The Role of Surface Hydrophobicity on the Structure and Dynamics of CO$_2$ and CH$_4$ Confined in Silica Nanopores

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Advancing a portfolio of technologies that range from the storage of excess renewable natural gas for distributed use to the capture and storage of CO$_2$ in geological formation are essential for meeting our energy needs while responding to challenges associated with climate change. Delineating the surface interactions and the organization of these gases in nanoporous environments is one of the less explored approaches to ground advances in novel materials for gas storage or predict the fate of stored gases in subsurface environments. To this end, the molecular scale interactions underlying the organization and transport behavior of CO$_2$ and CH$_4$ molecules in silica nanopores need to be investigated. To probe the influence of hydrophobic surfaces, a series of classical molecular dynamics (MD) simulations are performed to investigate the structure and dynamics of CO$_2$ and CH$_4$ confined in OH-terminated and CH$_3$-terminated silica pores with diameters of 2, 4, 6, 8, and 10 nm at 298 K and 10 MPa. Higher adsorption extents of CO$_2$ compared to CH$_4$ are noted on OH-terminated and CH$_3$-terminated pores. The adsorbed extents increase with the pore diameter. Further, the interfacial CO$_2$ and CH$_4$ molecules reside closer to the surface of OH-terminated pores compared to CH$_3$-terminated pores. The lower adsorption extents of CH$_4$ on OH-terminated and CH$_3$-terminated pores result in higher diffusion coefficients compared to CO$_2$ molecules. The diffusivities of both gases in OH-terminated and CH$_3$-terminated pores increase systematically with the pore diameter. The higher adsorption extents of CO$_2$ on OH-terminated and CH$_3$-terminated pores are driven by higher van der Waals and electrostatic interactions with the pore surfaces, while CH$_4$ adsorption is mainly due to van der Waals interactions with the pore walls. These findings provide the interfacial chemical basis underlying the organization and transport behavior of pressurized CO$_2$ and CH$_4$ gases in confinement.

Keywords: surface hydrophobicity, CO$_2$, CH$_4$, gas storage, structure, organization, dynamics, diffusivity
INTRODUCTION

Scientific advancements that enable us to harness renewable energy resources and facilitate the removal and storage of greenhouse gas emissions are essential for meeting our energy and resource needs in a sustainable manner while responding to challenges associated with climate change. One approach in the portfolio of strategies needed to address this challenge is the storage of renewable energy carriers such as hydrogen and biomethane. Storage of excess renewable energy carriers in natural and engineered environments is critical to meeting our energy needs on demand. In this context, there is an emerging interest in exploring subsurface environments (Pfeiffer and Bauer, 2015; Berta et al., 2018; Shi et al., 2020) and engineered materials (Yun et al., 2002; Düren et al., 2004; Dündar-Tekkaya and Yürüm, 2016) to store clean energy carriers such as biomethane and hydrogen. Further, safe and permanent storage of CO\(_2\) in geologic formations at the gigaton scale is essential if renewable and non-renewable carbon-bearing fuels continue to be used (Bachu et al., 2007; Aydin et al., 2010; Michael et al., 2010; Jiang, 2011; Zhang and Bachu, 2011).

Resolving the physical and chemical adsorption of carbon dioxide (CO\(_2\)) and methane (CH\(_4\)) on porous silica is an area of increasing interest due to its relevance in various energy and environmental fields, including CO\(_2\) capture and CO\(_2\) utilization and storage coupled with enhanced oil and gas recovery from subsurface environments (Kuuskraa et al., 2013; Huo et al., 2017; Mohammed and Gadikota, 2019a; Farajzadeh et al., 2020; Klewiah et al., 2020).

While prior studies reported the link between functionalized silica surfaces and the structure of CO\(_2\) and CH\(_4\) for applications related to gas separations (Wiheeb et al., 2015; Mafra et al., 2018), the coupled effects of confinement and surface hydrophobicity have not been systematically probed. The surfaces of silica nanopores and nanoparticles can be either hydrophilic or hydrophobic depending on the surface polarity and the chemistry of the functional groups on the surface (Jin et al., 2019). The hydrophobicity of silica surfaces has significant impacts on the organization and flow of confined fluids, including water (Jin et al., 2021), hydrocarbons (Ghoufi et al., 2013) and gases. Given the interest in storing gases in subsurface environments, delineating the mechanisms underlying the storage of gases in oil-wet vs. water-wet environments is essential. Further, the influence of nano-scale confinement on the organization of these gases needs to be further delineated given the abundance of nanoporous-rich environments in subsurface environments and the anomalous thermodynamics and transport behavior of nano-confined fluids.

Extensive progress has already been made toward explaining the physical and chemical interactions of CO\(_2\) with amine-functionalized porous silica using a wide range of experimental and computational characterization techniques (Chaikittisilp et al., 2011; Liu et al., 2014; Cogswell et al., 2015). Amine-functionalized porous silica provides the advantage of chemically binding CO\(_2\) with the impregnated amines in the porus silica that enhance the gas uptake (Serna-Guerrero et al., 2008), as opposed to OH-functionalized porous silica in which CO\(_2\) adsorbs physically through van der Waals interactions, electrostatic interactions, and hydrogen bonding. The chemical binding of CO\(_2\) with the amine groups results in high CO\(_2\) adsorption capacity, good selectivity, fast adsorption and desorption rates, and low energy consumption when compared to the porous materials that capture CO\(_2\) through physical adsorption (Li et al., 2014). Despite these advancements in developing functional materials, there have been no efforts to contrast the organization of CO\(_2\) and CH\(_4\) in pores with hydrophobic and hydrophilic silica surfaces.

The structure, dynamics and flow of CH\(_4\) in organic and inorganic confinement have also been studied using a range of experimental and computational tools, including small-angle neutron scattering (Chiang et al., 2016a,b; Mohammed et al., 2020b) and molecular simulations (Siderius et al., 2017; Xiong et al., 2017; Mohammed and Gadikota, 2020; Wang et al., 2020). The core-shell organization of pressurized CH\(_4\) molecules in confinement and their associated dimensions can be successfully determined using small-angle neutron scattering (Chiang et al., 2016a,b; Mohammed et al., 2020b), and these measurements can be used to validate molecular simulations. The differences in the spatial organization of confined gases contribute to anisotropic variations in their diffusivities (Wu et al., 2015; Xiong et al., 2016, 2017; Mohammed and Gadikota, 2019a). Confined effects influence the desorption of bound species such as water and CO\(_2\) (Baumgartner et al., 2019; Knight et al., 2019).

Prior work by Qin et al. (2008) used classical molecular dynamics (MD) simulations to show that supercritical CO\(_2\) is preferentially adsorbed on hydroxylated silica surfaces [-Si(OH)] instead of silylated [-Si(CH\(_3\))] silica pores due to the hydrogen bonding interactions between the confined CO\(_2\) and -OH groups on the pore. Although these insights provided by Qin and co-workers provide a crucial link to the fate of confined CO\(_2\) and the surface chemistry of silica pores, the effects of pore diameter remain unresolved.

To address this knowledge gap, we performed a series of classical MD simulations to investigate the structure, organization, dynamics, and energetics of CO\(_2\) and CH\(_4\) confined in OH-functionalized and CH\(_3\)-functionalized silica pores with diameters of 2, 4, 6, 8, and 10 nm. The hypothesis that the organization of CO\(_2\) and CH\(_4\) molecules is influenced by the hydrophobicity of the surfaces is investigated. The simulations are performed at 10 MPa and 298 K to mimic the mechanical and thermal conditions of subsurface environments.

COMPUTATIONAL METHODOLOGY

CO\(_2\), CH\(_4\), and β-cristobalite silica unit cells are built using Avogadro software. The structure of isolated cristobalite unit cell is optimized using density functional theory implemented in Quantum Espresso (Giannozzi et al., 2017). A kinetic energy cutoff for wavefunctions of 36 Ry and K-points mesh of (6 × 6 × 6) are used to optimize the β-cristobalite silica unit cell. These values are chosen based on the convergence of the total energy of the silica structure. Ultrasoft pseudopotentials are implemented in which the generalized gradient approximation (GGA) (Perdew et al., 1996) is selected for the exchange correlation functional. The Broyden-Fletcher-Goldfarb-Shanno
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**FIGURE 1** The initial configurations of confined CO$_2$ and CH$_4$ in silica pores with diameters 4 nm are shown in panels (A,B), respectively. Atoms in silica pores and confined gases molecules shown in CPK and VDW drawing methods, respectively, are implemented in VMD software.

(BFGS) (Head and Zerner, 1985) algorithm is utilized to perform the structural optimization of the silica unit cell. BFGS has been widely used to optimize the electronic structure of a wide range of materials in DFT calculations (Han et al., 2019; Sharma et al., 2019; Neupane and Adhikari, 2020).

Silica surfaces are constructed by replicating the optimized β-cristobalite unit cell in x, y, and z directions. Slit-shaped pores with heights of 2, 4, 6, 8, and 10 nm are cleaved in the constructed surfaces. The non-bridging oxygens on the interior pore surfaces are functionalized with -OH and -CH$_3$ groups to tune the surface hydrophobicity of the constructed pores. Each pore has a length of 9.95 nm along the X-axis and a depth of 3.98 nm along the Y-axis, while the pore height varies from 2 to 10 nm along the Z-axis.

The pressures of CO$_2$ and CH$_4$ inside the pores is set to 10 MPa. The number of CO$_2$ and CH$_4$ molecules are 193, 385, 578, 771, and 964 in 2, 4, 6, 8, and 10 nm pores, respectively (see Figure 1). Silica pores are modeled using ClayFF forcefield (Cygán et al., 2004). The TraPPE forcefield (Potoff and Steppmann, 2001) is used to model -CH$_3$ functional group. The CO$_2$ molecules are modeled using TraPPE forcefield, while CH$_4$ molecules are modeled using OPLS/AA forcefield (Jorgensen et al., 1996). These forcefields have been widely used to study the properties of CO$_2$ and CH$_4$ on silica surfaces because the governed adsorption extents, organizations and dynamics agree with the experimental data (Phan et al., 2014; Le et al., 2015; Mohammed et al., 2020b, 2021).

Energy minimization is performed on the initial configurations for 50,000 steps using the steepest descent method to remove inappropriate geometries and reduce the high energy of the randomly distributed gas molecules in the pore space. Constant number of molecules, constant volume and constant temperature (NVT) ensemble are performed on the optimized cells for 50 ns under 298 K. The temperature is controlled using Nose-Hoover thermostat with a relaxation time of 1 ps (Evans and Holian, 1985). The short-range interaction is calculated in a cutoff of 1.4 nm, while the long-range electrostatic interactions are treated using Particle Mesh Ewald (PME). The equation of motion is integrated by leapfrog integrator with a time step of 2 fs. Non-bonding interactions are accounted for van der Waals and electrostatic potentials. Bonding interactions are calculated from bond stretching, angle bending, and dihedrals in CO$_2$ and CH$_4$ molecules while only O-H and O-CH$_3$ bond stretching are considered in silica pores. MD simulations are performed and analyzed using GROMACS 2018 code (Abraham et al., 2015) and the visualization of the simulations inputs and outputs are performed using VDM software (Humphrey et al., 1996). Further information on the simulation details can be found in Mohammed and Gadikota (2018, 2019a,b); Mohammed and Gadikota (2020) and Mohammed et al. (2020a,b).

**RESULTS AND DISCUSSIONS**

**Structural Properties of Confined CO$_2$ and CH$_4$**

Insights into the organization of CO$_2$ and CH$_4$ molecules in silica nanopores are obtained from the density profiles of these gases. The density profiles of confined CO$_2$ and CH$_4$ along the pore height (z-axis) in OH-terminated and CH$_3$-terminated pores...
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**FIGURE 2** | Number density profiles of confined CO$_2$ and CH$_4$ molecules along the vector normal to the pore surface (z-axis) in (A,B) OH-terminated pores and (C,D) CH$_3$-terminated pores in pore diameter of 2 nm. The density profiles are averaged over the last 10 ns of the simulation time.

with diameter of 2 nm is shown in Figure 2 as a representative for the distribution of confined gases in slit pores with different pore hydrophobicity. The density profiles show a preferential adsorption of CO$_2$ and CH$_4$ on the pore surfaces in both OH-terminated and CH$_3$-terminated pores. The density profile of the confined gases decreases sharply on approaching the pore center where the minimum density values are observed for both gases. However, the number density of CO$_2$ molecules confined in OH-terminated pores is higher at the pore surface while the number density of CH$_4$ molecules is higher in the center of the pore (see Figures 2A,B). These observations suggest that CO$_2$ adsorbs preferentially on the OH-terminated silica pores compared to CH$_4$ at similar conditions of temperature, pressure and pore size. Prior studies probing the competitive adsorption of CO$_2$ on OH-terminated silica pores showed that CO$_2$ adsorbs preferentially over nonpolar aliphatic hydrocarbons (paraffins) such as ethane (C$_2$H$_6$) (Elola and Rodriguez, 2019), propane (C$_3$H$_8$) (Mohammed and Gadikota, 2019a), butane (C$_4$H$_{10}$) (Le et al., 2015) and octane (C$_8$H$_{18}$) (Le et al., 2016).

The preferential adsorption of CO$_2$ and CH$_4$ on the surfaces of the OH-terminated and CH$_3$-terminated pores compared to the pore center is evident from the 2D density maps of the gases’ distribution in the pore space (see Figures 3, 4). The density maps are averaged over the last 10 ns of the simulation time to ensure an equilibrium state. CO$_2$ showed higher density on the pore surfaces compared to CH$_4$ in OH-terminated and CH$_3$-terminated surfaces in all pore sizes. Further, the interactions with the functional groups on the pore surface influence the distribution of the interfacial molecules such that higher CO$_2$ densities are observed at the OH groups and higher CH$_4$ densities are noted at CH$_3$ groups.

Interestingly, the location of the adsorbed CO$_2$ and CH$_4$ peaks on the CH$_3$-terminated pores are shifted toward the pore center by about 0.34 and 0.27 nm, respectively, in 2 nm sized pores (see Table 1). The shift in the adsorbed peaks “exclusion region” in hydrophobic silica surfaces is evident for water (Jin et al., 2019), but studies on gases confined in CH$_3$-terminated silica are scarce, making it difficult to compare such observations with previous studies. The exclusion of CO$_2$ and CH$_4$ from the CH$_3$-terminated pore surface is also shown by the snapshots taken from the silica-CO$_2$ and silica-CH$_4$ interfaces (see Figure 5). Figure 5 shows that the interfacial CO$_2$ and CH$_4$
FIGURE 3 | 2D density maps of CO$_2$ confined in OH-terminated and CH$_3$-terminated pores as a function of the pore diameter. The density maps are averaged over the last 10 ns of the simulation times.

FIGURE 4 | 2D density maps of CH$_4$ confined in OH-terminated and CH$_3$-terminated pores as a function of the pore diameter. The density maps are averaged over the last 10 ns of the simulation times.
molecules can reside between the dangling OH groups on the OH-terminated surfaces, while there is a finite distance between the dangling CH$_3$ groups and the interfacial CO$_2$ and CH$_4$ molecules.

To contrast the adsorption behavior of CO$_2$ and CH$_4$, the adsorption extents (mmol/m$^2$) of CO$_2$ and CH$_4$ on the pore surfaces are calculated from the number density profiles in OH-terminated and CH$_3$-terminated pores and normalized by Avogadro number and the area of the pore surface (see Figure 6) as follows:

$$ \text{Adsorption extent} \left[ \frac{\text{mmol}}{\text{m}^2} \right] = \frac{\text{Number of adsorbed molecules}}{\text{Avogadro number} \times \text{Pore surface area}} \quad (1) $$

The adsorbed molecules were considered as the first peak in the density profile adjacent to the pore surface. This approach is consistent with prior studies (Mohammed and Gadikota, 2019a). The adsorption extent of CO$_2$ and CH$_4$ in OH-terminated and CH$_3$-terminated pores increases systematically with the increase in the pore diameter. However, the adsorption extent of CO$_2$ is higher than that of CH$_4$ in OH-terminated and CH$_3$-terminated pores. Further, the adsorption extent of CO$_2$ in OH-terminated pores is higher than that in CH$_3$-terminated pores. In contrast, the CH$_4$ molecules adsorb preferentially on CH$_3$-terminated pores compared to that in OH-terminated pores. As the pore diameter increases from 2 nm to 10 nm, the adsorption extent of CO$_2$ in OH-terminated pores increases from 0.48 ± 0.03 to 1 ± 0.05 mmol/m$^2$, while CO$_2$ adsorption extent on CH$_3$-terminated pores increases from 0.42 ± 0.01 to 0.92 ± 0.05 mmol/m$^2$. Similarly, increasing the pore diameter from 2 to 10 nm causes the adsorption extent of CH$_4$ to increase from 0.38 ± 0.03 to 0.66 ± 0.03 mmol/m$^2$ in OH-terminated pores and from 0.41 ± 0.04 to 0.70 ± 0.04 mmol/m$^2$ in CH$_3$-terminated pores. The profiles of the adsorption extents are consistent with previous studies after accounting for the difference in the compositions of confined gases (Mohammed and Gadikota, 2019a).

The structural properties are further analyzed by calculating the radial distribution function (RDF) of the carbon atoms of CO$_2$ and CH$_4$ with respect to the -OH and -CH$_3$ groups on the pore surface (Figure 7). RDFs are averaged over the last 10 ns of the simulations time to ensure equilibrium structure of the interfacial CO$_2$ and CH$_4$ molecules. RDF of C atoms of CO$_2$ and CH$_4$ showed two peaks with respect to the -OH and -CH$_3$ groups on the silica pores surfaces. However, the first peak of OH-CO$_2$ is higher than that of CH$_3$-CO$_2$ (see Figures 7A,C). Further, the first peak of OH-CO$_2$ is located at a radius of 0.34 nm while that of CH$_3$-CO$_2$ is located at 0.41 nm. The lower first peak of C$_{CH4}$ compared to C$_{CO2}$ with respect to -OH and -CH$_3$ functional groups (Figures 7B,D) on the pore surfaces agrees with the lower adsorption extent of CH$_4$ on OH-terminated and CH$_3$-terminated pores. The peak values of all RDFs decrease systematically as the pore diameter increases due to the larger number of gas molecules residing in the pore center compared the molecules adsorbed on the pore surface. Previous studies showed similar trends in the RDF of confined CO$_2$ in OH-terminated and CH$_3$-terminated pore surfaces (Qin et al., 2008).

The coordination numbers $n(r)$ of C$_{CO2}$ and C$_{CH4}$ with respect to -OH and -CH$_3$ groups on the pore surfaces (Figure 8) are calculated by integrating the radial distribution function as follows:

$$ n(r) = 4\pi \rho \int_0^r g(r)r^2dr \quad (2) $$

In the expression above, $\rho$ is the density, $r$ is the radius and $g(r)$ is the radial distribution function. The number of C$_{CO2}$ atoms in the first coordination shell of -OH and -CH$_3$ increase significantly as the pore diameter increases from 2 nm to 10 nm (see Figures 8A,C). However, the number of C$_{CO2}$ in the first coordination shell of OH is higher than that of CH$_3$. In contrast, a slight increase is noted in the number of C$_{CH4}$ in the first coordination shell of -OH and -CH$_3$ groups on the silica surface (Figures 8B,D). In addition, the number of C$_{CO2}$ in the first coordination shell of -OH and -CH$_3$ is higher than C$_{CH4}$ in all the pore sizes. The denser packing of the first coordination shell of C$_{CO2}$ agrees with higher adsorption extent on OH-terminated and CH$_3$-terminated pore surfaces.

**Diffusivity of Confined CO$_2$ and CH$_4$**

The hypothesis that the structure of confined fluids influences their transport is investigated. The self-diffusion coefficient of confined CO$_2$ and CH$_4$ is calculated in the plane perpendicular to the pore diameter (xy plane) due to the negligible dimensionality of the pore diameter compared to xy plane (infinite) (see Figure 9). The self-diffusion coefficients are calculated based on the mean square displacement ($l^2$) as follows (Gadikota et al., 2017):

$$ D = \frac{1}{2nt} \lim_{t \to \infty} \frac{dl^2}{dt} \quad (3) $$

In the expression above, $l^2$ was calculated in the xy plane ($n = 2$), and $t$ is the time. The diffusion coefficients of confined CO$_2$ and CH$_4$ increase systematically with the pore diameter in OH-terminated and CH$_3$-terminated pores. The diffusion coefficients of CO$_2$ in OH-terminated pores increased from
(1.29 ± 0.34) × 10^{-4} to (2.08 ± 0.29) × 10^{-4} cm^2/sec as the pore diameter increases from 2 nm to 10 nm. Similarly, the diffusion coefficient of CO_2 in CH_3-terminated pores increased from (0.86 ± 0.16) × 10^{-4} to (1.84 ± 0.50) × 10^{-4} cm^2/sec as the pore diameter increased from 2 to 10 nm. This increase in diffusivity with the pore diameter is attributed to the higher number of molecules confined in larger pores that occupy the adsorption sites on the pore surface and leave a large fraction of the confined molecules outside the attractive energy well near the pore surface. The non-adsorbed molecules on the pore surface can move freely along the xy direction due to the low molecular collisions and low
steric hinderance in the pore center. The values of the self-diffusion coefficient of confined CO$_2$ match those predicted by previous studies after accounting for the differences in the pore diameter, CO$_2$ loading and the applied temperature (Qin et al., 2008; Le et al., 2015).

Interestingly, the diffusion coefficients in OH-terminated pores are higher than those confined in CH$_3$-terminated pores. The higher diffusion coefficients in OH-terminated pores can be linked to the higher adsorption extent of CO$_2$ molecules on the pore surface, such that it results in lower molecular density in the center of the pore. The lower molecular density in the center of the pore contributes to fewer molecular collisions in the OH-terminated pores compared to those in the CH$_3$-terminated pores.

The lower adsorption extent of CH$_4$ on OH-terminated and CH$_3$-terminated silica pores, relative to CO$_2$, result in higher in-plane self-diffusion coefficients in all the pore sizes. As the pore diameter increase from 2 nm to 10 nm, CH$_4$ diffusion coefficients increase from (6.01 ± 0.13) × 10$^{-4}$ to (8.76 ± 0.34) × 10$^{-4}$ cm$^2$/sec, respectively, in OH-terminated pores and from (5.04 ± 0.12) × 10$^{-4}$ to (8.22 ± 0.21) × 10$^{-4}$ cm$^2$/sec, respectively, in CH$_3$-terminated pores. The higher diffusion coefficient of CH$_4$ in confinement is also attributed to the lower molecular weight and the lower intermolecular interactions with the pore walls that enable even the adsorbed atoms to move faster in the xy plane compared to the adsorbed CO$_2$ molecules that bind strongly to the pore surfaces.

In addition, the diffusion coefficients of CO$_2$ and CH$_4$ in OH-terminated and CH$_3$-terminated pores vary across the pore space such that the adsorbed molecules on the pore surface diffuse slower than the molecules in the center of the pore (see Table 2). The lower diffusion coefficients in the adsorbed layers are derived by the intermolecular interactions with the pore surface that results in the domination of surface diffusion. In contrast, the absence of surface interactions and lower density profiles in the pore center enable the gas molecules to diffuse faster relative to the adsorbed layers. The confined free gas molecules diffuse faster than the adsorbed molecules on the pore surfaces by an order of magnitude in the simulated pores.
Energetics of Confined CO\(_2\) and CH\(_4\)

The intermolecular interaction energies of CO\(_2\) and CH\(_4\) molecules with the silica surfaces are calculated to elucidate the energetic basis of the varying adsorption extents, organization of interfacial CO\(_2\) and CH\(_4\) molecules, and dynamics with changes in the functionalized surfaces and the pore diameter (see Figure 10). Van der Waals and electrostatic interactions are averaged over the last 10 ns of the simulations time as a function of the pore diameter. Error bars represent the standard deviation from the mean value of these three different simulations.

Van der Waals interactions of CO\(_2\) with OH-terminated pores increase systematically with the pore diameter (Figure 10A). Van der Waals interactions in OH-terminated pores increased from \(-956.6 \pm 13\) to \(-2,563.5 \pm 16\) kJ/mol as the pore diameter increased from 2 to 10 nm. Similarly, van der Waals interactions between confined CO\(_2\) molecules and CH\(_3\)-terminated pores have systematically increased from \(-972.6 \pm 5\) to \(-2,417.1 \pm 16\) kJ/mol as the pore diameter increased from 2 to 10 nm (Figure 10C). The increase in van der Waals interactions with the increase in pore diameter is attributed to the higher number of molecules in larger pores that are required to maintain the chemical potential. The larger number of molecules results in more intermolecular collisions between the interfacial CO\(_2\) molecules and functional groups (OH and CH\(_3\)) on the pore surface. However, the difference in the magnitude of van der Waals interactions between the confined CO\(_2\) molecules with OH-terminated and CH\(_3\)-terminated pores are not significant, suggesting that the intensity of intermolecular collisions between confined CO\(_2\) and pore surfaces is independent of the type of functional group on the pore surface.

Electrostatic interactions, on the other hand, showed a profound difference in OH-terminated pores compared to CH\(_3\)-terminated pores. The electrostatic interactions between CO\(_2\) and OH-terminated pores are higher compared to those between CO\(_2\) and CH\(_3\)-terminated pores by an order of magnitude. The electrostatic interactions between OH-terminated pores and the confined CO\(_2\) molecules increased from \(-267.5 \pm 4\) to \(-690.5 \pm 4\) kJ/mol as the pore diameter increased from 2 nm to 10 nm. The electrostatic interactions between CO\(_2\) molecules and CH\(_3\)-terminated pores showed a slight increase from \(-23.0 \pm 1\) to \(-35.4 \pm 1\) kJ/mol as the pore diameter increased.
from 2 nm to 10 nm. Since the differences in the van der Waals interactions are insignificant, the profound difference in electrostatic interactions between CO$_2$ and silica pores drives the preferential adsorption of confined CO$_2$ on OH-terminated pores. The higher electrostatic interactions between CO$_2$ and OH-terminated pores stems from the quadruple moment of CO$_2$ molecules.

Further, CO$_2$ molecules form hydrogen bonds with the OH-group on the silica surfaces that contribute positively to the overall intermolecular interactions. The hydrogen bonds between the confined CO$_2$ molecules and OH-terminated surfaces increases from $33 \pm 2$ to $102 \pm 4$ as the pore diameter increases from 2 to 10 nm, respectively. The energy of a hydrogen bond can vary from 1 to 40 kcal/mol. The observed electrostatic interactions and hydrogen bonding between confined CO$_2$ and OH-terminated silica surfaces are consistent with previous studies (Mohammed and Gadikota, 2019a).

The intermolecular interactions between the confined CH$_4$ and pore walls are driven by van der Waals interactions with negligible contributions from the electrostatic interactions (see Figures 10B,D) due to the non-polar characteristics of CH$_4$ molecules, and they slightly with the pore diameter. The intermolecular interactions of CH$_4$ with the CH$_3$-terminated pores are slightly lower than compared to the OH-terminated pores, which explains the higher adsorption extents of CH$_4$ on CH$_3$-terminated pores (see Figure 6). The higher van der Waals interactions combined with the contribution of the electrostatic interactions of CO$_2$ with the OH-terminated and CH$_3$-terminated pores results in a preferential adsorption of CO$_2$ on the silica pores with different surface chemistries over non-polar hydrocarbons. This data suggests that the hydrophilic surfaces aid the preferential adsorption of CO$_2$ and the displacement of hydrocarbons, including CH$_4$, away from the silica surfaces.

**CONCLUSIONS**

The structure, dynamics and energetics of confined CO$_2$ and CH$_4$ in OH-terminated and CH$_3$-terminated silica pores with diameters ranging from 2 nm to 10 nm are investigated using classical molecular dynamics simulations. In this study, anisotropic distribution of CO$_2$ and CH$_4$ molecules...
FIGURE 9 | The self-diffusion coefficient of (A) CO$_2$ and (B) CH$_4$ molecules in OH-terminated and CH$_3$-terminated pores as a function of the pore diameter. Diffusion coefficients are averaged over the last 10 ns of the simulation time. Error bars represent the standard deviation from the mean values of the three different simulations.
TABLE 2 | Self-diffusion coefficients (10^{-4} \text{ cm}^{-2}/\text{sec}) of interfacial and confined free gas molecules (bulk) in OH-terminated and CH₃-terminated pores as a function of the pore diameter.

| Diameter (nm) | OH-terminated | CH₃-terminated | OH-terminated | CH₃-terminated |
|--------------|---------------|----------------|---------------|----------------|
|              | \text{CO}_2   | \text{CH}_4     | \text{CO}_2   | \text{CH}_4     |
|              | \text{Interfacial} | \text{Bulk} | \text{Interfacial} | \text{Bulk} | \text{Interfacial} | \text{Bulk} | \text{Interfacial} | \text{Bulk} |
| 2            | 0.214 ± 0.01  | 2.921 ± 0.03   | 0.163 ± 0.03  | 2.574 ± 0.12   | 0.684 ± 0.01  | 7.421 ± 0.12   | 0.493 ± 0.04  | 6.012 ± 0.13 |
| 4            | 0.221 ± 0.01  | 2.960 ± 0.08   | 0.185 ± 0.04  | 2.582 ± 0.21   | 0.697 ± 0.03  | 7.613 ± 0.31   | 0.512 ± 0.03  | 6.123 ± 0.03 |
| 6            | 0.238 ± 0.03  | 2.974 ± 0.04   | 0.191 ± 0.02  | 2.691 ± 0.16   | 0.703 ± 0.02  | 7.712 ± 0.41   | 0.534 ± 0.01  | 6.214 ± 0.41 |
| 8            | 0.245 ± 0.02  | 3.023 ± 0.13   | 0.199 ± 0.08  | 2.732 ± 0.15   | 0.721 ± 0.03  | 7.792 ± 0.14   | 0.541 ± 0.05  | 6.274 ± 0.18 |
| 10           | 0.249 ± 0.04  | 3.102 ± 0.18   | 0.203 ± 0.05  | 2.813 ± 0.21   | 0.742 ± 0.05  | 7.821 ± 0.16   | 0.558 ± 0.05  | 6.301 ± 0.42 |

The error bars represent the standard deviation from the mean value of simulations performed in triplicates.

FIGURE 10 | Van der Waals and electrostatic interaction energies of \text{CO}_2 and \text{CH}_4 with (A,C) OH-terminated and (B,D) CH₃-terminated pores as a function of the pore diameter. The intermolecular interactions are averaged over the last 10 ns of the simulation time. Error bars represent the standard deviation from the means values of three different simulations.

in confinement is noted with higher number densities observed adjacent to the pore surfaces. Preferential adsorption of \text{CO}_2 on the surfaces of OH-terminated and CH₃-terminated pores over \text{CH}_4 is attributed to favorable intermolecular interactions with the hydroxyl functional groups. \text{CO}_2 and \text{CH}_4 molecules adsorb closer to the surfaces of OH-terminated pores than CH₃-terminated pores. Higher adsorption extents of \text{CO}_2 are noted compared to \text{CH}_4, and the adsorption extent increases with the pore diameter. The diffusion coefficients of confined \text{CO}_2 and \text{CH}_4 showed higher values in larger pores, and confined \text{CH}_4 diffuses faster than \text{CO}_2 in all pore sizes. The higher adsorption extent of \text{CO}_2 over \text{CH}_4 on the surfaces of OH-terminated and CH₃-terminated pores stems from significantly stronger van der Waals interactions with considerable contributions from
electrostatic interactions. Thus, delineating the organization and transport behavior of CO$_2$ and CH$_4$ molecules in confinement in hydrophobic and hydrophilic pores provides the basis for tuning surface chemical interactions for storing gases in engineered materials and for predicting the fate of multicomponent fluids in porous environments in subsurface geologic formations.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

SM constructed the simulations and completed the first draft of the manuscript. AS and CW contributed to the simulations and data analyses. GG developed the concept and edited the manuscript. All authors contributed to the article and approved the submitted version.

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