

Article

Exploring Methane Storage Capacities of $M_2(BDC)_2(DABCO)$ Sorbents: A Multiscale Computational Study

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Abstract: A promising solution for efficient methane (CH_4) storage and transport is a metal–organic framework (MOF)-based sorbent. Hence, searching for potential MOFs like $M_2(BDC)_2(DABCO)$ to enhance the CH_4 storage capacity in both gravimetric and volumetric uptakes is essential. Herein, we systematically elucidate the adsorption of CH_4 in $M_2(BDC)_2(DABCO)$ or $M(DABCO)$ ($M = Mg, Mn, Fe, Co, Ni, Cu, Zn$) MOFs using multiscale simulations that combined grand canonical Monte Carlo simulation with van der Waals density functional (vdW-DF) calculation. We find that, in the $M(DABCO)$ series, $Mg(DABCO)$ has the highest total CH_4 adsorption capacities, with $m_{tot} = 231.39$ mg/g at 298 K, for gravimetric uptake, and $V_{tot} = 231.43$ cc(STP)/cc, for volumetric uptake. The effects of temperature, pressure, and metal substitution on enhancing CH_4 storage are evaluated, and we predict that the volumetric CH_4 storage capacity on $M(DABCO)$ could meet the DOE target at temperatures of ca. 238 K–268 K and pressures of 35–100 bar. The interactions between CH_4 and $M(DABCO)$ are dominated by the vdW interactions, as shown by the vdW-DF calculations. The $Mg, Mn, Fe, Co,$ and Ni substitutions in $M(DABCO)$ result in a stronger interaction and thus, a higher CH_4 storage capacity, at higher pressures for $Mg, Mn, Ni,$ and Co and at lower pressures for Fe . This work may provide guidance for the rational design of CH_4 storage in $M_2(BDC)_2(DABCO)$ MOFs.

Keywords: methane storage; $M_2(BDC)_2(DABCO)$ sorbents; $M(DABCO)$ MOFs; CH_4 adsorption energies; CH_4 adsorption isotherms



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1. Introduction

Recently, the use of methane (CH_4) has received increasing attention as a potential fuel to resolve the global energy crisis and to mitigate greenhouse emissions [1–3]. This is because CH_4 exhibits a lower CO_2 emission and the highest H:C ratio. Moreover, CH_4 is abundant, as it is the major component of natural gas (about 85%) and is found in the emissions of fossil fuel combustion, caves, and deep rock wells. Therefore, CH_4 can provide an energy source for hundreds of years [4]. Although the energy from CH_4 is not entirely green like hydrogen, promising technologies for converting methane into basic chemicals will enable it to become a potential bridge fuel and the basis of organic substances in the future. Furthermore, methane can be obtained from synthesizing CO_2 and water, which contributes to reducing carbon emissions globally [4]. Nevertheless, the low energy density is a main drawback of employing CH_4 as a fuel in light-duty vehicles. The volumetric energy density of methane is nearly 900 times lower than that of gasoline at standard temperature and pressure (STP: the pressure of 1 atm and the temperature of

273.15 K) [5]. Sorbent-based technology is one potential solution to resolve this drawback and enhance the CH₄ storage efficiency [5]. For efficient storage and distribution, methane fuel technology needs to meet three objectives [2,6–8]: (i) a total gravimetric storage density of ($\geq 500 \text{ mg}_{\text{CH}_4} / \text{g}_{\text{sorbent}}$ or $700 \text{ cm}^3 / \text{g}$), (ii) a total container density of ($\geq 155 \text{ mg} / \text{cm}^3$ or $263 \text{ cc(STP)} / \text{cc}$), and (iii) a storage condition in the range of near ambient temperatures and moderate pressures (typical pressure is under 35 bar, but storage pressure is up to 65 bar). It is also important to note that when factoring in the 25% packaging loss, the capacity needs to reach $330 \text{ cc(STP)} / \text{cc}$ for the container [6]. Therefore, finding suitable sorbents for methane storage is attracting numerous researchers.

Among sorbents, metal–organic frameworks (MOFs) have received significant attention for CH₄ storage because they exhibit several prominent properties for CH₄ adsorption, e.g., high thermal and physical stability, changeable porosity, adjustable organic functionality, structural flexibility, and high-pressure resistance, etc. [2,9–11]. MOFs have been of interest in energy storage, especially methane storage, because of their significant enhancement of the volumetric density of methane [12].

Many works reported the methane storage capacity of sorbents, including MOFs, at room temperature [5,12–16]. Among them, several impressive MOFs recorded the highest CH₄ storage (gravimetric uptake or volumetric uptake) over time, such as Co₂(BPY)₃(NO₃)₄ (1997) [17], IRMOF-6 (2002) [18], HKUST-1 (2013) [6], Al-soc-MOF-1 (2015) [19], Cu-tbo-MOF-5 (2016) [20], and MFM-180 and MFM-185 (2017) [21]. Generally, at room temperature, the CH₄ storage in MOFs with outstanding gravimetric CH₄ uptake exhibits relatively low volumetric uptake or vice versa. So far, Al-soc-MOF-1 was reported to have the highest total gravimetric CH₄ storage capacity, with $579 (362) \text{ cm}^3 / \text{g}$ ca. $420 (263) \text{ mg} / \text{g}$ at 65 (35) bar. However, the volumetric uptake of CH₄ in Al-soc-MOF-1 was only $197 \text{ cc} / \text{cc}$ at 65 bar ($123 \text{ cc} / \text{cc}$ at 35 bar) [19]. It is speculated that an ultra-large pore volume and a high surface area of Al-soc-MOF-1 are responsible for its outstanding gravimetric CH₄ storage.

Shortening the organic linker in Al-soc-MOF-1 results in enhanced volumetric CH₄ storage due to the strengthening of the CH₄–MOF framework interaction. We noticed that the available data shows that gravimetric CH₄ uptake in MOF, with high surface area and pore volume, is always high, but its volumetric uptake is rather low due to a weak CH₄–MOF interaction (Table S1) [19,22–24]. In contrast, MOFs, having a moderate surface area and pore volume, show a high volumetric, but a limited gravimetric, uptake [8,25]. To date, only a few MOFs have simultaneously achieved high gravimetric and volumetric CH₄ storage capacities at room temperatures and moderate pressures under 100 bar. Some of the best MOFs that meet these criteria are NJU-Bai 43 [26], UTSA-76 [27], and UTSA-110a [28]. Therefore, finding MOFs that achieve both high gravimetric and volumetric adsorption simultaneously, at moderate temperature and pressure, is a challenging task.

The M₂(BDC)₂(DABCO) [M(DABCO)] MOFs are promising sorbents for many applications in the fields of gas storage and capture, including outstanding CH₄ storage capacity [29–35]. The M₂(BDC)₂(DABCO) consists of a metal node connected via the double ligands (BDC = benzene dicarboxylate and DABCO = 1,4-diazabicyclo [2,2,2] octane) (see Figure 1). BDC is among the most popular linkers for forming MOFs with simple cubic topologies [36]. Additionally, DABCO-containing materials are expected to exhibit unique physicochemical effects and properties [37]. So far, M(DABCO) with M = Zn, Co, Cu, Ni, and Fe has been successfully synthesized [38–42], in which M(DABCO) (M = Zn, Co, Cu, Ni) has shown high gravimetric and volumetric CH₄ sorption capacities at room temperatures (see Table S2) [38–41]; however, CH₄ adsorption in Fe(DABCO) has not yet been evaluated [42]. Although some experimental results have shown that M(DBACO) MOFs obtain high CH₄ adsorption capacity, the roles of metal substitution in enhancing CH₄ uptakes in both volumetric and gravimetric units remain elusive. Previous works show that metal substitution is an effective way to tune the CH₄ capacity in MOFs [5,43], as MOFs contain paddlewheel units, such as M-HKUST-1, and M₂(BDC)₂(TED) enhances CH₄ adsorption compared to many other MOFs, especially in regards to volumetric density [6,8,41,44]. Among paddle-wheel MOFs, the M-HKUST-1 series (M = transition metals or alkaline

earth metals) has been experimentally studied and theoretically predicted to exhibit potential for various applications, including gas adsorption [45–49]. More importantly, several available studies show that M-modified HKUST-1 ($M = \text{Mg}, \text{Mn}$) or porph@MOM MOFs ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$), having the same space group and topology as HKUST-1 with paddlewheel units, have been successfully synthesized, enhancing the efficiency of gas adsorption or gas reduction [50–53]. Meanwhile, research on metal-substituted M(DABCO) used to enhance CH_4 storage capacity has received less attention than has HKUST-1. We also note that experimentally, the CH_4 adsorption on available M(DABCO) is studied in a limited temperature and pressure range.

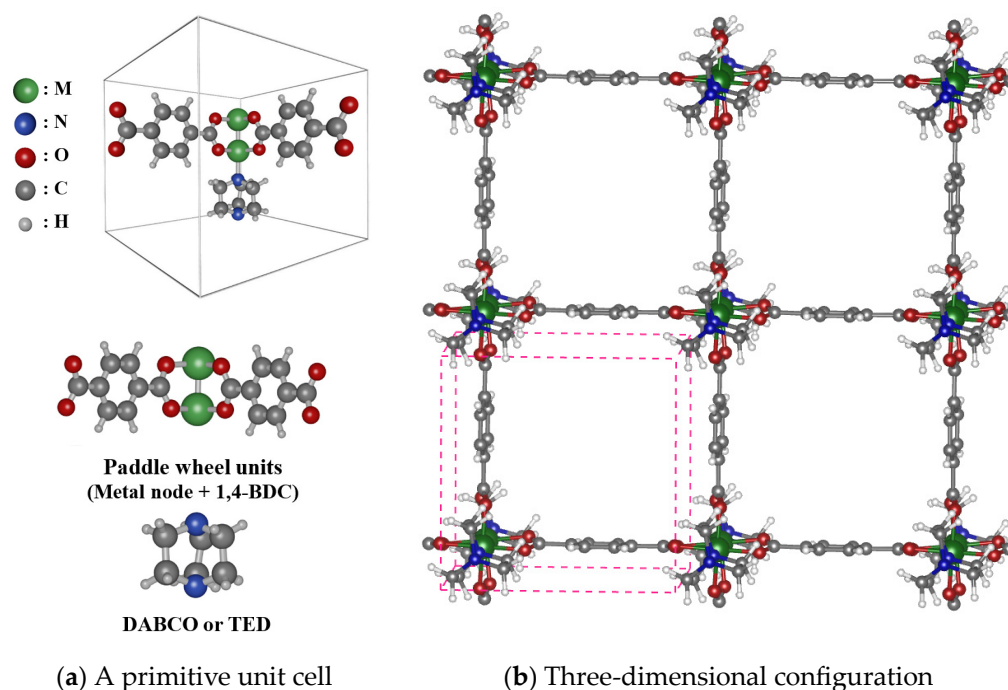


Figure 1. The configuration of (a) a primitive unit cell and (b) a three-dimensional view of $\text{M}_2(\text{BDC})_2(\text{DABCO})$ or $\text{M}(\text{DABCO})$.

For the above reasons, we selected the metals, including Co, Ni, Cu, Zn, and Fe, achieving the experimentally synthesized M(DABCO) and other potential predicted metals (Mg, Mn) in M(DABCO) to explore the methane adsorption capacity. Herein, we employed multiscale simulation, combining grand canonical Monte Carlo simulation and density functional theory calculations to study the effect of metal substitution on CH_4 uptake in M(DABCO) and to gain physical insights into the interactions between CH_4 and M(DABCO).

2. Methods and Modeling

2.1. Modeling of $\text{M}_2(\text{BDC})_2(\text{DABCO})$ MOFs

The configuration of $\text{M}_2(\text{BDC})_2(\text{DABCO})$ or $\text{M}_2(\text{BDC})_2(\text{TED})$ is shown in Figure 1. Hereafter, we denote $\text{M}_2(\text{BDC})_2(\text{DABCO})$ as M(DABCO) for simplicity. The chemical formula of M(DABCO) is $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_8\text{M}_2$. The unit cell of M(DABCO) consists of divalent metal ions M^{2+} ($M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) and two linkers, namely DABCO and BDC. DABCO is 1,4-diazabicyclo[2,2,2]octane with the formula of $\text{C}_6\text{H}_{12}\text{N}_2$, exhibiting a cage-like structure; BDC^{2-} is 1,4-benzenedicarboxylate, with the formula of $\text{C}_8\text{H}_4\text{O}_4$. The lattice constants and atomic positions of M(DABCO) were fully optimized using the DFT calculation (the DFT detail will be provided later) and the Murnaghan equation of state [54–56].

2.2. Grand Canonical Monte Carlo Simulation

The adsorbed amount of CH₄ (methane) and the adsorption isotherms of N₂ (nitrogen) and CH₄ in M(DABCO) were computed using grand canonical Monte Carlo (GCMC) simulation at room temperature and various pressures up to 100 bar using the RASPA code [57]. The GCMC simulations were performed using the μ VT ensemble (constant chemical potential, volume, and temperature). First, we performed 1.5×10^5 equilibration cycles and then performed 3.5×10^5 MC steps for random insertion, random deletion, translation, or rotation of molecules (N₂, CH₄) in the M₂(BDC)₂(DABCO) box (repeated three times, with the primitive unit cell in three dimensions) to obtain the equilibrium systems.

The van der Waals interaction mainly dominates the interaction between CH₄ and the MOF, while electrostatic interaction plays a minor role [3]. Therefore, the interaction between CH₄ and M(DABCO) is described by the 12-6 Lennard Jones (LJ) potential for the van der Waals interaction. We further verified this by elucidating the point charge of CH₄ adsorption in M(DABCO) using the DFT calculation. The charge of methane is thus modeled as an uncharged single-atom model. Therefore, the interaction between the atoms of the CH₄ molecule and the M(DABCO) is calculated as

$$V = \sum_{(i,j)} V_{ij} = \sum_{(i,j)} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where r_{ij} denotes the distance between the atoms i and j . The parameters σ_{ij} and ϵ_{ij} were determined by the mixing rule of Lorentz and Berthelot [58,59] as

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad \epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}. \quad (2)$$

Herein, the parameters σ_i and ϵ_i , the size and strength parameters, are selected from the generic force fields, which are tabulated in Table 1 [57]. The V_{ij} was truncated with the cutoff radius (r_{cut}) of 20 Å. During GCMC simulations, the M(DABCO) framework was fixed, while CH₄ could move freely in the pores of the MOF until reaching the equilibrium state. We modeled the CH₄ molecules using the TraPPE force field (also known as TraPPE-UA), developed by Martin et al. [60]. The accuracy of our approach is validated because it shows a good agreement between the GCMC and the experimental results for M(DABCO) (M = Co, Cu, Ni, Zn) [38,39,41] (Figure S1). Furthermore, a good agreement between the GCMC and the experimental results has been shown for previous flexible MOFs such as Co₃(NDC)₃(DABCO) and MIL-53 [3,61]. Here, it should also be noted that the results obtained via adsorption equilibrium using GCMC simulations are predictive.

For evaluating the adsorption capacity of CH₄ on M(DABCO) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn), GCMC simulations were performed with various pressures up to 100 bar and at room temperature. Here, we determined both gravimetric and volumetric uptakes of CH₄ in M(DABCO). We denoted total and excess gravimetric uptakes as m_{tot} and m_{exc} , respectively. On the other hand, total and excess volumetric uptakes are denoted as V_{tot} and V_{exc} , respectively. The total uptake (m_{tot}) and excess uptake (m_{exc}) are related through the equation:

$$m_{tot} = m_{exc} + d_{CH_4} \times V_p \quad (3)$$

where, d_{CH_4} is methane density, and V_p is the total pore volume of M(DABCO). In order to elucidate the strength of the CH₄-M(DABCO) interaction, the total heat of adsorption was calculated using the following expression [62]

$$-Q_{st} = \Delta H_{ads} = \Delta U - RT, \quad (4)$$

Herein, ΔU is the internal energy, which is estimated by the formula:

$$\Delta U = \langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle \quad (5)$$

where $\langle U_h \rangle$, $\langle U_g \rangle$, and $\langle U_{hg} \rangle$ are the average energy of the M(DABCO) (host), the CH₄ (gas), and the (host + gas) system, respectively. T is the temperature, and R is the gas constant.

The specific surface area (A_{BET}) and pore volume (V_p) are important structural factors of M(DABCO). The A_{BET} and V_p of M(DABCO) were determined from the nitrogen (N₂) adsorption isotherms at 77 K, which can be considered similar to the experimental sample using the BET (Brunauer–Emmett–Teller) model. The pore-size distribution (PSD) was calculated geometrically using Gelb and Gubbins' method [57].

Table 1. Lennard-Jones parameters (ϵ , σ) of the atoms of M(DABCO).

Atoms	ϵ/k_B (K)	σ (Å)
H ^a	7.65	2.85
C ^a	47.86	3.47
N ^a	38.95	3.26
O ^a	48.16	3.03
Mg ^b	55.86	2.69
Mn ^b	6.54	2.64
Fe ^b	6.54	2.59
Co ^b	7.05	2.56
Ni ^b	7.55	2.52
Cu ^b	2.52	3.11
Zn ^b	62.40	2.46
CH ₄ (Dubbeldam et al.) [62,63]	158.50	3.72
CH ₄ (TraPPE-UA) (Martin et al.) [60]	148.00	3.73

^a DREIDING force field; ^b the universal force field (UFF).

2.3. Density Functional Theory Calculation

We employed the DFT calculation to optimize the M(DABCO) structures and to accurately elucidate the interaction between CH₄ and M(DABCO) [64–66]. These DFT calculations were performed using the Vienna ab initio simulation package (VASP) code [67,68], with the projected augmented wave (PAW) method [69,70] and the plane-wave basis set, with a cut of energy of 700 eV. The van der Waal density functional (vdW-DF) method, with the revised Perdew–Burke–Ernzerhof exchange–correlation functionals [71], was employed to accurately describe the CH₄–M(DABCO) interaction, denoted as CH₄@M(DABCO). The Brillouin zone was sampled using Monkhorst–Pack meshes [72] of $3 \times 3 \times 3$, for atomic optimization, and $5 \times 5 \times 5$, for calculating the total energies and electronic properties (charges, density of state, etc.). The atomic charge was elucidated using charge Bader partitioning [73,74], while electronic structure analysis was performed using the density of states (DOS). The adsorption energy (E_{ads}) of the CH₄ molecule adsorbed on the M(DABCO) was estimated as

$$E_{\text{ads}} = E_{\text{MOF}+\text{CH}_4} - (E_{\text{MOF}} + E_{\text{CH}_4}) \quad (6)$$

Here, $E_{\text{MOF}+\text{CH}_4}$, E_{MOF} , and E_{CH_4} are the total energies of the CH₄ adsorbed-MOF, the pristine M(DABCO), and the isolated methane molecule, respectively.

3. Results and Discussion

3.1. Porosity and Surface Analysis of M(DABCO)

Firstly, we discuss the porosity and surface area of the M(DABCO) frameworks. The N₂ sorption isotherms in M(DABCO) and their pore-size distribution (PSD) are shown in Figures 2a and 2b, respectively. These N₂ sorption isotherms indicate the type-I adsorption isotherms, similar to the N₂ isotherm on Zn(BDC)(DABCO)_{0.5} [75] and Co(BDC)(DABCO)_{0.5} [39] (these increased rapidly at a pressure near 0 bar and saturated at ca. 500 cm³/g). Herein, the results show that Mg(DABCO) is superior to the remaining M(DABCO) MOFs in regards to N₂ adsorption.

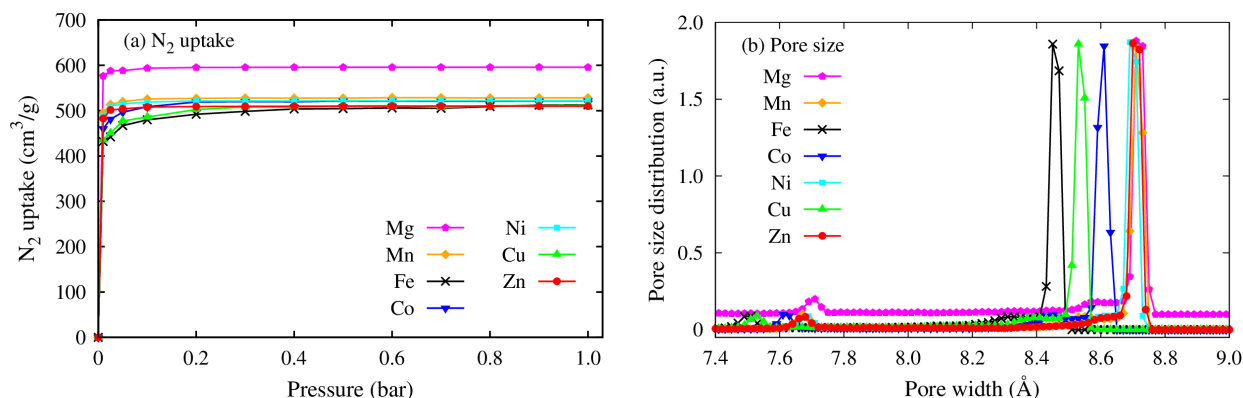


Figure 2. (a) The simulated N₂ adsorption isotherms of the M(DABCO) at 77 K and (b) the corresponding pore size distribution (PSD) of the M(DABCO).

The results of the geometrical features of M(DABCO) are listed in Table 2. Our results for PSD, pore size, surface area, and pore volume are relatively consistent with the experimental reference values for M(DABCO) (M = Zn, Co) [39,75]. The surface area and pore volume are in ascending order of metal: Cu < Fe < Zn < Co < Ni < Mn < Mg, in which Cu (1561 m²/g, 0.71 cm³/g) and Mg (1931 m²/g, 0.87 cm³/g) exhibit the smallest and the largest surface area and pore volume of M(DABCO), respectively. The results are comparable with the experimental data [30,39,75,76], where the A_{BET} and V_p of Ni exhibited the largest values in the experimentally measured metals (Cu, Co, Zn, and Ni) (Table 2). From the data for A_{BET} and V_p in Table 2, we also find the linear relationship between A_{BET} and V_p , i.e., $A_{BET} = a \cdot V_p$, with the fitted linear coefficient (a) equal to 2204 ± 6 , with an error of 0.25% (Figure S2). Moreover, we also calculate the pore sizes of M(DABCO), and they are about 8.45 to 8.72 Å, which are close to the results in the experiment data (ca. 8.0 Å) (see Table 2).

Table 2. The simulated geometrical features, including specific surface area, pore volumes, and pore sizes of M(DABCO), compared to the available simulated and experimental data.

MOFs	A_{BET} (m ² /g)	V_p (cm ³ /g)	Pore Size (Å)
Cu(DABCO)	1561	0.71	8.53
Fe(DABCO)	1571	0.72	8.45
Zn(DABCO)	1597	0.73	8.72
Co(DABCO)	1628	0.74	8.61
Ni(DABCO)	1686	0.76	8.69
Mn(DABCO)	1701	0.77	8.71
Mg(DABCO)	1931	0.87	8.72
Cu(DABCO)	1631 [30], 1572 [76]	0.63 [30], 0.65 [76]	7.98 [76]
Zn(DABCO)	1781 [30], 1523 [76], 1904 [75]	0.65 [30], 0.56 [76], 0.73 [75]	8.00 [75]
Co(DABCO)	1708 [30], 1600 [39]	0.62 [30], 0.82 [39]	
Ni(DABCO)	1905 [30], 1698 [76]	0.76 [30], 0.71 [76]	7.88 [76]
HKUST-1 [6]	1850	0.78	

3.2. Methane Adsorption on M(DABCO)

Because the force field parameters are important to accurately evaluate the adsorption capacity of CH₄ on M(DABCO) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn) in GCMC simulation, we first validate our approach using available experimental CH₄ uptake results for Co(DABCO), Cu(DABCO), Ni(DABCO), and Zn(DABCO) [38,39,41] (Figure S1). The results indicate that our GCMC results using the TraPPE-UA force field for CH₄ and the LJ parameters for MOFs, taken from the universal force field (UFF) for metals and the DREIDING force field for other atoms, achieve reliability compared to the experimental

data [38,39,41]. In particular, under the same conditions, with a temperature of 303 K and a pressure of 75 bar, the simulation indicates that the CH₄ uptake of Co(DABCO) is $m_{exc} = 139$ mg/g, compared to that of Co(DABCO) measured by the experiment (140 mg/g), with an error of ca. 0.7% [39]. Additionally, under the same conditions of 298 K and 35 bar, the CH₄ adsorption of Cu(DABCO) achieved 181 cm³/g by our simulation and 186 cm³/g by the experiment in Ref. [38], with an error of ca. 3.2%. Moreover, our GCMC simulations are more consistent with the experimental results than those carried out by the force field proposed by Dubbeldam et al. [62,63].

The CH₄ storage capacities are shown in Figure 3, for low pressures under 1 bar, and in Figure 4, for higher pressures up to 100 bar, respectively. Among these MOFs, under 1 bar, Mg(DABCO) yields the largest gravimetric uptakes, with $m_{tot} = 15.15$ mg/g and $m_{exc} = 14.58$ mg/g. Moreover, Fe(DABCO) expresses the largest volumetric uptakes with $V_{tot} = 16.98$ cc/cc and $V_{exc} = 16.42$ cc/cc. On the other hand, Ni(DABCO) exhibits the lowest CH₄ uptakes. However, the deviation between the highest and lowest M(DABCO) for the gravimetric [volumetric] CH₄ uptake is small, with a difference of 2.5 mg/g (2.6 cc/cc) when comparing the Ni(DABCO) results with those for Mg(DABCO) [Fe(DABCO)].

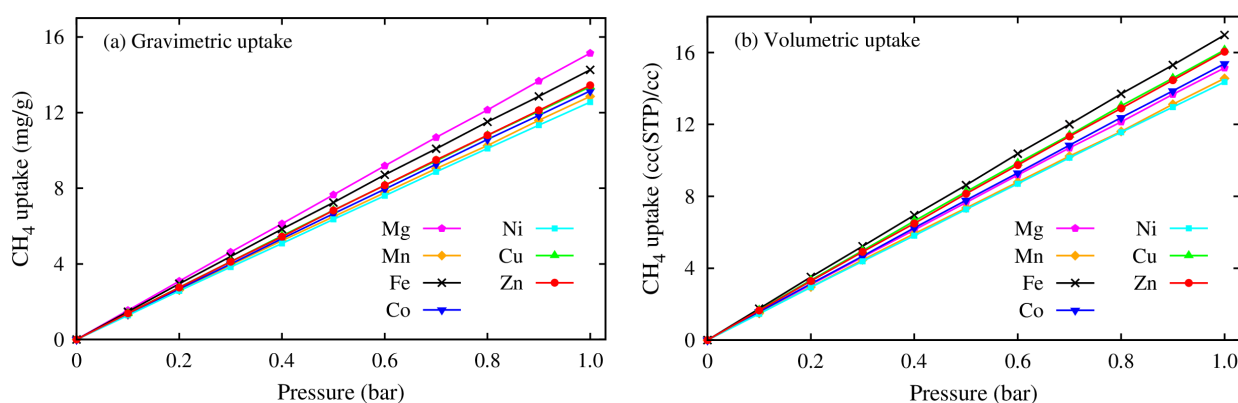


Figure 3. The simulated CH₄ adsorption isotherms of M(DABCO) with the total uptake (solid lines) and the excess uptake (dashed lines) at 298 K and pressures under 1 bar: (a) gravimetric adsorption and (b) volumetric adsorption.

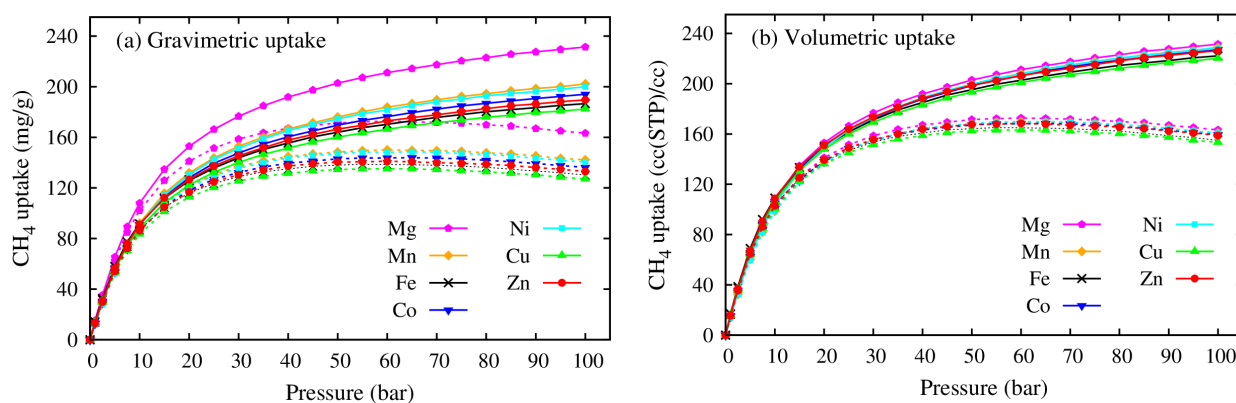


Figure 4. The simulated CH₄ adsorption isotherms of M(DABCO) with the total uptake (solid lines) and the excess uptake (dashed lines) at 298 K and pressures up to 100 bar: (a) gravimetric adsorption and (b) volumetric adsorption.

When the pressure increases to 100 bar, the difference in the CH₄ adsorption capacity of M(DABCO) becomes more apparent (Figure 4). The total CH₄ sorption isotherms show a strong dependence on pressure up to 100 bar, while excess CH₄ sorption isotherms nearly saturate at 35 bar, then increase slightly and reach maximum values at about 60–65 bar. Methane storage capacities are listed in detail in Table 3. For comparison with available experimental

data, we listed the most outstanding adsorption capacities of CH₄ on MOFs for the gravimetric and volumetric uptakes in Table 3. Our results for the CH₄ storage in M(DABCO) show that the gravimetric uptakes of M(DABCO) [182–231 mg/g] are lower than that of Al-soc-MOF-1 [420 mg/g], recorded the highest gravimetric uptake thus far. However, comparing to the volumetric uptake of Al-soc-MOF-1 (197 cc/cc), the CH₄ volumetric uptakes of M(DABCO) [220–231 cc/cc] are larger, showing that M(DABCO) is a promising candidate for CH₄ storage in terms of the volumetric uptake. This can be further confirmed by comparing both uptakes of the M(DABCO) series and HKUST-1, which is recorded to yield the highest volumetric capacity, along with a relatively high gravimetric uptake, in the literature. The CH₄ storage in HKUST-1 is 216 mg/g and 267 cc/cc at 65 bar, which is comparable with that noted in the M(DABCO) series (182–231 mg/g and 220–231 cc/cc) at 100 bar. Compared to the best available data (Table 3), our results show that the CH₄ adsorption capacities on M(DABCO) MOFs are remarkably enhanced, especially in regards to their volumetric density.

Table 3. The simulated maximum gravimetric and volumetric CH₄ adsorption on M(DABCO) for the total uptake (at 100 bar) and excess uptake (at 60 bar for M = Cu, Fe, Zn and 65 bar for M = Co, Ni, Mn, Mg), compared with available highest recorded data for CH₄ adsorption of MOFs.

MOFs	CH ₄ Adsorption				Volumetric Uptake cc(STP)/cc		Heat Adsorption, $Q_{st} = -\Delta H_{ads}$ (kJ/mol)
	Gravimetric Uptake		cm ³ /g				
	mg/g						
	m_{tot}	n_{exc}	m_{tot}	m_{exc}	V_{tot}	V_{exc}	
Cu(DABCO)	182.39	135.12	254.83	188.79	220.26	163.17	17.14
Fe(DABCO)	186.58	138.71	260.69	193.80	222.14	165.14	17.19
Zn(DABCO)	189.59	141.12	264.89	197.17	226.30	168.44	17.21
Co(DABCO)	194.05	143.93	271.12	201.09	227.03	168.39	17.17
Ni(DABCO)	199.90	148.48	279.30	207.46	228.68	169.86	17.10
Mn(DABCO)	202.22	150.06	282.53	209.65	228.94	169.89	17.13
Mg(DABCO)	231.39	172.30	323.29	240.73	231.43	172.33	17.27
Co(DABCO) [39]	14 wt.% (75 bar) ^a						
Cu(DABCO) [38]	<i>ca.</i> 185 (35 bar)				188 (35 bar) ^a		16.25
HKUST-1 [6]	216 (184) ^b	178 (165) ^c			267 (227) ^b	220 (204) ^b	17
PCN-14 [6]	197 (169) ^b	157 (146) ^c			230 (195) ^b	183 (171) ^b	18.7
MIL-101(Cr)					215 (150) ^b		
Al-soc-MOF-1 [13,19]	420 (263) ^b	-	579 (362) ^b			197 (123) ^b	10.5
NJU-Bai 43 [26]			396 (315) ^b			254 (202) ^b	14.45
UTSA-76 [27]	263 (216) ^b			302 (257) ^b	257 (211) ^b	15.44	
UTSA-110a [8]			402 (312) ^b			241 (187) ^b	15.49
DOE	500					263	

^a at a temperature of 303 K; ^b at a temperature of 298 K and a pressure of 65 (35) bar.

Here, we also discuss the effect of metal substitution on CH₄ storage capacities in M(DABCO). The CH₄ adsorption capacity of M(DABCO) varies in the order of Cu(DABCO) < Fe(DABCO) < Zn(DABCO) < Co(DABCO) < Ni(DABCO) < Mn(DABCO) < Mg(DABCO). Among them, Cu(DABCO) yields the lowest CH₄ adsorption capacity in regards to both mass and volume density, while Mg(DABCO) achieves the highest gravimetric and volumetric CH₄ adsorption capacity. The results for Mg(DABCO) are m_{tot} = 231.39 mg/g and m_{exc} = 172.30 mg/g; V_{tot} = 231.43 cc/cc and V_{exc} = 172.33 cc/cc in STP. The volumetric uptake of Mg(DABCO) is higher than that of Al-soc-MOF-1 and is comparable to that of HKUST-1. To identify the best gravimetric CH₄ adsorption of Mg(DABCO) compared to other M(DABCO), we evaluated the total amount of CH₄ adsorption per mole of M(DABCO) at 298 K and 100 bar and the molar mass of M(DABCO). The results are shown in Figure S3 and Table S3. The highest gravimetric CH₄ uptake in Mg(DABCO) arises from both a smaller molar mass and a higher amount of CH₄ adsorption per mole of Mg(DABCO). We find that the molar mass effect is dominant when comparing the results

of Mg(DABCO) with Mn(DABCO) and Ni(DABCO), showing that light metal substitution is an effective strategy to enhance gravimetric CH₄ uptake.

Although the results obtained for adsorption capacities, especially volumetric uptakes, of CH₄ in M(DABCO) are remarkable, they have not yet reached the DOE's standards (500 mg/g and 263 cc/cc). Therefore, we further elucidate CH₄ uptakes in M(DABCO) in the temperature range from 298 K to 238 K to strengthen CH₄ adsorption. Here, we only considered Mg(DABCO), which is the best candidate for CH₄ storage in the M(DABCO) series. The results are shown in Figure 5a. If the packing efficiency loss of CH₄ is ignored, at 238 K and 35 bar, V_{tot} is 270.61 cc/cc, which could meet the DOE target (263 cc/cc). At higher pressures (65 bar and 100 bar), the temperatures at which the V_{tot} reaches the DOE standard are 258 K and 268 K, respectively, showing that elevating the pressure could increase the temperature at which the volumetric uptake meets the DOE requirement. We also note that this relationship between pressure and temperature is linear (see details in Table 4). Figure 5b shows that the total CH₄ uptakes (at 35 bar, 65 bar, and 100 bar) and the maximum excess CH₄ uptake depend linearly on the temperature. These trends could be seen in many MOFs for methane uptakes available at 1 bar, especially for CH₄ adsorbed on M(BDP) (M = Co, Fe; BDP = 1,4-benzenedipyrazolate) [13].

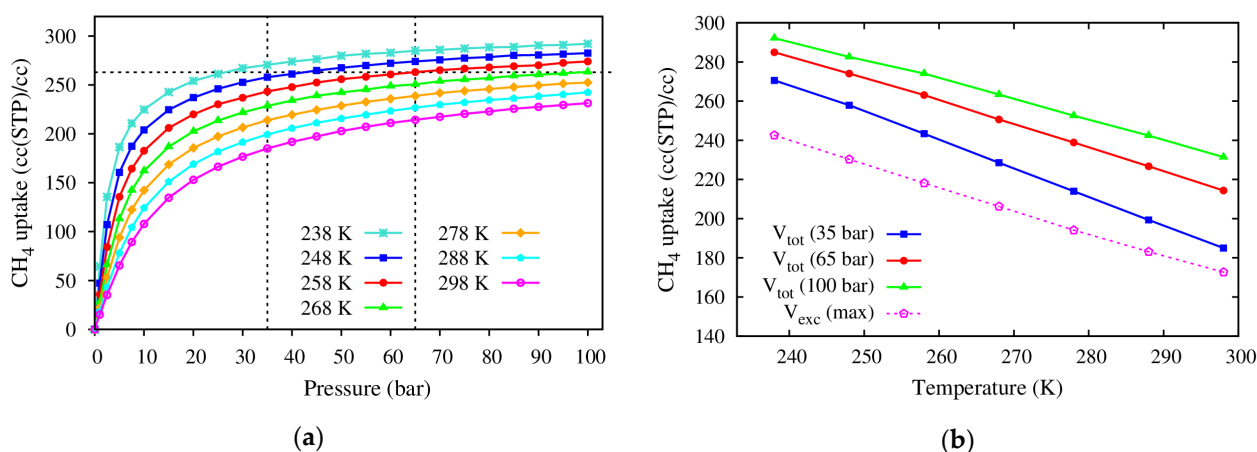


Figure 5. (a) The simulated total volumetric CH₄ sorption isotherms of M(DABCO) at 238 K–298 K and pressures up to 100 bar and (b) the dependence of the simulated volumetric CH₄ uptakes of M(DABCO) on the temperature.

Table 4. The simulated total and excess volumetric uptakes (cc/cc at STP) of CH₄ on M(DABCO) at other pressures and temperatures.

Temperature (K)	V_{tot}			V_{exc} (Max)
	35 bar	65 bar	100 bar (Max)	
238	270.61	284.95	292.15	242.58 (30.0 bar)
248	257.89	274.09	282.54	230.32 (35.0 bar)
258	243.37	263.09	274.05	218.13 (37.5 bar)
268	228.56	250.63	263.34	206.24 (42.5 bar)
278	214.01	238.87	252.54	194.15 (47.5 bar)
288	199.34	226.72	242.40	183.14 (52.5 bar)
298	184.99	214.38	231.43	172.71 (60.0 bar)

We further find a correlation between the CH₄ uptakes with the porosity and surface area of M(DABCO). The M(DABCO), with a higher surface area, shows a higher gravimetric uptake (Figure 6a), while M(DABCO), with a higher pore volume, exhibits a higher volumetric uptake (Figure 6b). Figure 6a shows the total and excess gravimetric uptake of CH₄ adsorbed on M(DABCO), as a function of its surface area (A_{BET}). The results show a linear behavior between gravimetric uptakes and surface areas. Similarly, we also find a linear

relationship between the volumetric uptakes of CH₄ in M(DABCO) and its pore volume. These relationship trends are also found in the high-pressure range in the literature [8,19]. This shows that improving the structural features (A_{BET} and V_p) of the MOF increases the storage ability of CH₄ on M(DABCO), especially in regards to gravimetric uptakes.

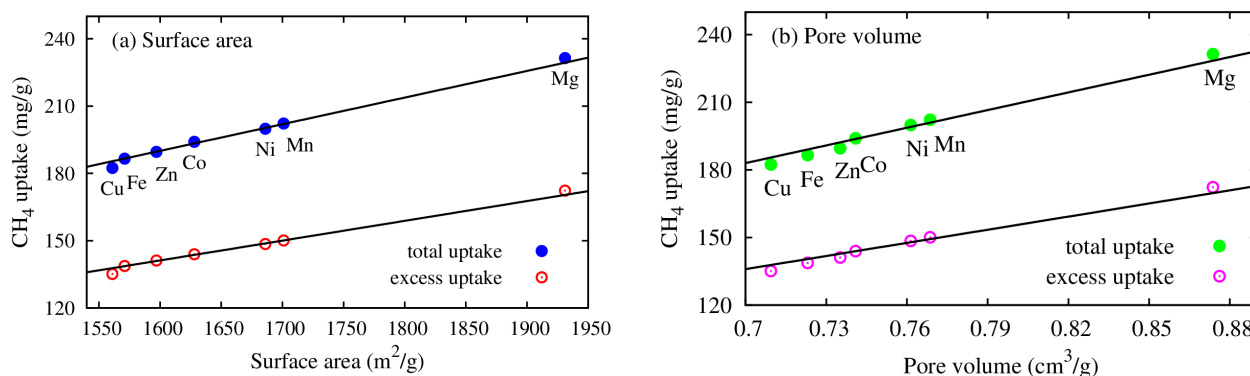


Figure 6. The dependence of the simulated maximum total and excess CH₄ uptakes (at 298 K) on (a) surface area and (b) pore volume (solid and empty circles). Herein, solid lines denote the linear fitting with the maximum uptakes.

3.3. Adsorption Heat of Methane on M(DABCO)

In order to elucidate the average interaction between the CH₄ molecules and the M(DABCO) MOFs (CH₄@M(DABCO)), the isosteric heat of adsorption ($Q_{st} = -\Delta H_{ads}$) at room temperature was calculated and visualized (see Figure 7). The results reveal that the values of Q_{st} for CH₄@M(DABCO) are about 16 to 18 kJ/mol, with the average of $Q_{st} \approx 17$ kJ/mol. Generally, the heat of adsorption of CH₄ physisorption is about 15 to 25 kJ/mol for sorbents recording the highest volumetric CH₄ capacities [77], and the Q_{st} of CH₄@M(DABCO) is also within this range. Hence, we conclude that M(DABCO) is promising for CH₄ storage, based on physisorption. It is also noted that at the pressures below 1 bar, the Q_{st} of CH₄@Fe(DABCO) is also higher than that of the remaining metals, explaining the stronger CH₄ adsorption on Fe(DABCO) sorbents below 1 bar (the inset of Figure 7). The relatively small difference between the adsorption heats of M(DABCO) explains the reason for the insignificant change in the volumetric CH₄ adsorption capacity of M(DABCO) (Figure 4b).

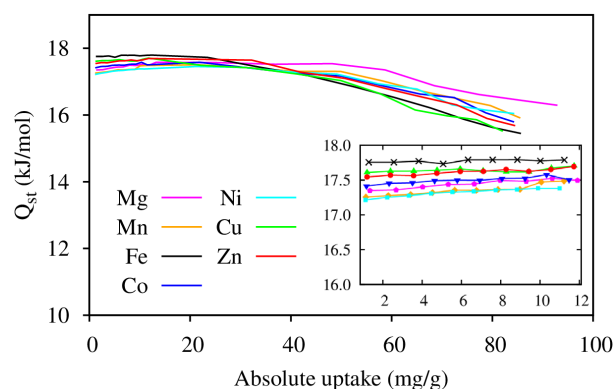


Figure 7. The simulated adsorption heat (Q_{st}) of CH₄ on M(DABCO). Inset: calculated Q_{st} at low pressures below 1 bar.

3.4. Stable CH₄ Adsorption Sites on M(DABCO)

To gain insight into the stable adsorption sites of CH₄@M(DABCO), we search the adsorption sites of CH₄ in M(DABCO) and evaluate the adsorption energies of the CH₄@M(DABCO)

based on vdW-DF calculations. Here, we aim to reveal the influence of the metal substitution in M(DABCO) in regards to CH₄-M(DABCO) interaction. Hence, we considered two adsorption sites of CH₄, i.e., site 1, where CH₄ is adsorbed at the metal oxide cluster site (Figure S4), and site 2, where CH₄ is located at the interface region between the M-O-C cluster and the TED group (Figure S5).

The adsorption energies (E_{ads}) and the nearest distance between CH₄ and M(DABCO) of the CH₄@M(DABCO) adsorption configurations are tabulated in Table 5. The average interaction strength of CH₄@M(DABCO) for two adsorption sites is in order of Mn > Co $\approx$ Mg $\approx$ Fe > Ni > Zn > Cu. The E_{ads} of CH₄@M(DABCO), with M = Mn, Co, Mg, Fe, and Ni, are similar (−73 to −78 kJ/mol), whereas the E_{ads} of CH₄@Zn(DABCO) are slightly smaller (−62 kJ/mol). In contrast, the E_{ads} of CH₄@Cu(DABCO) are the smallest (−20.31 and −45.33 kJ/mol for sites 1 and 2, respectively). The nearest distances (d_1 and d_2) between CH₄ and M(DABCO) are more than 2.5 Å (Table 5). Our calculated E_{ads} , d_1 , and d_2 of CH₄@M(DABCO) show that the interactions between CH₄ and the M(DABCO) series are primarily physisorption interactions, in agreement with the heat of adsorption recorded in the GCMC simulations. We find that the CH₄@M(DABCO) interactions are almost unaltered by the metal substitutions because this change in E_{ads} is small for Mn, Co, Mg, Fe, Ni, and Zn. In contrast, Cu yields a weaker CH₄ binding to Cu(DABCO) [78,79].

Table 5. The vdW-DF-based calculated adsorption energy (E_{ads}) of CH₄ on sites close to the metals of M(DABCO) and the nearest distance between the methane molecule and M(DABCO).

Adsorption Configurations	Site 1 (Metal Cluster)		Site 2 (M-O-C Cluster—TED Interface)	
	E_{ads} (kJ/mol)	d_1 (Å)	E_{ads} (kJ/mol)	d_2 (Å)
Mg	−76.58	2.92	−76.23	2.46
Mn	−77.73	3.08	−76.15	2.58
Fe	−76.97	3.00	−75.78	2.50
Co	−76.56	2.97	−76.55	2.59
Ni	−73.35	3.01	−75.40	2.46
Cu	−20.31	2.87	−45.33	2.74
Zn	−61.46	2.89	−62.13	2.49

Bader charges for the adsorption sites are listed in Tables 6 and 7, where symbols C1, C2, and C3 represent the C atoms linked with other C, O, and N atoms of MOF, respectively (Figure S6). The results show a tiny charge exchange between the atoms of CH₄ and M(DABCO), within the error range of 0.005 e in the Bader analysis. The magnitude of the Bader charge of C in CH₄ is less than 0.038 e , whereas that of four H atoms in CH₄ is less than 0.037 e . Overall, the CH₄ adsorbed on CH₄@M(DABCO) is almost neutral because the total Bader charge of CH₄ is almost zero. Therefore, the contribution of the electrostatic interaction between CH₄ and M(DABCO) could be ignored. This result further validates our GCMC approach, in which the interaction between CH₄-M(DABCO) is modeled by LJ potentials, leading to a good agreement between our GCMC results and those of the available experimental data from Refs. [38,39,41] (Figure S1).

A DOS analysis of CH₄ and M(DABCO) shows that the $1t_2$ (or σ_p) state of CH₄ is the main contributor to the interaction between CH₄ and M(DABCO). However, these changes in DOS are not significant, and include mainly the fact that the DOS peaks are shifted toward the negative energy, in which the $1\alpha_1$ (or σ_s) state barely changes its shapes after CH₄ adsorption (Figure 8). The slight difference in adsorption energies can also explain the small change in volumetric CH₄ adsorption capacity when substituting metal in M(DABCO) due to the good correlation between the CH₄ uptake and the adsorption energy on MOFs [5]. The origin of the strongest and weakest interactions of CH₄ in Mn(DABCO) and Cu(DABCO) can be seen from the overlap between the DOS of CH₄ and the DOS of M(DABCO) (Figures S7 and S8). Generally speaking, a larger overlap in the DOS of CH₄ and the MOF framework gives rise to a stronger interaction [54]. We see that the

overlap between the DOS of CH₄ and Cu(DABCO) is the smallest, while that of CH₄ and Mn(DABCO) is the largest, confirming a difference in the binding strength of CH₄ to these frameworks.

Table 6. The Bader charges of the CH₄ molecule sorbed on M(DABCO) MOFs (in *e*) compared those of the isolated corresponding compounds on the adsorption site of the metal cluster (site 1).

CH ₄ @M(DABCO) at Site 1		M = Mg	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn
CH ₄ molecule	4 H	+0.011	−0.011	+0.037	−0.028	−0.011	−0.007	−0.001
	1 C	−0.018	+0.005	−0.030	+0.016	+0.001	+0.012	−0.006
	Total	−0.007	−0.006	+0.007	−0.012	−0.010	−0.011	−0.007
M(DABCO)	20 H	−0.008	+0.053	−0.043	+0.020	−0.053	−0.007	+0.013
	12 C1	−0.052	+0.021	+0.017	+0.035	+0.151	+0.165	−0.091
	4 C2	+0.081	+0.024	+0.023	−0.029	−0.160	−0.178	+0.108
	6 C3	−0.016	−0.056	+0.016	−0.021	−0.003	−0.034	+0.033
	2 N	+0.014	+0.011	−0.0004	−0.010	+0.006	−0.002	−0.019
	8 O	−0.013	−0.036	−0.010	+0.059	+0.066	+0.099	−0.043
	2 M	+0.001	−0.012	−0.009	−0.042	+0.003	−0.035	+0.004
	Total	+0.007	+0.006	−0.006	+0.012	+0.010	+0.011	+0.007

Table 7. The Bader charges of the CH₄ molecule sorbed on M(DABCO) MOFs (in *e*) compared those of the isolated corresponding compounds on the adsorption site of the bridge between the metal cluster and the TED (site 2).

CH ₄ @M(DABCO) at Site 2		M = Mg	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn
CH ₄ molecule	4 H	+0.032	+0.022	+0.033	−0.004	+0.028	+0.022	−0.043
	1 C	−0.038	−0.027	−0.024	−0.001	−0.036	−0.031	+0.036
	Total	−0.006	−0.005	+0.009	−0.005	−0.008	−0.009	−0.007
M(DABCO)	20 H	+0.060	+0.008	−0.077	+0.061	+0.009	+0.034	+0.020
	12 C1	−0.044	+0.037	+0.069	−0.016	+0.130	+0.096	−0.089
	4 C2	−0.011	+0.007	−0.015	−0.023	−0.170	−0.162	+0.111
	6 C3	−0.032	−0.020	+0.0003	−0.042	−0.022	−0.001	+0.023
	2 N	+0.016	+0.015	+0.006	+0.002	+0.006	+0.032	−0.034
	8 O	+0.016	−0.034	+0.012	+0.047	+0.054	+0.042	−0.054
	2 M	+0.001	−0.007	−0.001	−0.025	+0.001	−0.032	+0.031
	Total	+0.006	+0.005	−0.006	+0.005	+0.008	+0.009	+0.007

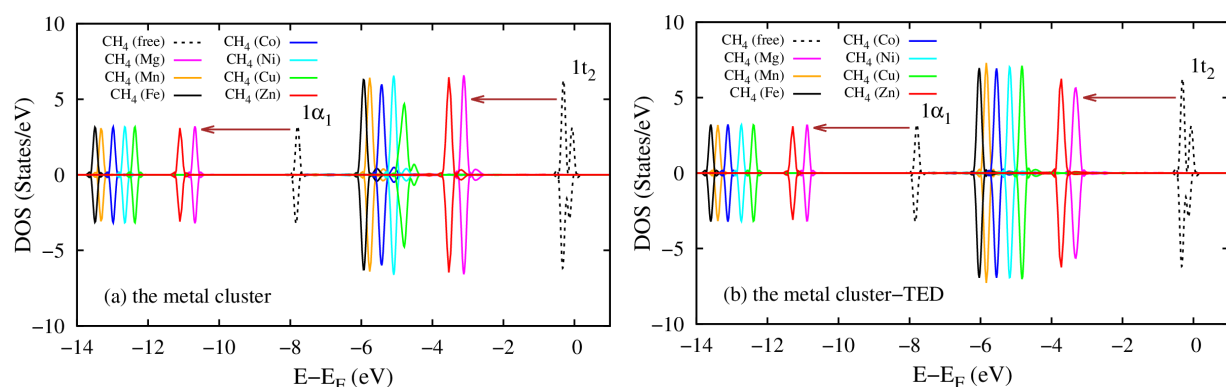


Figure 8. DOS of the adsorbed CH₄ molecule on M(DABCO) compared to that of the free CH₄ molecule: (a) on adsorption site 1 (the M-O-C cluster) and (b) on adsorption site 2 (the interface between the M-O-C cluster and TED).

Finally, we discuss the stability of M(DABCO) with M = Mg and Mn because these MOFs have not yet been synthesized by experiments. To this end, we elucidated the enthalpies of the formation of M(DABCO) with M = Mg and Mn, and the results are shown in

Table S4. We find that the enthalpies of formation of M(DABCO) with M = Mg and Mn are negative, showing that at least these MOFs are stable with respect to isolated metal ions and their constituent organic linkers. Therefore, our calculated results raise the possibility of those MOF formations, and we encourage experiments to explore the synthesis of M(DABCO) with M = Mg and Mn due to their remarkable CH₄ storage capacity and stable CH₄ adsorption. Recently, Mn-HKUST-1 or Mn- and Mg-based MOFs like HKUST-1 with similar paddlewheel building units have been successfully synthesized, further supporting our hypothesis [50,53].

4. Conclusions

Using a multiscale simulation that combined GCMC and DFT, this work elucidated the CH₄ storage capacity of the M(DABCO) series (M = Mg, Mn, Fe, Co, Ni, Cu, Zn). We obtained the following important results:

- (i) The CH₄ storage capacities in regards to both the gravimetric and volumetric uptakes of the M(DABCO) series are evaluated, and the volumetric uptakes of CH₄ in M(DABCO) are remarkable. Both uptakes are in the increasing order of M(DABCO), as: Cu < Fe < Zn < Co < Ni < Mn < Mg. Among these MOFs, Mg (DABCO) shows the highest CH₄ adsorption, with the maximum total and excess uptakes of 231.39 mg/g (at 100 bar) and 172.30 mg/g (at 65 bar), for gravimetric uptakes, and 231.43 cc(STP)/cc (at 100 bar) and 172.33 cc(STP)/cc (at 65 bar), for volumetric uptakes. Moreover, the methane adsorption capacities increase almost linearly with temperature, and the gravimetric methane adsorption strongly depends on the geometrical features (specific surface area and pore volume) of the M(DABCO) MOFs. Our simulations predicted that the volumetric CH₄ storage capacity could meet the DOE target at lower temperatures, ca. 238 K–268 K in the 35–100 bar pressure range.
- (ii) The interaction between CH₄ and M(DABCO) is mainly governed by the vdW interaction, and electrostatic interactions play a minor role, as indicated by the DFT calculations.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst14070596/s1>, Table S1: Several well-known MOFs for gravimetric CH₄ adsorption capacity at 298 K; Table S2: Excess gravimetric and volumetric CH₄ uptakes adsorbed on M(DABCO) at room temperature; Figure S1: Isotherms for methane compared with available experimental (exp.) data; Figure S2: The correlation between the surface area (A_{BET}) and the pore volume (V_p) of M(DABCO) sorbents. Points indicate the pairs of V_p and A_{BET} . The solid line indicates the linear fitting; Figure S3: The simulated CH₄ adsorption isotherms of M(DABCO) with the total uptake (solid lines) and the excess uptake (dashed lines) at 298 K and pressures up to 100 bar (in CH₄ molecules/unit cell); Table S3: The amount of CH₄ adsorption in M(DABCO) at 100 bar, 298 K in many different units compared to the molar mass of M(DABCO); Table S4: Formation enthalpy (ΔH_f) of M₂(BDC)₂(TED) or M(DABCO) compounds; Figure S4: The most stable CH₄ adsorption sites on the metal cluster of M(DABCO); Figure S5: The most stable CH₄ adsorption sites on the interface between the M-O-C cluster and TED of M(DABCO); Figure S6: The symbols for the atoms (C1, C2, C3, O, N, and M) of M(DABCO) with M = Mg, Mn, Fe, Co, Ni, Cu, or Zn. Here, H atoms are omitted; Figure S7: The overlap between the DOS of CH₄ and the atoms of M(DABCO) on the adsorption site of the metal cluster; Figure S8: The overlap between the DOS of CH₄ and the atoms of M(DABCO) on the adsorption site of the M-O-C cluster—TED interface.

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