Metal–Organic Frameworks

Extraordinary Separation of Acetylene-Containing Mixtures with Microporous Metal–Organic Frameworks with Open O Donor Sites and Tunable Robustness through Control of the Helical Chain Secondary Building Units


Abstract: Acetylene separation is a very important but challenging industrial separation task. Here, through the solvo-thermal reaction of Cul and 5-triazole isophthalic acid in different solvents, two metal–organic frameworks (MOFs, FJU-21 and FJU-22) with open O donor sites and controllable robustness have been obtained for acetylene separation. They contain the same paddle-wheel (Cu₂(COO)₄)₄ nodes and metal–ligand connection modes, but with different helical chains as secondary building units (SBUs), leading to different structural robustness for the MOFs. FJU-21 and FJU-22 are the first examples in which the MOFs’ robustness is controlled by adjusting the helical chain SBUs. Good robustness gives the activated FJU-22a, which has higher surface area and gas uptakes than the flexible FJU-21a. Importantly, FJU-22a shows extraordinary separation of acetylene mixtures under ambient conditions.

Introduction

Removal of acetylene from C₂H₂/C₂H₄ mixtures is an important and highly challenging industrial process.[1–5] Ethylene, the largest volume organic chemical, is widely used for the production of polymers. Ethylene produced in steam crackers typically contains on the order of 1% of acetylene,[6] which should be reduced to an accepted level in the ethylene feed before polymerization, because acetylene can poison Ziegler–Natta catalysts and also lower the resulting product quality.[7] Current approaches to remove acetylene include partial hydrogenation over a noble metal catalyst[8] and the solvent extraction of cracked olefins,[9] but both of these are cost and energy consumptive.

The emerging microporous metal–organic frameworks (MOFs)[10–13] based on physical adsorption are promising as cost-effective and efficient materials for gas separation, which has been a topic of interest because the ability to rationally design and chemically tune their architecture of the MOFs allows chemists to establish various methods to achieve highly selective gas adsorption.[10–29] Since the pioneering work of Kitagawa and co-workers,[14] some MOFs with high acetylene storage have been realized by using immobilized open metal sites (OMS).[30, 31] For C₂H₂/C₂H₄ separation, after the first work realized by using the flexible MOFs on the basis of metalloiligands in 2011,[32] the series of MOF-74[33] with high densities of open
metal sites and NOTT-300 with multiple weak supramolecular interactions were also employed. However, these three kinds of MOFs are not the ideal materials; the former exhibit very low acetylene uptake and the latter two show very low selectivity toward acetylene. A recent MOF, UTSA-100, containing amino groups is a unique example for actual column breakthrough experiments of C2H2/C2H4 mixtures, giving moderate selectivity and moderate acetylene uptake. Additionally, owing to the similar fluid properties of acetylene and CO2, the efficient separation of C2H2/CO2 mixture is another technologically interesting issue. A few MOFs and zeolites with relevant differences in capacity for C2H2/CO2 have been developed, mainly through tuning the cross-section size of the pore. To date, no MOFs or other porous materials have been found with actual C2H2/CO2 breakthrough experiments, except one hydrogen-bonded organic framework (HOF-3), however, this has low separation capacity. The MOFs for the separation of C2H2 mixtures have not been fully explored. It is still desirable to explore new ways to construct the MOFs with excellent performance for the challenging separations of C2H2/CO2 and C2H2/C2H4 mixtures.

In this work, through solvothermal reactions of 5-triazole isophthalic acid (H2L), CuI, and various solvents, two MOFs ([Cu(L)][DMF]/(H2O)2, (FJU-21, DMF = N,N-dimethylformamide) and ([Cu(L)][DMA]/(H2O)2), (FJU-22, DMA = N,N-dimethylacetamide) with open O donor sites and controllable robustness have been obtained for the highly selective separation of both C2H2/CO2 and C2H2/C2H4 mixtures. This was done on the base of the following considerations. (1) The remarkable difference between C2H2 and other adsors including CO2 and ethylene is the acidic hydrogen atoms at both ends of acetylene. Thus, the different framework flexibilities, different OMS and amino groups, and the open O donors can endow the MOFs with exclusive recognition ability for C2H2 through extra hydrogen-bonding interactions. (2) The use of 5-triazole isophthalic acid (H2L) containing one heterocyclic and two carboxylate groups to construct the MOFs may generate rich open O donor sites (without H riding) standing on the framework wall to recognize acetylene. (3) Solvent-induced structure diversity with controllable robustness may be observed to further control the acetylene separation capacity. As expected, the open O donors can provide the MOFs better recognition ability for C2H2 than other functional sites, including the OMS and amino groups. The activated FJU-22a with open O donors and good robustness exhibits extraordinary separation performances for both C2H2/CO2 and C2H2/C2H4 mixtures at ambient conditions as demonstrated by gas adsorption, breakthrough simulations, actual column breakthrough experiments, and first-principles calculations.

Results and Discussion

Solvent-induced structure diversity

Green needle-like crystals of FJU-21 could be obtained in DMF/H2O (3:2, v/v) mixed solvent at 85 °C for 1 day, and bulk crystals of FJU-22 could be obtained by the same method except that DMA was replaced by DMA. Single-crystal X-ray diffraction analyses reveal that FJU-21 and FJU-22 have the same metal nodes and metal–ligand connection modes (Figure 1). In each crystallographically independent unit, there is one CuII ion and one ligand. The CuII ion is fivefold coordinated by four oxygen atoms and one triazolyl N donor from five ligands and has a square-pyramidal coordination environment. Two CuII ions are bridged by four carboxylate groups to give a paddle-wheel node (PWN). The axial site of the PWN is occupied by triazolyl N donors. The ligand L employs its one triazole N and four carboxylate O atoms to link three PWNs. In FJU-22, the twist angle between the triazole ring and the plane of the benzene ring of the ligand in FJU-21 (b) and FJU-22 (i); the two kinds of helical chain SBUs of FJU-21 (c and d) along the b axis; the unique kind of helical chain SBUs with various pitches along the a and c axes in FJU-22 (j and k); the triazole-pillared [CuII(isophthalate)2] bilayers in the orientation of the (200) plane of FJU-21 (f); 3D framework of FJU-21 along the b axis (l) and 3D framework of FJU-22 view along the a and c axes (m and n). Color code: Cu, green; C, gray; O, red; N, blue.
Gas adsorption

To assess the permanent porosity, the N<sub>2</sub> sorption isotherms of the activated FJU-21a and FJU-22a materials were examined at 77 K (Figure 2), which yielded a reversible type I isotherm for the microporous nature of the samples with Brunauer–Emmett–Teller (BET) surface areas of 369.10 and 828.19 m<sup>2</sup> g<sup>−1</sup>, respectively. FJU-21a shows a bimodal pore size distribution centered at 5.2 and 8.7 Å, and FJU-22a has a distribution centered at 8.0 Å, as calculated by the non-local (NL)-DFT method; these values are close to the pore sizes determined from the crystal structures (Figure S1 in the Supporting Information). Although their void volumes from the Platon calculations are close, the BET surface area for FJU-21a, with the dynamic framework, is only about half that for FJU-22a. The flexible character of FJU-21 is further confirmed by a hysteresis loop in the N<sub>2</sub> adsorption isotherm at 77 K.

The unique pore structures encouraged us to examine the capacities of the two MOFs for gas adsorption. The low-pressure sorption isotherms of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were collected at 296 K (Figure S3 in the Supporting Information). Adsorption isotherms for C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> on FJU-21a are very similar to those for FJU-22a and the adsorption capacity follows the same hierarchy: C<sub>3</sub>H<sub>8</sub> > C<sub>2</sub>H<sub>6</sub> > C<sub>2</sub>H<sub>4</sub>. This phenomena may be attributed to the same pore surface structure resulting from the same metal node and ligand connection mode. However, the halved BET surface area for FJU-21a makes its various gas uptakes fall to half the corresponding values of FJU-22a. Furthermore, it is worth noting that the acetylene uptake isotherms for FJU-21a and FJU-22a at 296 K show a very sharp uptake at low pressure, whereas carbon dioxide uptake is much lower at this pressure. This discovery motivated us to examine their feasibility for the industrially important C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> separation.

C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> column breakthrough experiments

We first performed breakthrough simulations for a 50:50 (v/v) C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> mixture on FJU-21a and FJU-22a by using the established methodology. As shown in Figure S4 (in the Supporting Information), FJU-21a and FJU-22a are able to separate C<sub>2</sub>H<sub>4</sub> from the C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> mixture at room temperature. Clearly, FJU-22a, with good robustness, is more effective than FJU-21a for the C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> separation. Thus, we only studied the actual performance of FJU-22a in the experimental column breakthrough.

In the actual column breakthrough experiment, an equimolar C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> mixture was flowed over a packed column of the FJU-22a solid with a total flow of 5 cm<sup>3</sup> min<sup>−1</sup> at 296 K (Figure 3). CO<sub>2</sub> was detected after the gas mixture has been introduced into the column for about 12 min, whereas C<sub>2</sub>H<sub>4</sub> was not detected until a breakthrough time of 23 min was reached. Thus, the separation of C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> mixture gases through a column packed with FJU-22a solid can be achieved efficiently. The breakthrough times of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on the unique...
pore material HOF-3 were 5.5 and 9 min, respectively. From the breakthrough curve, the separation selectivity, $\alpha = \frac{q_1 y_2}{y_1 q_2}$, for FJU-22 a is 1.9, and close to 2.0 for HOF-3. However, FJU-22 a has a separation capacity of 44.13 cm$^3$ g$^{-1}$, which is much higher than the value of 25.54 cm$^3$ g$^{-1}$ for HOF-3. At the same separation conditions, FJU-22 a, with the open O donors, shows better performance than HOF-3, containing functional amino groups. FJU-22 a is the first example of a MOF whose separation of a C$_2$H$_2$/CO$_2$ mixture has been clearly established by column breakthrough experiments.

First-principles calculations

To further understand the C$_2$H$_2$ and CO$_2$ adsorption on FJU-22 a, detailed computational investigations were performed. We first optimized the bare FJU-22 a structure by first-principles DFT-D (dispersion-corrected density-functional theory) calculations, and then carried out Grand Canonical Monte Carlo (GCMC) simulations using the classical force-field method. Based on the probability distribution of adsorbed gas molecules generated from the GCMC simulations, we introduced C$_2$H$_2$/CO$_2$ accordingly into the FJU-22 a channel pore, and further optimized the structures using DFT-D. We found that the guest molecules are associated with particular adsorption sites. Upon adsorption, both C$_2$H$_2$ and CO$_2$ sit right at the small cage connecting the two adjacent channel pores (Figure 4 and Figure S5 in the Supporting Information). Although the linker triazole ring has van der Waals (vdW) interactions with C$_2$H$_2$, the relatively strong binding between C$_2$H$_2$ and FJU-22 a clearly comes from the hydrogen-bonding interactions between the C$_2$H$_2$ and the framework O (d(O(1)-C(2))=2.290 Å); this interaction does not exist between CO$_2$ and FJU-22 a and CO$_2$ adsorption in the structure is mainly vdW-type in nature. The static C$_2$H$_2$ and CO$_2$ binding energies for FJU-22 a, derived from the DFT-D calculations, are 33.3 and 22.6 kJ mol$^{-1}$, respectively. This difference in the gas/MOF framework interaction strength is likely the reason why the performance of separation for C$_2$H$_2$/CO$_2$ is outstanding in FJU-22 a at room temperature.
C$_2$H$_4$/C$_2$H$_2$ breakthrough experiments

The performance of FJU-22a for the removal of acetylene from C$_2$H$_4$/C$_2$H$_2$ mixtures containing 1% acetylene was examined through experimental column breakthrough in which a C$_2$H$_4$/C$_2$H$_2$ (1:99, v/v) mixture was flowed over a packed column of the FJU-22a solid with a total flow of 1.8 cm$^3$ min$^{-1}$ at 296 K. As shown in Figure 5, the separation of the C$_2$H$_4$/C$_2$H$_2$ mixture gases through a column packed with FJU-22a solid can be efficiently achieved, and the separation selectivity, $\alpha$, for C$_2$H$_4$/C$_2$H$_2$ is 25.8. The adsorption and separation data for C$_2$H$_4$ and C$_2$H$_2$ gases on FJU-22a and some representative MOFs are given in Figure 6 and Table S4 (in the Supporting Information). M’MOF-3a, with a flexible framework, exhibits relatively high separation selectivity (24.0), but very low acetylene uptake, because of narrow pores and high sieving effects.[5] High densities of open metal sites can significantly endow the series of MOF-74 with high acetylene uptakes, but their selectivities for C$_2$H$_4$/C$_2$H$_2$ separation are systemically quite low[11] as the open metal sites have quite strong interactions toward both ethylene and acetylene molecules. NOTT-300 has multiple weak supramolecular interactions aligned within the host to form an optimal geometry for the selective binding of hydrocarbons, but the selectivity toward C$_2$H$_4$/C$_2$H$_2$ is still very low.[6] The multiple supramolecular interactions in NOTT-300 include the hydrogen-bonding interactions between C(C$_2$H$_4$ or C$_2$H$_2$) and H-O(framework), which are clearly distinct from those between O(framework) and H-C(C$_2$H$_2$) in FJU-22a. The former cannot recognize acetylene and ethylene very well, whereas the latter endows FJU-22a with exceptionally high selectivity. UTSA-100a,[5] containing amino groups with dual functionalities to simultaneously bind acetylene and sieve ethylene, has a relative high selectivity, about five times that for MOFs containing OMS. It is worth noting that FJU-22a is isostuctural with UTSA-100. The enthalpies of acetylene adsorption on both MOFs are almost same, but the separation selectivity, $\alpha$, of FJU-22a is more than twice that for UTSA-100a, indicating that even in UTSA-100a (Figure S6 in the Supporting Information), the main contribution for its high selectivity toward acetylene may also come from the open O donor sites on the framework wall, rather than the amino groups. Conversely, the extra amino groups of UTSA-100a, to a certain extent, decrease its static C$_2$H$_4$ uptake. Despite its moderate static acetylene uptake, FJU-22a has the highest separation selectivity for the C$_2$H$_4$/C$_2$H$_2$ mixture among the reported porous materials. Based on the discussion above, open O donors on the pore wall can provide MOFs with better recognition for C$_2$H$_4$/C$_2$H$_2$ mixtures than the OMS and amino groups. FJU-22a is thus superior to the other MOFs, exhibiting highly efficient removal of acetylene from ethylene/acetylene mixtures containing 1% acetylene.

Conclusions

We have observed solvent-induced topological diversity enabling controllable robustness in two metal–organic frameworks (FJU-21 and FJU-22) and have demonstrated that microporous...
MOFs with open O sites are highly selective for the separation of $\text{C}_2\text{H}_2/\text{CO}_2$ and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ at ambient conditions. Control of the MOFs' robustness through tuning the helical chain SBUs is shown to be an efficient design approach for the first time. The good robustness of the activated FJU-22a, with open O donors, results in the extraordinary separation performance for mixtures of $\text{C}_2\text{H}_2/\text{CO}_2$ and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$; this performance is superior to all the reported MOFs including the flexible FJU-21a. The separation capacity of FJU-22a for 50:50 $\text{C}_2\text{H}_2/\text{CO}_2$ mixtures is about twice that of HOF-3, the unique example for separation before our experiments. The actual selectivity of FJU-22a for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixtures containing 1% $\text{C}_2\text{H}_6$ is highest among the reported porous materials. Such preferential adsorption for $\text{C}_2\text{H}_2$ by FJU-22a rather than $\text{CO}_2$ and $\text{C}_2\text{H}_4$ is attributed to the open O donor sites on its framework wall. Open O donors can provide MOFs with better recognition ability for $\text{C}_2\text{H}_6$ than other functional sites, including open metal sites (OMS) and amino groups. It is expected that extensive research endeavors on porous MOFs will facilitate the discoveries of better $\text{C}_2\text{H}_6$ separation materials.

**Experimental Section**

**General**

All reagents and solvents were used as received from commercial suppliers without further purification. Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851+ analyzer with a nitrogen flow and a heating rate of 10 K min\(^{-1}\) from 30°C to 600°C. Elemental analysis was collected with a Vario EL III elemental analyzer to give a ratio of C/H/N. Powder X-ray diffraction (PXRD) was carried out with a PANalytical X'Pert powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA over the 2θ range 5°–25°.

**Synthesis**

$\text{N,N-Dimethylformamide azine dihydrochloride (DMAz):}$ The DMAz used in this study was synthesized by a modified version of the method in refs. [42, 43]. Thionyl chloride (SOCl\(_2\); 28.6 mL, 0.4 mol) was added with stirring to DMF (150 mL) at 5°C. After addition, the mixture was stirred at room temperature for 0.4 s. Supercritical CO\(_2\) (SOCl\(_2\); 28.6 mL, 0.4 mol) was added slowly. After addition, the mixture was stirred at room temperature for 48 h and the white precipitate of $\text{N,N-dimethylformamide azine dihydrochloride}$ was collected by filtration and washed with DMF and diethyl ether. Yield: 19.1 g; m.p.: 251°C.

$\text{5-Triazole isophthalic acid (H}_2\text{L):}$ A mixture of $\text{N,N-dimethylformamide azine dihydrochloride}$ (4.0 g, 18.66 mmol) and 5-aminoisophthalic acid (3.38 g, 18.66 mmol) was heated in reflux in 1.2-dimethylbenzene (50 mL) for 16 h to obtain a white solid. The solid was filtered and washed with ethanol (2×15 mL) and diethyl ether (1×17 mL). Yield: 1.62 g, 37.3%.

$$\{[\text{Cu(L)}](\text{DMA})\text{(H}_2\text{O})_3\}_{\infty} \text{(FJU-21): A mixture of Cu(0.1 mmol, 0.0191 g), H}_2\text{L (0.1 mmol, 0.0223 g), DMF (3 mL), and H}_2\text{O (2 mL) was stirred for 10 min. Then, the solution was transferred to a 23 mL glass reactor and heated to 85°C. After 24 h, the system was cooled to room temperature and green needle-like crystals were obtained (32% yield with regard to H}_2\text{L}.$$


**Single-crystal X-ray structure determination**

Data collection and structural analysis of the crystals were collected on an Agilent Technologies SuperNova Single Crystal Diffra-ctometer equipped with graphite monochromatic Cu K\(_\alpha\) radiation (λ = 1.54184 Å). The crystal was kept at 293(10) K during data collection. Using Olex2,[44] the structure was solved with the Superflip structure solution program by using charge flipping and refined with the ShelXL refinement package by using least-squares minimization. The hydrogen atoms on the ligands were placed in idealized positions and refined by using a riding model. We employed PLATON/SQUEEZE[45] to calculate the diffraction contribution of the solvent molecules in FJU-21 and FJU-22 and thereby produce a set of solvent-free diffraction intensities. The formulae of the crystals were calculated by elemental analysis. The detailed crystallographic data and structure refinement parameters for these compounds are summarized in the Supporting Information, Table S1.

**Gas adsorption measurements**

A Micromeritics ASAP 2020 surface area analyzer was used to measure the gas adsorption. The sorption measurements were performed at 77 K with liquid nitrogen and at 273 K with an ice/water bath (slush). A water bath was used for adsorption isotherms at 296 K. DFT pore size distributions and pore sizes were calculated from the N\(_2\) adsorption at 77 K.

**Transient breakthrough simulations**

The performance of industrial fixed-bed adsorbers is dictated by a combination of adsorption selectivity and uptake capacity. For a proper comparison of various MOFs, we performed transient breakthrough simulations by using the simulation methodology.[46] For the breakthrough simulations, the following parameter values were used: length of packed bed, L = 0.3 m; voidage of packed bed = 0.4; superficial gas velocity at inlet, u = 0.04 m s\(^{-1}\). The framework density of FJU-21 is 1104 kg m\(^{-3}\) and for FJU-22 it is 1083 kg m\(^{-3}\).

**Column breakthrough test set-up, procedures, and measurements**

The mixed-gas breakthrough separation experiment was conducted at 296 K by using a laboratory-scale fixed-bed reactor. In a typical breakthrough experiment (Figure S7 in the Supporting Information) for the $\text{C}_2\text{H}_2/\text{CO}_2$ mixture, FJU-22 powder (1.2 g) was packed into a quartz column (5.8 mm I.D.×150 mm) with silica wool filling the void space. The sorbent was activated in situ in the column with a vacuum pump at 333 K for 24 h. A helium flow (5 cm\(^3\) min\(^{-1}\)) was introduced after the activation process to purge the adsorbent. The flow of He was then turned off while a gas mixture of $\text{C}_2\text{H}_2/\text{CO}_2$ (50:50, v/v) at 5 cm\(^3\) min\(^{-1}\) was allowed to flow into the column. The effluent from the column was monitored by...
using a mass spectrometer (MS). The absolute adsorbed amount of gas \(i\) (\(q_i\)) is calculated from the breakthrough curve by Equation (1):

\[
q_i = \frac{F_i t_s - V_{\text{dead}}}{m} \int_0^{t_r} F_i \Delta t
\]

(1)

in which \(F_i\) is the influent flow rate of the specific gas (cm\(^3\) min\(^{-1}\)), \(t_s\) is the adsorption time (min), \(V_{\text{dead}}\) is the dead volume of the system (cm\(^3\)), \(F_e\) is the effluent flow rate of the specific gas (cm\(^3\) min\(^{-1}\)), and \(m\) is the mass of the sorbent (g). The separation factor (\(\alpha\)) of the breakthrough experiment is determined as:

\[
\alpha = \frac{q_i y_i}{y_i q_i}
\]

(2)

Details of DFT-D calculations and GC/MS simulations

First-principles calculations based on density-functional theory were performed by using the PWSCF package. A semiempirical addition of dispersive forces to conventional DFT was included in the calculation to account for van der Waals interactions. We used Vanderbilt-type ultrasoft pseudopotentials and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation. A cutoff energy of 544 eV and a 2 \(\times\) 2 \(\times\) 2 \(\times\) sampling were sufficient for the total energy to converge within 0.5 meV per atom. We first optimized the bare FJU-22 structure. The optimized structure is fairly close to the experimental structure determined from XRD. \(\text{C}_2\text{H}_4\) or \(\text{CO}_2\) molecules were then introduced to the optimized HOF structure (guided by the GC/MS result), followed by a full structural relaxation. To obtain the gas binding energies, a free gas molecule placed in a supercell with the same cell dimensions was also relaxed as a reference. The static binding energy was then calculated by using: \(E_b = \langle \text{E(MOF)} + n\text{E(gas)} - \text{E(MOF + n gas)} \rangle/n\). Grand Canonical Monte Carlo (GCMC) simulations were performed for \(\text{C}_2\text{H}_4/\text{CO}_2\) adsorption on FJU-22 with the gas molecules and the MOF frameworks both treated as rigid bodies. A 2 \(\times\) 2 \(\times\) 2 \(\times\) supercell was used as the simulation box to ensure the simulation accuracy. A total of 2 \(\times\) 10\(^5\) steps were used for equilibration and an additional 2 \(\times\) 10\(^5\) steps were used to calculate the ensemble average of gas adsorption sites and thermodynamic properties. We used the standard universal force field (UFF) to describe the gas–framework interaction and the gas–gas interaction. Atomic partial charges derived from first-principles calculations were included in the simulation to account for electrostatic interactions. The cut-off radius used for the Lennard–Jones interactions is 12.8 Å. The long-range electrostatic interactions were treated by using the Ewald summation technique with tin–foil boundary condition. Simulations were performed at various temperatures and pressures. The probability distributions of adsorbed \(\text{C}_2\text{H}_4\) and \(\text{CO}_2\) were generated from the simulation after the equilibrium stage.

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