

Adsorption and separation of methane/hydrogen in octaphenylsilsesquioxane based covalently-linked organic-inorganic hybrid framework

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The adsorption and separation of CH₄/H₂ in two covalently-linked organic-inorganic hybrid frameworks polyoctaphenylsilsesquioxane (JUC-Z1) were computationally studied using the Grand Canonical Monte Carlo (GCMC) simulations. The results show that JUC-Z1 with Linde type A (LTA) and polycubane (zeolite code ACO) net topologies can adsorb up to 20.32, 18.57 mmol/g of CH₄ and 19.04, 17.89 mmol/g of H₂ at 298 K and 10 MPa, respectively. For the adsorption of binary mixture, the selectivity of CH₄ over H₂ in LTA-JUC-Z1 decrease gradually with the increase of the pressure or the CH₄ mole fraction of the mixture. As to ACO-JUC-Z1, the selectivity first increases at low pressure or CH₄ mole fraction, and then begins to decrease with the further increase of the corresponding amount. Anyhow, the two materials both exhibit excellent adsorption and separation capacities of CH₄/H₂.

Keywords adsorption and separation, selectivity, GCMC, octaphenylsilsesquioxane

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1 Introduction

Nanoporous materials have currently gained great attention because of their potential applications in gas storage [1–4], efficient separation [5–7], chemical catalysis [8–10], etc. Towards a use in gas storage or separation, they must have large enough specific surface area and suitable pore structure with desired size and shape. Moving in this direction, many researchers try their best to design and synthesize new materials, or develop already existing materials with specific properties both in the experiment and theory [11–15]. Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are two typical candidates that possess the characteristics required.

MOFs are 3D crystalline porous coordination materials that are built from metal clusters and organic ligands [4, 16]. Meanwhile, special framework topologies and pore structures can be targeted through felicitous choosing and designing of metal nodes and organic bridging linkers [17–19]. Because of their exceptional charac-

teristics, such as tunable porosity and high surface area, MOFs are regarded as excellent candidates for gas adsorption and separation. For example, by introducing various functionalities to the organic ligands of MOFs, Deng *et al.* found that both the adsorption amounts of pure components and the selectivity of mixtures of CO₂, CO, and H₂ can be highly improved [17]. At the same time, Martin-Calvo *et al.* performed a comprehensive investigation on adsorption and separation of natural gas in IRMOF-1 and Cu-BTC metal organic frameworks [20]. In addition, There are also many other studies on the adsorption and separation of gases in MOFs [18, 21–23]. However, some studies demonstrated that the coordination-bond based MOFs are vulnerable to humid air [24–26], which is a disadvantage for practical applications in gas storage and separation.

COFs are constructed from the light elements (H, B, C, N, and O, etc.) by the strong covalent bonds which form 1D, 2D, or 3D frameworks [27, 28]. Compared to MOFs, COFs exhibit many superior properties for gas adsorption and separation, such as lower den-

sity, larger surface area, better thermodynamic stability, among others. Hence, many studies were performed to explore COFs as gas storage and separation media [29–32]. Besides MOFs and COFs, many other porous materials have been also designed and prepared [2, 3, 6, 33–35]. However, none of them can satisfy all the requirements for the practical gas adsorption and separation application up to now. Therefore, to design, synthesize new materials and investigate their gas adsorption and separation capacity remains a pressing issue in the present situation.

Recently, a new class of organic-inorganic hybrid frameworks materials comprised of polyhedral oligomeric silsesquioxanes (POSS) and rigid organic linkers has been reported [36–41]. Among the POSS units, cube-octameric silsesquioxane Si_8O_{12} , commonly termed double four-ring (D4R), is of particular interest as an ideal chemical building block unit [39, 40]. Linking D4R by linear organic units along the octant directions can generate ideal LTA and ACO nets. Recently, various polyoctaphenylsilsesquioxanes have been synthesized by D4R and other linkers in experiment [37–40]. The high porosity of these frameworks makes them the excellent candidates as gas adsorption or separation media. However, due to the fact that getting experimental data of gas adsorption and separation is very complicated, few relevant experiments are reported. Hence, in the present work, we have investigated the adsorption and separation of CH_4/H_2 in two typical polyoctaphenylsilsesquioxanes, LTA-JUC-Z1 and ACO-JUC-Z1 [37], using the molecular simulation method. Here, the LTA or ACO implies that the corresponding framework is built from the D4R cages with the LTA or ACO net topology, respectively.

2 Materials and methods

2.1 JUC-Z1 structures

The structures of $2 \times 2 \times 2$ supercells of LTA-JUC-Z1 and

ACO-JUC-Z1 are shown in Figs. 1(a) and (d). Since there are no ready-made structural data for two frameworks [37], we built their ideal models in the Material Studio [42]. The construction process was conducted by the database of Euclidean Patterns in Non-Euclidean Tilings (EPINET) [43]. Then the energy minimization was performed using the force field method in the Forcite Plus module of Material Studio [42]. During the process of optimization, no symmetry restriction is imposed to modify the frameworks with rational bond lengths and angles. The final unit cells of LTA-JUC-Z1 and ACO-JUC-Z1 both belong to the cubic lattices with cell lengths of 22.92 Å and 18.84 Å, respectively. For comparison, the adsorption and separation of CH_4/H_2 are also simulated in MOF-5, the unit cell of which was constructed from the powder X-ray diffraction (PXRD) data [16].

As presented in Fig. 1(a), LTA-JUC-Z1 framework is comprised of two types of cages, marked by the yellow and blue spheres. Each small cage (yellow sphere) is comprised of eight triangle units [Fig. 1(b)] to form an octahedral cage structure. While the large cage (blue sphere) is comprised of eight triangle units [Fig. 1(b)] and six square units [Fig. 1(c)] to form a polyhedral cage structure. Every large cage is adjoined and surrounded by eight small cages, and vice versa. Compared to the LTA-JUC-Z1, the ACO-JUC-Z1 framework is simple, formed just by linking the D4R and biphenyl with the ACO net topology [see Fig. 1(d)]. The yellow spheres in the ACO-JUC-Z1 framework mark the void space in this framework. The structural characteristics of MOF-5 have been discussed elsewhere [23], and we do not illustrate it here.

2.2 Force fields

During the GCMC simulations, the Van der Waals (VDW) interactions between the adsorbate molecules and the adsorbent frameworks were calculated by the 12-6 Lennard-Jones (LJ) potential, $U_{\text{LJ}} = -4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^6 - (\sigma_{ij}/r_{ij})^{12}]$. All the cross-interaction parameters between the different types of atoms were

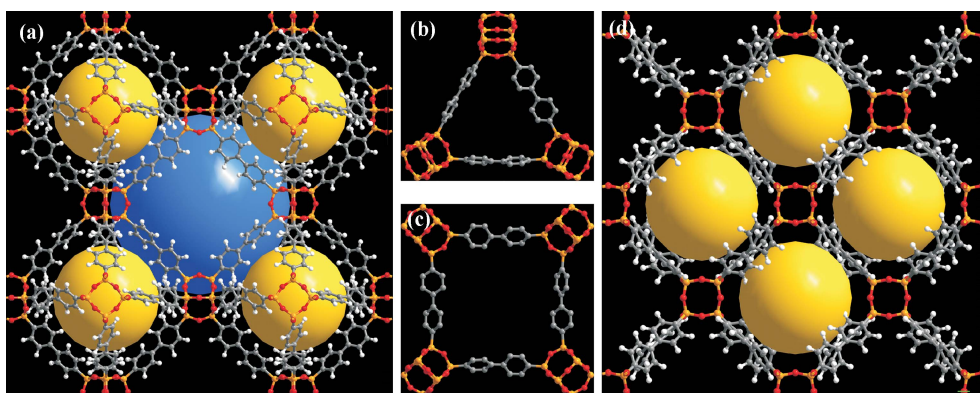


Fig. 1 The $2 \times 2 \times 2$ supercells of (a) LTA-JUC-Z1 and (d) ACO-JUC-Z1, and two small units (b, c) extracted from the LTA-JUC-Z1 (Si: orange, O: red, C: gray, and H: white). The large yellow and blue spheres denote the void space in LTA-JUC-Z1 and ACO-JUC-Z1.

treated by Lorentz–Berthelot mixing rules, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\varepsilon_{ij} = (\varepsilon_{ii} \times \varepsilon_{jj})^{1/2}$. The potential parameters for the framework atoms were taken from the universal force field (UFF) of Rappe *et al.* [44]. A simple LJ interaction site model was used to stand for a CH₄ molecule, and the potential parameters were taken from the TraPPE force field [45]. H₂ molecule was treated as a triatomic molecule with two hydrogen atoms placed at two points with the H–H distance of 0.741 Å but without LJ potential parameters. A third pseudoatom is located at the mass center of the hydrogen molecule with the potential parameters of $\sigma_{\text{PA}} = 2.958$ Å and $\varepsilon_{\text{PA}}/k_{\text{B}} = 36.7$ Å [46]. This mode of hydrogen molecule is equivalent to the united atom mode, and the two added hydrogen atoms are just convenient to display the snapshots for the future. All the LJ potential parameters used in the present work are listed in Table 1.

Table 1 The LJ potential parameters for CH₄, H₂ molecules, and the framework atoms used in this work. Here, H₂ and PA₂ represent the hydrogen atom and pseudoatom in the model hydrogen molecule and CH₄ represents methane molecule.

	H ₂	PA ₂	CH ₄	C	H	O	Si	He
$\sigma/\text{Å}$	0	2.96	3.73	3.43	2.57	3.12	3.83	2.64
$\varepsilon/k_{\text{B}}/\text{K}$	0	36.70	148.00	52.84	22.14	30.19	202.27	10.90

2.3 Molecular simulation methods

The adsorption of pure methane, hydrogen components, and their mixture in LTA-JUC-Z1, ACO-JUC-Z1, and MOF-5 frameworks were calculated using the GCMC simulation with the multipurpose simulation code Music [47]. The gas-phase fugacity for methane and hydrogen were computed with the Peng–Robinson equation of state [48]. The $2 \times 2 \times 2$ supercells of the frameworks and periodic boundary condition for all the adsorbent materials were adopted. The frameworks were kept rigid with frozen atoms during simulation. The LJ interactions were evaluated with a spherical cut off of 12.8 Å. One Monte Carlo step consisted of three types of trial moves: insertion of a new molecule, deletion of an existing molecule, or translation of an existing molecule. The first 1×10^7 steps were used for equilibration, and the subsequent 1×10^7 steps were used to calculate the ensemble averages.

The pore volumes of these materials were estimated with the method proposed by Talu and Myers [49]. They suggested that the pore volume can be calculated by the amounts of helium molecules contained in a unit mass adsorbent (N_a) obtained from GCMC simulation at low pressures (P) and room temperature (T_0) with Eq. (1)

$$V_p = N_a k_{\text{B}} T_0 / P \quad (1)$$

where k_{B} refers to the Boltzmann constant. We used the same LJ parameters for Helium molecule with Talu and Myers [49]. The values of the parameters were also pre-

sented in Table 1.

For adsorption separation of binary mixtures, the selectivity for component A relative to component B is defined by Eq. (2):

$$S = (x_{\text{A}}/x_{\text{B}})/(y_{\text{A}}/y_{\text{B}}) \quad (2)$$

where x_{A} and x_{B} are the mole fractions of components A and B in the adsorbed phase, respectively, while y_{A} and y_{B} are the mole fractions of components A and B in the bulk phase, respectively.

3 Results and discussions

3.1 The validation of the methods

In order to validate the employed force fields and the simulation methods, simulated adsorption isotherms of CH₄ and H₂ on the MOF-5 at 298 K are compared to the experimental data. As shown in Fig. 2, our calculated results well reproduced the experimental results of the methane and hydrogen [50, 51]. Therefore, the force field based on the LJ potential and the simulation methods is rational and will be utilized for the future in the present work. The same force field parameters for the framework atoms and the gas molecules have also been widely used in other studies on gas adsorption in porous materials [52–55]. And their simulated results can well reproduce the experimental results. All these facts demonstrate the validity of study method used in this work.

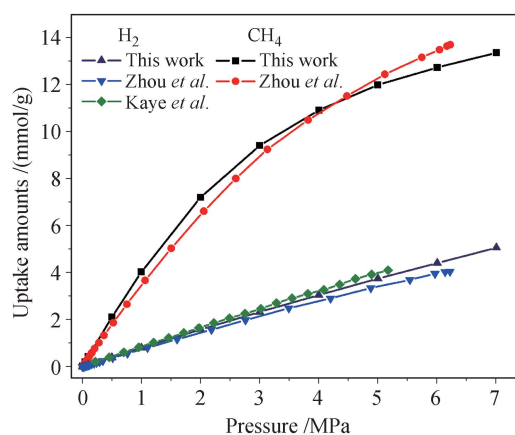


Fig. 2 Comparison of simulated and experimental adsorption isotherms of CH₄ and H₂ in MOF-5 at 298 K.

3.2 Adsorption of pure components

We first estimated the pore volumes for three porous materials by Eq. (1) with the helium adsorption amounts at the pressure of 0.01–0.1 MPa in 298 K. The calculated pore volumes for LTA-JUC-Z1, ACO-JUC-Z1, and MOF-5 are 2.04 cm³/g, 1.65 cm³/g, and 1.39 cm³/g, respectively. At the same time, the porosity percents in LTA-JUC-Z1, ACO-JUC-Z1, and MOF-5 are 86%, 83%

and 82%, respectively, which reflects that they are all high porosity materials. The different pore volumes of LTA-JUC-Z1 and ACO-JUC-Z1 are mainly attributed to the different net topology of two frameworks. The LTA net topology generates the larger pore size than ACO net topology during the forming of JUC-Z1 frameworks. Further, the two JUC-Z1 frameworks have the higher porosity than that of MOF-5. Hence, we inferred that they may own better gas adsorption and separation capacity consequently.

Methane and hydrogen adsorption isotherms of LTA-JUC-Z1, ACO-JUC-Z1, and MOF-5 were obtained at 298 K with the pressure up to 10 MPa, as shown in Fig. 3. The isotherms reflect that the adsorbed amount of CH_4 and H_2 increases gradually with the increasing pressure. It is noticeable that LTA-JUC-Z1 and ACO-JUC-Z1 can adsorb much more CH_4 and H_2 than MOF-5. Remarkably, at 10 MPa, the CH_4 (or H_2) uptakes in LTA-JUC-Z1, ACO-JUC-Z1, and MOF-5 are 20.32 mmol/g, 18.57 mmol/g, and 14.45 mmol/g (19.04 mmol/g, 17.89 mmol/g, and 6.85 mmol/g), respectively. The different gas adsorption capacities in these materials can be attributed to the fact that the material with larger pore volume can accommodate more gas molecules. From the results of pure gas adsorption, we conclude that the two new materials are excellent gas adsorption media for CH_4 and H_2 .

In order to understand the adsorption behaviors of CH_4 and H_2 gas in the two frameworks at a molecular level, we probed the snapshots of the LTA-JUC-Z1 and ACO-JUC-Z1 structures with adsorbed gas molecules. Four snapshots for LTA-JUC-Z1 with methane or hydrogen adsorbed are given in Fig. 4. Inferred from Fig. 4, the mechanism of gas adsorption in LTA-JUC-Z1 is the case as follows. The gas molecules are first adsorbed near the organic linkers in the small cages. Then they

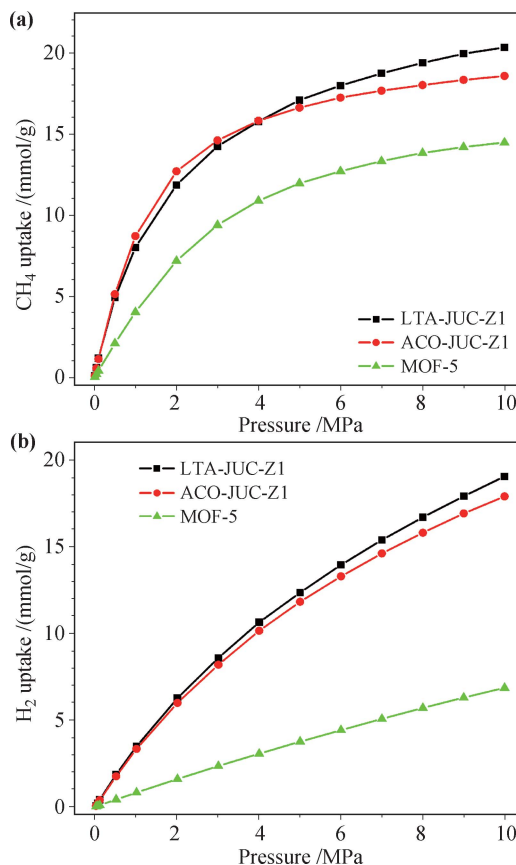


Fig. 3 The simulated adsorption isotherms of (a) CH_4 and (b) H_2 in LTA-JUC-Z1, ACO-JUC-Z1 and MOF-5 at 298 K.

are adsorbed near the organic linkers in the large cages, which meanwhile begin to saturate the small cages at the higher pressure. At last, they occupy the large cages with the further increase of the pressure. As to ACO-JUC-Z1 (see Fig. 5), the mechanism of gas adsorption is not so complicated. As shown in Fig. 5, the gas molecules first occupy the corner of the framework at low pressure. Then they cover the organic units at higher pressure, followed

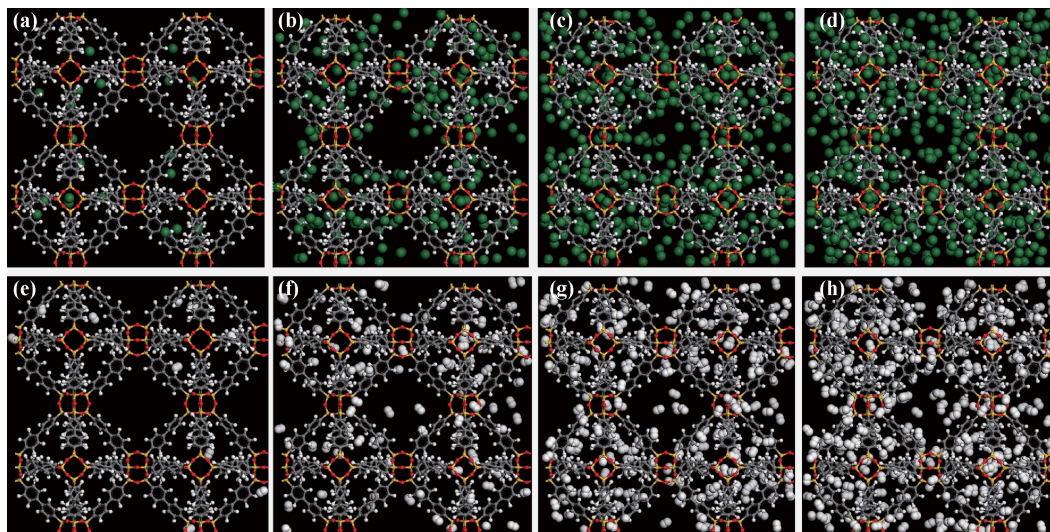


Fig. 4 Snapshots of the structures of LTA-JUC-Z1 with adsorbed CH_4 or H_2 at four pressures: (a, e) $P = 0.1$ MPa, (b, f) $P = 1$ MPa, (c, g) $P = 3$ MPa, and (d, h) $P = 5$ MPa. (Si: orange, O: red, C: gray, H: white, and CH_4 : green)

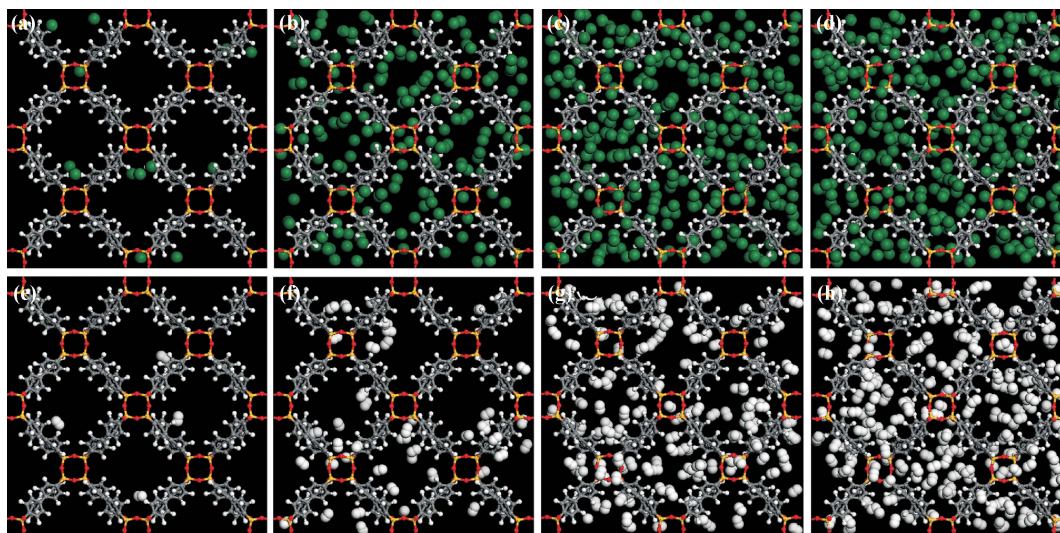


Fig. 5 Snapshots of the structures of ACO-JUC-Z1 with adsorbed CH₄ or H₂ at four pressures: (a, e) $P = 0.1$ MPa, (b, f) $P = 1$ MPa, (c, g) $P = 3$ MPa, and (d, h) $P = 5$ MPa. (Si: orange, O: red, C: gray, H: white, and CH₄: green)

by filling the channel space of the framework. These snapshots indicate that the adsorption process of gas in ACO-JUC-Z1 is more “homogeneous” than that of LTA-JUC-Z1.

3.3 Binary mixture separation

In this section, the effects of pressure and the gas composition on the selectivity of CH₄/H₂ for three materials at 298 K are discussed, respectively.

Figure 6 shows the GCMC simulated adsorption selectivity of CH₄/H₂ in three frameworks with three different gas compositions ($y_{\text{CH}_4}/y_{\text{H}_2} = 0.05:0.95$, $0.50:0.50$, and $0.95:0.05$) at 298 K with the pressure up to 10 MPa. Figure 6(a) reveals that the selectivity of CH₄/H₂ in LTA-JUC-Z1 decreases gradually with increasing pressure under all three gas compositions. On the other hand, the higher the CH₄ mole fraction, the faster does the selectivity decrease. On these grounds, we conclude that the LTA-JUC-Z1 is more appropriate to separate the CH₄ from H₂ at low CH₄ mole fraction and pressure. For the ACO-JUC-Z1, the case is very different. As can be seen in Fig. 6(b), the selectivity almost keeps unchanged with the increasing pressure of the mixture with $y_{\text{CH}_4}/y_{\text{H}_2}=0.05:0.95$. However, two different steps of selectivity exist in the mixture with $y_{\text{CH}_4}/y_{\text{H}_2}=0.5:0.5$ or $0.95:0.05$. The CH₄ selectivity first increases at low pressure and then begins to decrease with the further increase of the pressure. Further analyzing Fig. 6(b), we have found that the mixture with $y_{\text{CH}_4}/y_{\text{H}_2} = 0.95:0.05$ has the highest selectivity below the pressure of 3 MPa in ACO-JUC-Z1. While at the higher pressure (3–10 MPa), the mixture with $y_{\text{CH}_4}/y_{\text{H}_2} = 0.5:0.5$ has the highest selectivity. The change of selectivity in the MOF-5 is similar to that of the ACO-JUC-Z1 [see Fig. 6(c)], with merely a different at the changed ranges of the pressure.

The different performances of CH₄ selectivity can be explained by the different pore structures and surface areas of these materials. Among the three materials, LTA-JUC-Z1 owns more complicated net topology than ACO-JUC-Z1 and MOF-5. Duo to its complicated net topology, LTA-JUC-Z1 can provide more surface area for both CH₄ and H₂ at low pressure. However, ACO-JUC-Z1 and MOF-5 have net topologies with simply one type of pore structures, so they have a change of CH₄/H₂ selectivity similar to each other but different from that of LTA-JUC-Z1. To thoroughly investigate the effect of gas compositions on the selectivity, we have performed the simulations with a series of CH₄/H₂ compositions under three determined pressures (0.1 MPa, 2 MPa, and 10 MPa). The results are displayed in Fig. 7. For LTA-JUC-Z1 [see Fig. 7(a)], the mixture with the pressure of 0.1 MPa has the highest CH₄ selectivity, while the mixture with the pressure of 10 MPa has the lowest CH₄ selectivity. On the other hand, the cases for ACO-JUC-Z1 and MOF-5 are similar again [see Figs. 7(b) and (c)] and we simply discuss the case of ACO-JUC-Z1 typically. Figure 7(b) shows that when the mole fraction of CH₄ in the mixture is lower than 0.25, the mixture with the pressure of 10 MPa has the highest CH₄ selectivity in ACO-JUC-Z1. As the CH₄ mole fraction further increases, the mixture with the pressure of 2 MPa owns the highest CH₄ selectivity. All these results are consistent with the results in the previous part and so the discussions are valid.

In order to understand visually the structures of the materials with adsorbed binary mixture, the snapshots for the three materials with $y_{\text{CH}_4}/y_{\text{H}_2} = 0.5:0.5$ at 298 K and 2 MPa are shown in Fig. 8. For LTA-JUC-Z1, the CH₄ molecules mainly occupy the small cages, and the H₂ molecules sporadically scatter near the organic units in the large cages. As to ACO-JUC-Z1 and MOF-5, the CH₄ aggregate around the corner and the organic linkers,

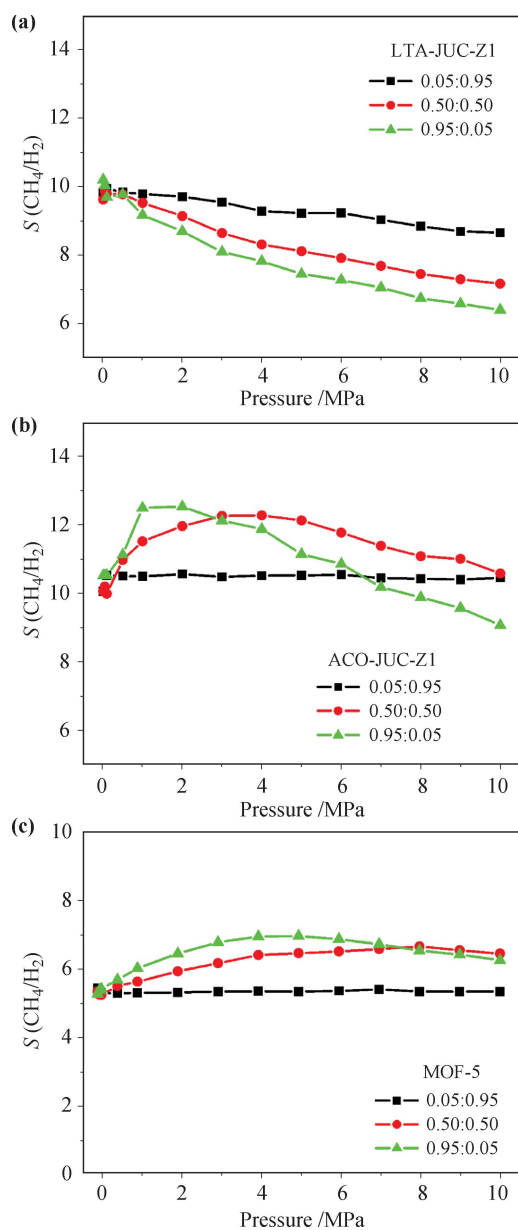


Fig. 6 Selectivity of methane over hydrogen for three different mixture ratio, $y_{\text{CH}_4}/y_{\text{H}_2} = 0.05:0.95, 0.50:0.50$, and $0.95:0.05$, in (a) LTA-JUC-Z1, (b) ACO-JUC-Z1, and (c) MOF-5 at 298 K and the pressure up to 10 MPa.

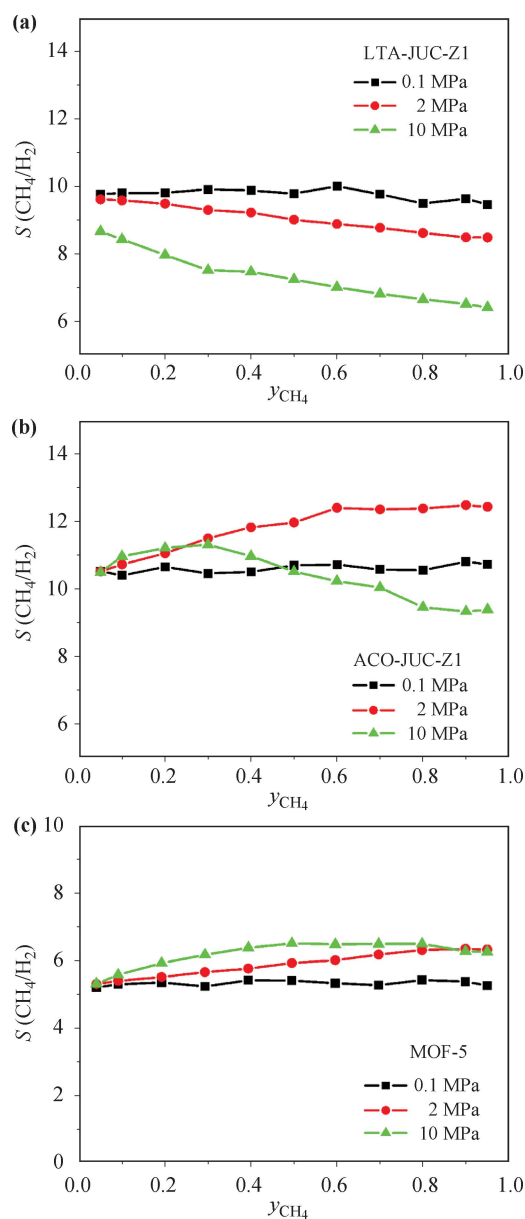


Fig. 7 Selectivity of methane over hydrogen for three different mixture pressure, $P = 0.1$ MPa, 2 MPa, and 10 MPa, in (a) LTA-JUC-Z1, (b) ACO-JUC-Z1, and (c) MOF-5 as the change of CH_4 ratio in the mixture at 298 K.

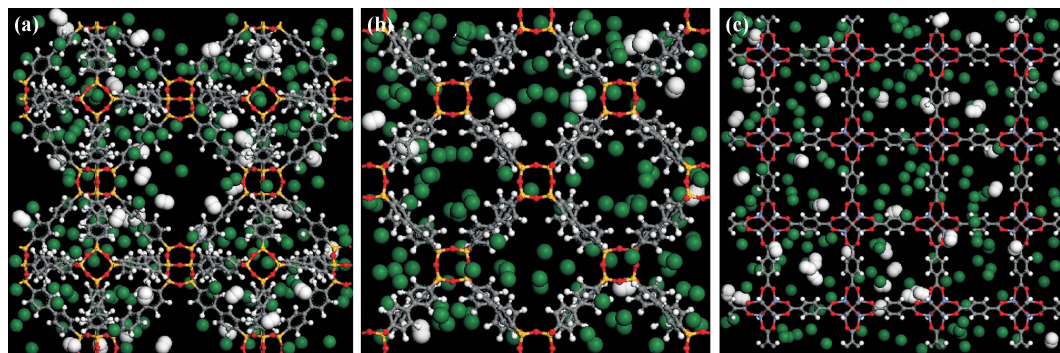


Fig. 8 Snapshots of the structures of (a) LTA-JUC-Z1, (b) ACO-JUC-Z1 and (c) MOF-5 with adsorbed CH_4 and H_2 at the pressure of 2 MPa. (Si: orange, O: red, C: gray, Zn: blue, H: white, and CH_4 : green)

with the hydrogen molecules sitting mainly in the channels or the interspaces of CH₄ molecules. The snapshots support the results discussed before once again. In addition, the selectivity of CH₄ over H₂ in three materials reflects that the separation efficiency of LTA-JUC-Z1 and ACO-JUC-Z1 is much better than that of MOF-5.

4 Conclusions

The present work shows that the two polyoctaphenylsilsesquioxane frameworks exhibit excellent potential as CH₄/H₂ adsorption and separation media at 298 K. Due to their different net topologies, LTA-JUC-Z1 and ACO-JUC-Z1 have different pore volume and porosity percentage, and hence, have different gas adsorption and separation characteristics. For LTA-JUC-Z1, the gas molecules are first adsorbed near the organic linkers, and then occupy the small cages, followed by accommodating the large cages. While for ACO-JUC-Z1, the gas molecules first aggregate near the corners and the organic linkers, and then fill the channels. Due to the different gas adsorption processes, the adsorption selectivity of CH₄ over H₂ for two frameworks displays different characteristics. This work not only reveals some adsorption and separation characteristics of LTA-JUC-Z1 and ACO-JUC-Z1, but also elucidates the underlying mechanisms at a molecular level. We hope that our study can supply some general design strategies of synthesizing new POSS based porous organic-inorganic hybrid materials with tailored properties for gas adsorption and separation.

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