The Equilibrium Stability of CH_4 and CO_2 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 CH_4/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 CH_4/calcite (10.4) demonstrated remarkable stability throughout a wide range of chemical potentials. The predominant stable forms for CO_2/calcite (10.4) systems are the 1.0 ML-B2 and 1.0 ML-A4 structures. The surface free energy phase diagrams demonstrate that CO_2 is more favourable than CH_4 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 CH_4 and CO_2 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 ($CaCO_3$) (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 (CO_2) into virtually depleted wells to stimulate the release of remaining hydrocarbons from the rock, hence enhancing the gas production output. Meanwhile, carbon dioxide (CO_2) 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 CO_2 and methane in the sedimentary rock layer of a reservoir via calculating the surface free energy diagram for the CO_2/calcite(10.4) and CH_4/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 CO_2 and CH_4 on calcium carbonates. Eliebid et al. (Eliebid *et al.*, 2018b) carried out a study on the adsorption of carbon dioxide (CO_2) and methane (CH_4) in limestone using the Rubotherm magnetic suspension balance. According to their findings, the limestone has a threefold higher capacity to absorb gaseous CO_2 compared to gaseous methane, which improves the EGR process. The adsorption of both species was determined to be exothermic.

Theoretical approaches were utilized to study the adsorption of CO_2 and CH_4 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 CO_2 adsorption, while the B3 location is the most advantageous site for CH_4 adsorption. Additionally, they investigated the impact of the CO_2 and CH_4 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 CO_2, resulting in the liberation of adsorbed CH_4 molecules. This is a result of the low affinity between CH_4 and calcite. Zhang et al. (Zhang *et al.*, 2020) conducted a study on the adsorption of CH_4 and CO_2 on various $CaCO_3$ polymorphs, including calcite(10.4), aragonite(011)Ca, and vaterite(010)CO_3. Their findings indicated that the order of adsorption sequences for CH_4 and CO_2 on these surfaces are aragonite(011)Ca > vaterite(010)CO_3 > calcite(10.4), and vaterite(010)CO_3 > aragonite(011)Ca > calcite(10.4), respectively. Furthermore, they demonstrated that the adsorption of CO_2 is more advantageous compared to that of CH_4, which aligns with the findings of Carchini et al. (Carchini *et al.*, 2020a).

This study investigates the stability of several CO_2/calcite(10.4) and CH_4/calcite(10.4) systems using the ab initio atomistic thermodynamics technique. The data illustrates the progression of CO_2 and CH_4 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 CO_2/calcite(10.4) and CH_4/calcite(10.4) systems. A structure with lower surface energy exhibits greater stability. The surface energy, γ^{ads}, is defined as

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

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 CO_2/calcite(10.4) and CH_4/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

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

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 CH_4/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 CH_4 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 $\Delta\mu_{CH_4} = -0.29eV$, 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 CH_4/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 CH_4 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 CO_2/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 CO_2 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 CO_2/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 CO_2 is adsorbed over the B1 site.

A comparison between Figs 1 and 2 shows that CO_2/calcite(10.4) forms a stable structure at lower value of chemical potential than CH_4/calcite(10.4). This gives an advantage for CO_2 adsorption over CH_4 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 CO_2/calcite(10.4) and CH_4/calcite(10.4) systems.

Experimental evidence demonstrated that the addition of 10% CO_2 to CH_4 led to an increase in the adsorption energy of methane at a temperature of 150°C (Zhang *et al.*, 2020). The adsorption capacity of CO_2 on limestone was found to be four times greater than that of CH_4. The greater inherent selectivity of carbonate for CO_2 was thermodynamically justified by the higher exothermic behaviour of CO_2 adsorption. Therefore a better understanding of competitive adsorption between CO_2 and CH_4, a 2-D free energy phase diagram should be calculated for CO_2/CH_4 co-adsorbed systems at different coverages. The wettability of the rock is one of the major factors that would affect the adsorption of CO_2 and CH_4. Eliebid et al. (Eliebid *et al.*, 2018b) reported that surfactant-treated limestone has a much lower capacity for CO_2 and CH_4 adsorption compared to surfactant-untreated minerals.
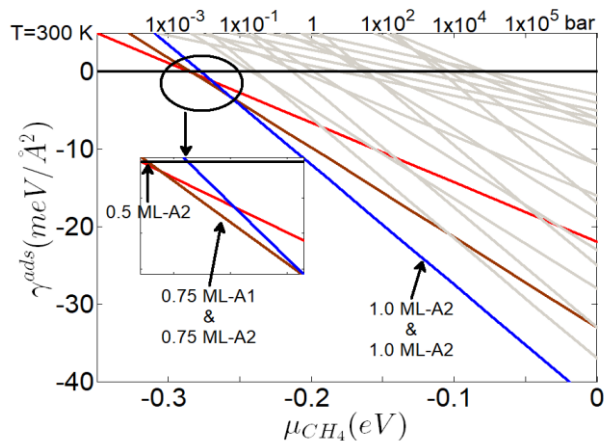

Fig. 1 Surface free energy for CH_4/calcite(10.4) structures reported by Carchini et al. (Carchini *et al.*, 2020b).
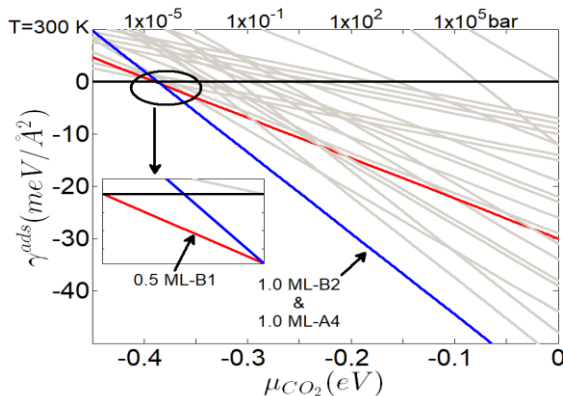
Fig. 2 Surface free energy for CO_2/calcite(10.4) structures reported by Carchini et al. (Carchini *et al.*, 2020b).

Conclusions

The stability of CO_2/calcite(10.4) and CH_4/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 CH_4/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 CO_2/calcite(10.4). The phase diagrams also indicated that the adsorption of CO_2 on the surface is more advantageous compared to CH_4, increasing EGR.

Nomenclature

A	=Surface Area	[Å²]
E_b	=Binding Energy	[eV]
γ^{ads}	=Surface Energy	[$\frac{meV}{Å^2}$]
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]

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).