



The Equilibrium Stability of CH₄ and CO₂ on the Calcite (10.4) Surface: an Atomistic Thermodynamics Investigation

Niveen Assaf, Ibrahim Suleiman*, and Bassam Malkawi

Al-Balqa Applied University, Faculty of Engineering Technology, Chemical Engineering Department, Amman, 11134, Jordan.

Abstract

The present study utilized the ab initio atomistic thermodynamics technique to assess the stability of pure carbon dioxide and pure methane on the calcite(10.4) systems. The stability of configurations 0.5 ML-A2, 0.75 ML-A2, and 0.75 ML-A1 in CH₄/calcite (10.4) systems was shown to be considerable, but only within a limited range of chemical potential. The 1.0 ML-A1 and 1.0 ML-A2 systems of CH₄/calcite (10.4) demonstrated remarkable stability throughout a wide range of chemical potentials. The predominant stable forms for CO₂/calcite (10.4) systems are the 1.0 ML-B2 and 1.0 ML-A4 structures. The surface free energy phase diagrams demonstrate that CO₂ is more favourable than CH₄ for adsorption on the calcite (10.4) surface.

Paper type: Short communication paper

Keywords: EGR, atomistic thermodynamics, methane, carbon monoxide.

Citation: Assaf, N., Suleiman, I., and Malkawi, B. "The Equilibrium Stability of CH₄ and CO₂ on the Calcite (10.4) Surface: An Atomistic Thermodynamics Investigation", Jordanian Journal of Engineering and Chemical Industries, Vol. 7, No.1, pp: 1-4 (2024).

Introduction

Permeable rocks can retain and accumulate gas molecules and can be classified as gas reservoirs. Sedimentary rocks are the primary constituent of natural gas reservoirs, which contain significant amounts of calcium carbonate (CaCO₃) (Jiang *et al.*, 2021; Song *et al.*, 2022). Calcite is the most thermodynamically stable form of calcium carbonate and is the main component of the reservoir rocks (Morse *et al.*, 2007). The gaseous molecules can be found either within the porous cavities of the rocks or attached to the solid nanopores through adsorption (Song *et al.*, 2020).

Carbon capture and utilization (CCU) involves injecting significant amounts of gaseous carbon dioxide (CO₂) into virtually depleted wells to stimulate the release of remaining hydrocarbons from the rock, hence enhancing the gas production output. Meanwhile, carbon dioxide (CO₂) is sequestered in the rocks, resulting in the reduction of greenhouse gases (Garcia-Garcia *et al.*, 2021). Enhanced gas recovery (EGR) refers to the process of preserving the residual fuel from wells that have been exhausted (Hamza *et al.*, 2021). The objective of this work is to examine the adsorption of CO₂ and methane in the sedimentary rock layer of a reservoir via calculating the surface free energy diagram for the CO₂/calcite(10.4) and CH₄/calcite(10.4) systems.

Both experimental (Eliebid *et al.*, 2018b; Eliebid *et al.*, 2018a) and theoretical (Wang *et al.*, 2016; Carchini *et al.*, 2020a; Carchini *et al.*, 2020b; Zhang *et al.*, 2020) investigations have been attempted to study the adsorption of CO₂ and CH₄ on calcium carbonates. Eliebid *et al.* (Eliebid *et al.*, 2018b) carried out a study on the adsorption of carbon dioxide (CO₂) and methane (CH₄) in limestone using the Rubotherm magnetic suspension balance. According to their findings, the limestone has a threefold higher capacity to absorb gaseous CO₂ compared to gaseous methane, which improves the EGR process. The adsorption of both species was determined to be exothermic.

* Corresponding author: E-mail: dr.ibrahim.suleiman@bau.edu.jo

Received on March 5, 2024.

Jordanian Journal of Engineering and Chemical Industries (JJECI), Vol.7, No.1, 2024, pp: 1-4.

ORCID: <https://orcid.org/0000-0002-7311-9227>

Accepted on March 30, 2024.

Revised: March, 23, 2024.



Theoretical approaches were utilized to study the adsorption of CO₂ and CH₄ on the calcite(10.4) surface including density functional theory (DFT) calculation and molecular dynamic (MD) simulation (Wang *et al.*, 2016; Carchini *et al.*, 2020a; Carchini *et al.*, 2020b; Zhang *et al.*, 2020). Carchini *et al.* (Carchini *et al.*, 2020b) showed through DFT calculations that the A4 position has the highest affinity for molecular CO₂ adsorption, while the B3 location is the most advantageous site for CH₄ adsorption. Additionally, they investigated the impact of the CO₂ and CH₄ coverage on their adsorption on the surface. Carchini *et al.* (Carchini *et al.*, 2020a) showed in their MD investigation that calcite can absorb greater amounts of CO₂, resulting in the liberation of adsorbed CH₄ molecules. This is a result of the low affinity between CH₄ and calcite. Zhang *et al.* (Zhang *et al.*, 2020) conducted a study on the adsorption of CH₄ and CO₂ on various CaCO₃ polymorphs, including calcite(10.4), aragonite(011)Ca, and vaterite(010)CO₃. Their findings indicated that the order of adsorption sequences for CH₄ and CO₂ on these surfaces are aragonite(011)Ca > vaterite(010)CO₃ > calcite(10.4), and vaterite(010)CO₃ > aragonite(011)Ca > calcite(10.4), respectively. Furthermore, they demonstrated that the adsorption of CO₂ is more advantageous compared to that of CH₄, which aligns with the findings of Carchini *et al.* (Carchini *et al.*, 2020a).

This study investigates the stability of several CO₂/calcite(10.4) and CH₄/calcite(10.4) systems using the ab initio atomistic thermodynamics technique. The data illustrates the progression of CO₂ and CH₄ adsorption on the calcite(10.4) surface, as well as the specific pressure conditions necessary to see each stable configuration at a temperature of 300 K.

1 Materials and Methods:

The ab initio atomistic thermodynamics technique is employed to compute the surface free energy of different CO₂/calcite(10.4) and CH₄/calcite(10.4) systems. A structure with lower surface energy exhibits greater stability. The surface energy, γ^{ads} , is defined as

$$\gamma^{ads} = \frac{1}{A} [N_i E_b - N_i \Delta\mu_i(T, p)] \quad (1)$$

where E_b denotes the binding energy. This work utilizes the findings of Carchini *et al.* (Carchini *et al.*, 2020b), who provided data on the binding energies of CO₂/calcite(10.4) and CH₄/calcite(10.4) systems at various coverage levels, up to 1.0 ML. The symbol $\Delta\mu_i$ represents the chemical potential, while N_i denotes the number of species i that have been adsorbed onto the surface.

If the surrounding gaseous environment acts as an ideal gas reservoir, then the change in chemical potential ($\Delta\mu_i$) concerning temperature (T) and pressure (p) can be calculated using the formula

$$\Delta\mu_i(T, p) = \mu_i(T, p^o) + \frac{1}{2} kT \ln \left(\frac{p}{p^o} \right) \quad (2)$$

where k is the Boltzmann constant. Additional information regarding the technique is available in the references (Suleiman *et al.*, 2020; Assaf *et al.*, 2022; Suleiman *et al.*, 2022)

2 Results and Discussion

The diagram in **Figure 1** shows the phase diagram of the surface energy of CH₄/calcite(10.4). The most stable structures discovered were the 0.75ML-A1, 1.0ML-A1, 0.5ML-A2, 0.75ML-A2, and 1.0ML-A2 configurations, all of which had a binding energy of -0.28 eV per CH₄ molecule. The clean calcite10.4 surface was determined to be the most stable structure in a dilute methane environment. When the concentration of methane is increased above the value $\Delta\mu_{CH_4} = -0.29 eV$, the 0.5ML-A2 configuration becomes the most stable. However, this stability is only observed for a very limited range of chemical potential. Once the value of $\Delta\mu_{CH_4}$ reaches -0.28 eV, the structures 0.75ML-A1 and 0.75ML-A2 become the prevailing structures, where their stability lines are overlapping. The configurations 1.0 ML-A1 and 1.0ML-A2 exhibit the exact same greatest stability compared to all other CH₄/calcite(10.4) structures when $\Delta\mu_{CH_4} > -0.26 eV$. They also remain stable over the whole range of $\Delta\mu_{CH_4}$. Fig. 1 also includes the surface energy as a function of pressure at a temperature of 300K. Considering the error margin of the used technique, it can be confidently said that the structure 1.0ML-A2 is the most suitable for observation under ultra-high-vacuum to extremely high-pressure conditions. These results are consistent with the findings of Carchini *et al.* (Carchini *et al.*, 2020b), however, they focused on the structures where CH₄ is adsorbed on the A2 site only, ignoring the possibility of the presence of other stable configurations. **Figure 2** depicts the phase diagram of the surface energy of CO₂/calcite(10.4). Out of all the structures that were examined, the only configurations that were discovered to be stable were 0.5ML-B1, 1.0ML-B2 and 1.0ML-A4. All of these configurations have a binding energy of -0.39 eV per CO₂ molecule. The clean surface demonstrates maximum stability until the chemical potential reaches -0.39 eV. At a change in chemical potential of carbon dioxide $\Delta\mu_{CO_2}$ of -0.39 eV, the 0.5ML-B1 structure begins to exhibit greater stability compared to the clean surface, however only for a marginal period. The 1.0ML-B2 and 1.0ML-A4 configurations are overlapping and have the greatest stability for the remaining values of chemical potential, beyond $\Delta\mu_{CO_2} = -0.38 eV$. Considering the error margin of these

methodologies, it can be concluded that the 1.0ML-B2 and 1.0ML-A4 configurations are the most stable structure among all CO₂/calcite(10.4) configurations, regardless of the operating pressure settings. These results are consistent with the findings of Carchini et al. (Carchini *et al.*, 2020b). However, our results highlighted the stability of structures where CO₂ is adsorbed over the B1 site.

A comparison between Figs 1 and 2 shows that CO₂/calcite(10.4) forms a stable structure at lower value of chemical potential than CH₄/calcite(10.4). This gives an advantage for CO₂ adsorption over CH₄ on the calcite (10.4) surface. This is consistent with the results of Carchini et al. (Carchini *et al.*, 2020b) and Zhang et al. (Zhang *et al.*, 2020). A 1.0 ML coverage was found to be a stable structure for both CO₂/calcite(10.4) and CH₄/calcite(10.4) systems.

Experimental evidence demonstrated that the addition of 10% CO₂ to CH₄ led to an increase in the adsorption energy of methane at a temperature of 150°C (Zhang *et al.*, 2020). The adsorption capacity of CO₂ on limestone was found to be four times greater than that of CH₄. The greater inherent selectivity of carbonate for CO₂ was thermodynamically justified by the higher exothermic behaviour of CO₂ adsorption. Therefore a better understanding of competitive adsorption between CO₂ and CH₄, a 2-D free energy phase diagram should be calculated for CO₂/CH₄ co-adsorbed systems at different coverages. The wettability of the rock is one of the major factors that would affect the adsorption of CO₂ and CH₄. Eliebid et al. (Eliebid *et al.*, 2018b) reported that surfactant-treated limestone has a much lower capacity for CO₂ and CH₄ adsorption compared to surfactant-untreated minerals.

Conclusions

The stability of CO₂/calcite(10.4) and CH₄/calcite(10.4) systems was investigated using the ab initio atomistic thermodynamics technique. The systems were examined at coverages of 0.25, 0.5, 0.75, and 1.0 ML. Within CH₄/calcite(10.4) systems, the stability of both the 1.0 ML-B2 and 1.0 ML-A4 configurations was determined to be equal and the highest throughout a wide range of chemical potential. The configurations 1.0 ML -A2 and 1.0 ML - A4 were determined to be the most stable for a broad range of chemical potential in the case of CO₂/calcite(10.4). The phase diagrams also indicated that the adsorption of CO₂ on the surface is more advantageous compared to CH₄, increasing EGR.

Nomenclature

A	=Surface Area	[Å ²]
E_b	=Binding Energy	[eV]
γ^{ads}	=Surface Energy	$\left[\frac{meV}{\text{Å}^2}\right]$
k	=Boltzmann Constant	[eV/K]
ML	=Monolayer	[-]
μ_i	=Chemical Potential of CO ₂ and CH ₄ molecules	[eV]
N_i	=Number of CO ₂ and CH ₄ molecules	[-]
p	=Pressure	[Bar]
p^o	=Standard Pressure	[bar]
T	=Temperature	[K]

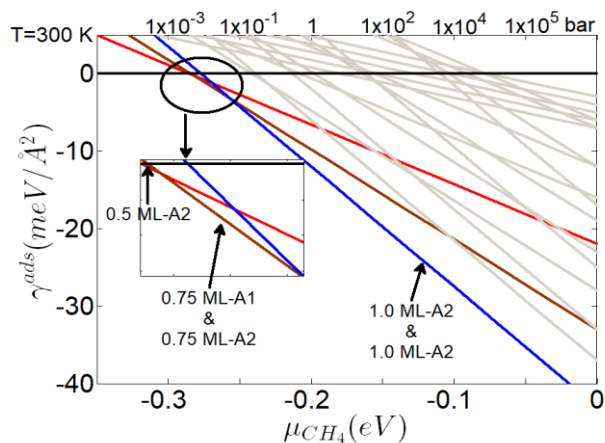


Fig. 1 Surface free energy for CH₄/calcite(10.4) structures reported by Carchini et al. (Carchini *et al.*, 2020b).

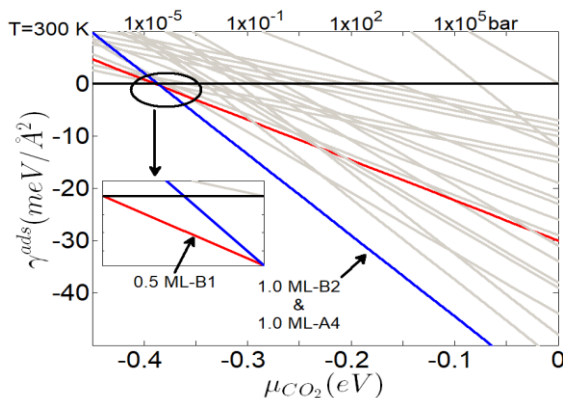


Fig. 2 Surface free energy for CO₂/calcite(10.4) structures reported by Carchini et al. (Carchini *et al.*, 2020b).

References

- Assaf, N. W., Suleiman, I. A., and A.T., Shawaqfeh "The surface energy phase diagrams of CO adsorption on the low index iridium surfaces and the morphology of iridium nanoparticles", *J. of Crystal Growth*, **593**, 126774, (2022).
- Carchini, G., Al-Marri, M. J., Hussein, I. A. and S., Aparicio "Ab Initio Molecular Dynamics Investigation of CH₄/CO₂ Adsorption on Calcite: Improving the Enhanced Gas Recovery Process", *ACS Omega*, **5**, 30226-30236, (2020a).
- Carchini, G., Hussein, I., Al-Marri, M. J., Shawabkeh, R., Mahmoud, M., and S., Aparicio "A theoretical study of gas adsorption on calcite for CO₂ enhanced natural gas recovery". *Appl. Surface Sci.*, **504**, 144575. (2020b).
- Eliebid, M., Mahmoud, M., Shawabkeh, R., Elkatatny, S., and I. A., Hussein "Effect of CO₂ adsorption on enhanced natural gas recovery and sequestration in carbonate reservoirs", *J. of Natural Gas Sci. and Eng.*, **55**, 575-584, (2018a).
- Eliebid, M., Mahmoud, M., Hussein, I., Elkatatny, S., Shawabkeh, R., Sultan, A., and M. J., Al-Marri "Impact of Surfactant on the Retention of CO₂ and Methane in Carbonate Reservoirs", *Energy & Fuels*, **32**, 5355-5363, (2018b).
- Garcia-Garcia, G., Fernandez, M.C., Armstrong, K., Woolass, S., and P., Styring "Analytical review of life-cycle environmental impacts of carbon capture and utilization technologies", *Chem. Sus. Chem.*, **14**, 995-1015, (2021).
- Hamza, A., Hussein, I. A., Al-Marri, M. J., Mahmoud, M., Shawabkeh, R., and P., Aparicio "CO₂ enhanced gas recovery and sequestration in depleted gas reservoirs: A review", *J. of Petroleum Sci. and Eng.*, **196**, 107685, (2021).
- Jiang, Z., Xiangxin, K., Yepeng, Y., Zhang, J., Zhang, Y., Li, W., and Y., Xiaodong "Multi-source genesis of continental carbonate-rich fine-grained sedimentary rocks and hydrocarbon sweet spots", *Petroleum Exploration and Development*, **48**, 30-42, (2021).
- Morse, J. W., Arvidson, R. S., and A., Lüttge "Calcium Carbonate Formation and Dissolution", *Chem. Reviews*, **107**, 342-381, (2007).
- Song, C., Elsworth, D., Jia, Y., and J., Lin "Permeable rock matrix sealed with microbially-induced calcium carbonate precipitation: Evolutions of mechanical behaviors and associated microstructure", *Eng. Geology*, **304**, 106697, (2022).
- Song, Z., Li, Y., Song, Y., Bai, B., Hou, J., Song, K., Jiang, A., and S., Su "A critical review of CO₂ enhanced oil recovery in tight oil reservoirs of North America and China", *SPE Asia Pacific Oil and Gas Conference and Exhibition*, (2020).
- Suleiman, I. A., Assaf, N.W., and A. T., Shawaqfeh "An equilibrium ab initio atomistic thermodynamics investigation of hydrogen adsorption on the low index iridium surfaces and the morphology of iridium nanoparticles", *J. of Phy. and Chem. of Solids*, **167**, 110736, (2022).
- Suleiman, I. A., Shawaqfeh, A. T., Stockenhuber, M., and E. M., Kennedy "Insights on the stability of cuprous chloride under high pressure: An equilibrium ab initio atomistic thermodynamics study", *J. of Phy. and Chem. of Solids*, **136**, 109158, (2020).
- Wang, S., Zhou, G., Ma, Y., Gao, L., Song, R., Jiang, G., and G., Lu "Molecular dynamics investigation on the adsorption behaviors of H₂O, CO₂, CH₄ and N₂ gases on calcite (1 1-0) surface", *Appl. Surface Sci.*, **385**, 616-621, (2016).
- Zhang, M., Li, J., Zhao, J., Cui, Y. and X., Luo "Comparison of CH₄ and CO₂ Adsorptions onto Calcite(10.4), Aragonite(011)Ca, and Vaterite(010)CO₃ Surfaces: An MD and DFT Investigation", *ACS Omega*, **5**, 11369-11377, (2020).