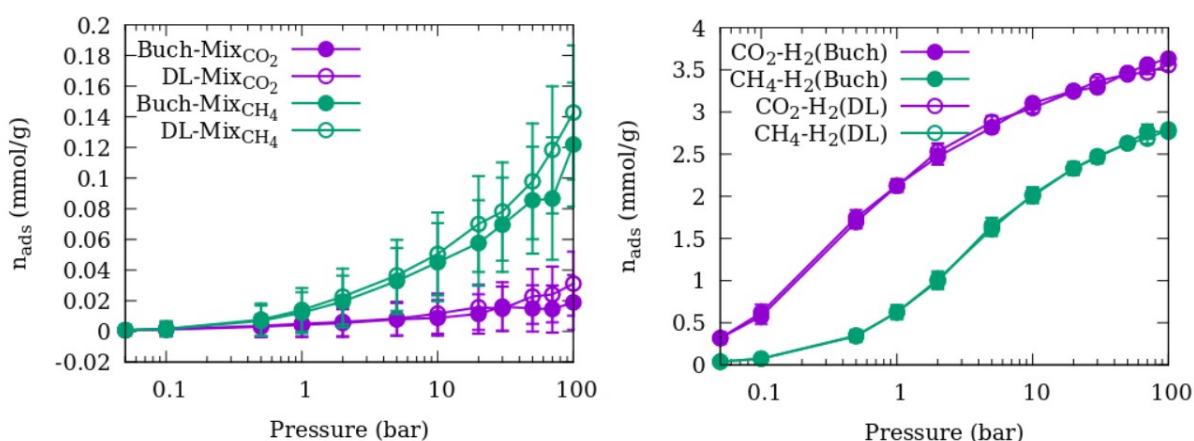
The complete adsorption isotherms of the 9 adsorbents not shown in the main article are shown here in Figures S1 (for hydrogen) and S2 (for carbon fluids)



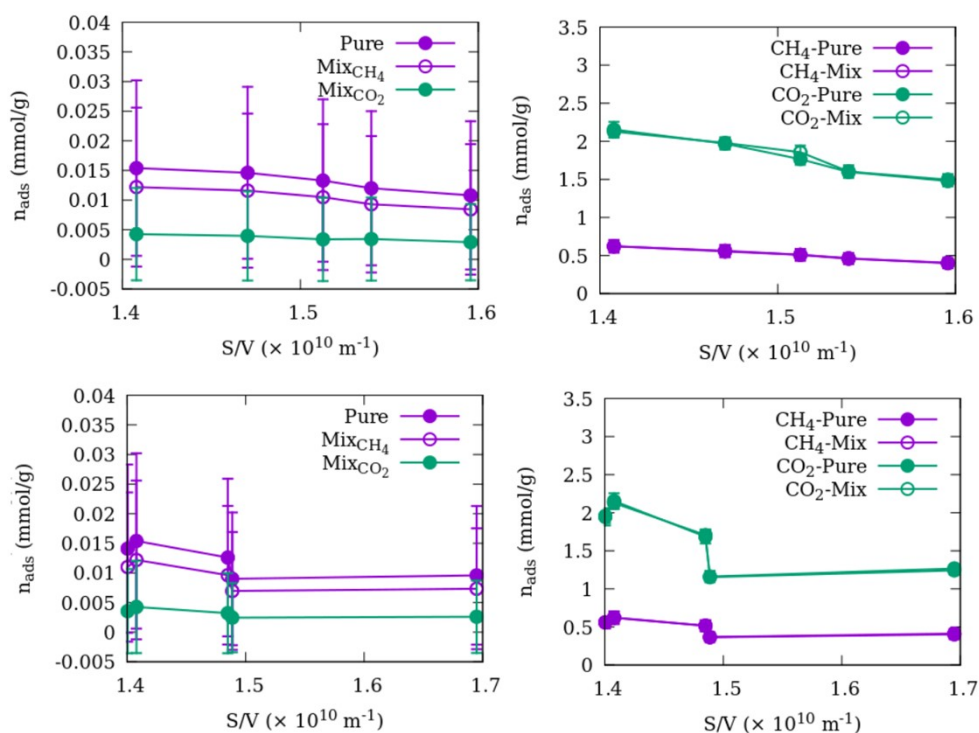
**Figure S1** Simulated adsorption isotherms of hydrogen in nine adsorbents based on silicalite as indicated. Data corresponding to both pure fluid adsorption and hydrogen in the mixture with methane or  $\text{CO}_2$  is shown for comparison.



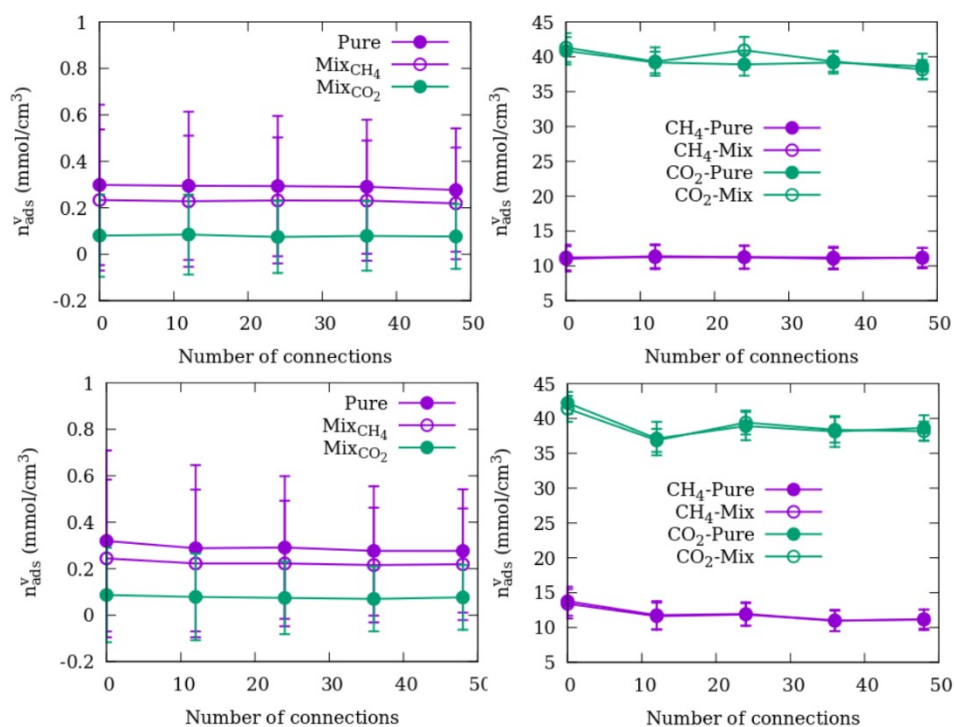
**Figure S2** Simulated adsorption isotherms of the carbon fluids in nine adsorbents based on silicalite as indicated. Data corresponding to both pure fluid adsorption and the carbon fluids in the mixture with hydrogen are shown for comparison.



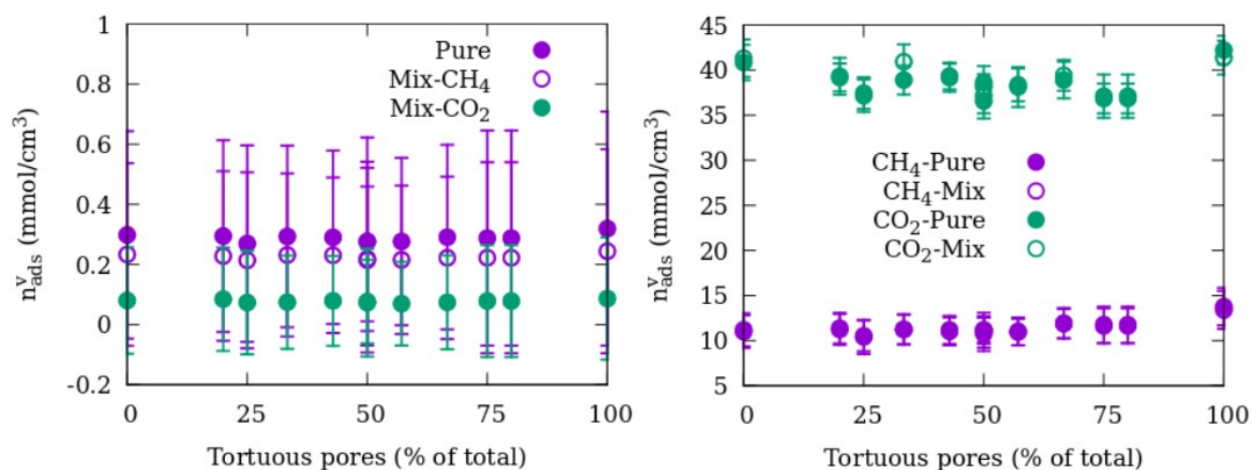
**Figure S3** Adsorption isotherms of hydrogen (left) and the carbon fluids (right) in S4Z4 when hydrogen in the mixture adsorption is modeled using the force-field proposed by Buch (solid symbols) or Darkrim and Levesque (open symbols).



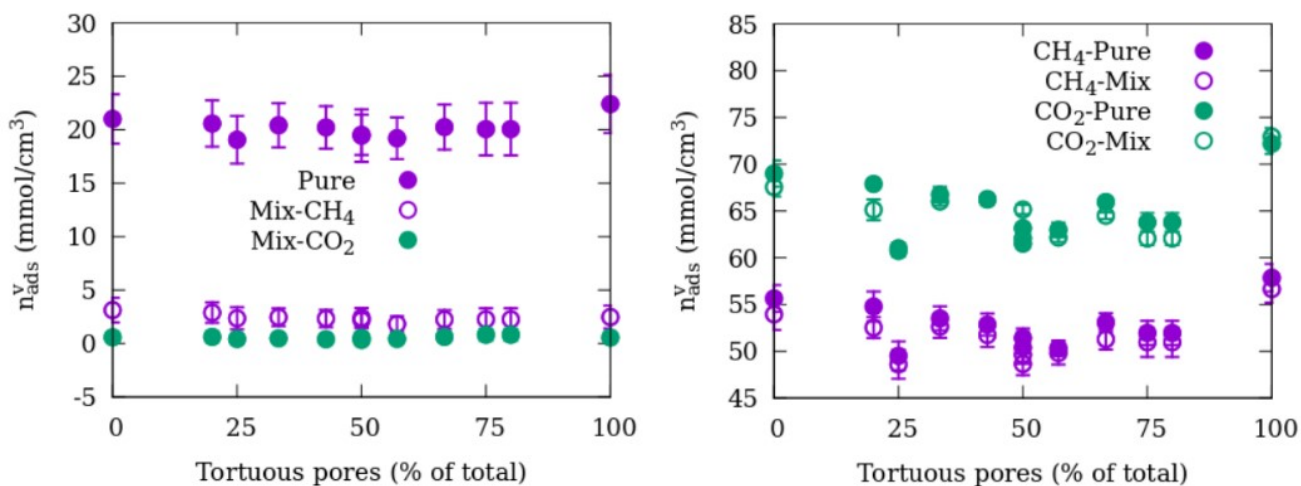
**Figure S4** Variation of adsorption amounts of hydrogen (left) and carbon fluids (right) at 1 atm with  $S/V$  of the adsorbents. The top panels show the data for S-major adsorbents while the data for Z-major adsorbents are shown in the bottom panels.



**Figure S5** Variation of adsorption amounts of hydrogen (left) and carbon fluids (right) at 1 atm with the number of pore connections in the adsorbents. The top panels show the data for S-major adsorbents while the data for Z-major adsorbents are shown in the bottom panels.

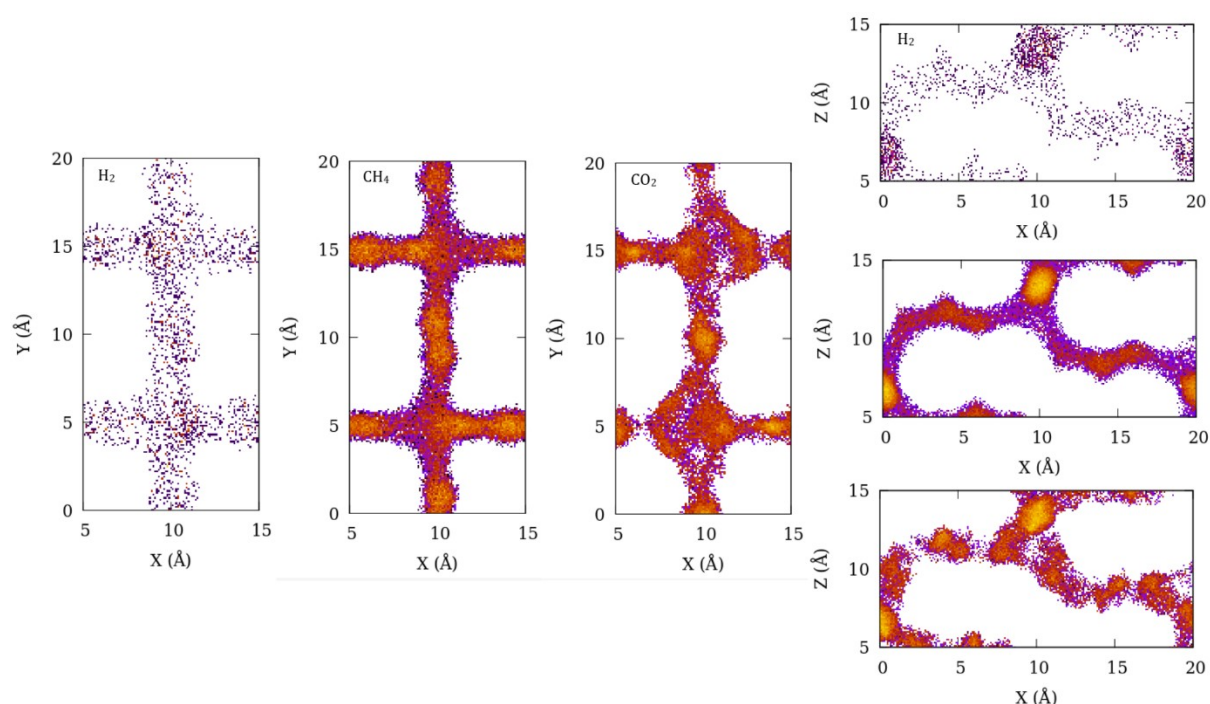


**Figure S6** Variation of adsorption amounts of hydrogen (left) and carbon fluids (right) at 1 atm with the percentage of tortuous pores.



**Figure S7** Variation of adsorption amounts of hydrogen (left) and carbon fluids (right) at 100 atm with the percentage of tortuous pores.

## Distribution of the adsorbate molecules in the adsorbent pores



**Figure S8** Probability distribution maps of the three fluid molecules in the straight (left vertical panels) and zigzag (right horizontal panels) channels of S4Z4 at 1 atm. The intensity represents the probability of finding a molecule at a given location and varies logarithmically between lower probabilities represented by bluer hues and higher probabilities represented by yellower hues. White regions represent zero probability.

## REFERENCES

- [SR1] Cygan, R. T., Liang, J. J., & Kalinichev, A. G. (2004). Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. *The Journal of Physical Chemistry B*, 108(4), 1255-1266.
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- [SR4] Potoff, J. J., & Siepmann, J. I. (2001). Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE journal*, 47(7), 1676-1682.
- [SR5] Darkrim, F., & Levesque, D. (1998). Monte Carlo simulations of hydrogen adsorption in single-walled carbon nanotubes. *The Journal of chemical physics*, 109(12), 4981-4984.