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The condensation behaviours of carbon dioxide on MgO surface

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Abstract. Various separation methods for carbon dioxide gas have been proposed to control its release to the atmosphere, including the separation using an inorganic membranes such as ceramic MgO. In this work, molecular dynamics simulations are performed to clarify the condensation behaviour of carbon dioxide, in its pure and mixture state, onto the surface of MgO at a high operational temperature. The results show that no condensation of pure carbon dioxide is observed on MgO surface. However, the presence of methane impurity can promote the condensation of carbon dioxide on MgO surface as a single layer with an ordered configuration.

1. Introduction

Carbon dioxide, CO₂, is an important family member of greenhouse gases (GHG). With estimated growth rate of 2.2 ppm/year [1], the increasing amount of CO₂ in the atmosphere over the past years has been primarily caused by the emission of carbon dioxide from deforestation and human activities [2-4]. High amount of carbon dioxide in the atmosphere comes with a consequence that earth's surface absorb additional heat, raising its temperature, and change the global climate in a harmful direction. The anthropogenic emission of carbon dioxide from fossil fuel combustion has been started before industrial revolution and its increase is projected to continue in the future, unless efforts are made to replace the fossil fuel or control the release of carbon dioxide.

Along with the effort to find a renewable energy source, many research works have been dedicated to develop new technologies to control the release of carbon dioxide to the atmosphere. Electrocatalysts materials such as doped graphene and molecular metal catalysts have been reported to be useful in converting carbon dioxide into another useful compound by reduction reaction [5-6]. Other researches have reported about the inclusion of carbon dioxide inside ice, producing a carbon dioxide hydrate as one method of trapping carbon dioxide at the high pressure [7-9]. On the other hand, the separation of carbon dioxide using a membrane has become a promising technology that allows continuous separation in industrial scale at a low cost process. Membranes such as modified graphene, mesoporous carbon, zeolite, polymer, and polymer based ionic liquid membrane have been reported for the separation of carbon dioxide with a very high selectivity [10-13]. From the view point of its material, inorganic membrane allows the separation of carbon dioxide to be carried out continuously under high temperature and pressure, which are kinetically favorable for gas system. Recently, Lukman et al [14] reported a molecular dynamics simulation of carbon dioxide separation using a ceramic MgO membrane at high temperature to allow higher transport rate. However, they observed that the carbon dioxide tends to



condensate near the cylindrical pore opening on MgO membrane under low concentration of methane even at a temperature as high as 100 °C. This conditions led to an incomplete separation of carbon dioxide and methane in their mixture and thus largely hampered the advantages of inorganic membrane for carbon dioxide separation and controlled release. From the scientific view point, the condensation of carbon dioxide at high operational temperature is intriguing.

In this research, a constant-density molecular dynamics (MD) simulations are performed to clarify the condensation of carbon dioxide on MgO surface at high temperature. The MD simulation have become an important method to examine the influence of molecular properties in nanoscale confinement and the method has been used to study the condensation of various compounds, such as n-dodecane [15] and water molecule [16]. The understanding of carbon dioxide condensation behavior is important in developing new technologies for gas separation to control carbon dioxide emission and the utilization of supercritical carbon dioxide as a green solvent.

2. Research Methods

2.1. Simulation cells

The simulation cell is a rectangle consists of a gas container with dimension of 4.212 nm × 2.5272 nm × 5.00 nm. An MgO crystal having rock-salt configuration with 6.7392 nm thickness, and without any pore opening, is located at the bottom of the container. A layer of “repulsive” graphene is placed at the top of the container as a wall. A two-dimensional periodic boundary condition is then implemented in lateral directions to the plane of MgO surface. The container is occupied by a pure carbon dioxide with varied density of ρ_0 , $2\rho_0$, and $4\rho_0$; with $\rho_0 = 0.25534 \text{ g cm}^{-3}$ to mimic the condition that was reported by Lukman et al [14]. In separated simulations, the container consists of a mixture of carbon dioxide and methane with 1:1 mole ratio and each with ρ_0 density.

2.2. Potential Models

In the present study, the potential energy is described as the sum of non-bonded pair-interaction that consists of the Lennard-Jones (LJ) 12-6 potential model and the electrostatic interaction,

$$\phi_{ij} = \sum_i \sum_{j>i} \left[4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{Z_i Z_j e^2}{r_{ij}} \right] \quad (1)$$

Carbon dioxide is modeled as a linear rigid rotor that interacts according to Zhigang Zhang and Zhenhao Duan (Z3D) parameter [17]. As a comparison to the previous report, the MSM-Modified [14] potential model is also employed. Both models consist of three LJ potential sites: one at C atom and two at each O atom. A single positive-charge site is located at C and two negative charge sites are located at each O. Methane is modeled as a spherical LJ atom. The MgO structure is modeled with rock-salt configuration. Mg and O are each modeled as a spherical LJ, with Mg carries positive charge and O carries negative charge. The site-site potential parameters are shown in **Table 1**. The potential parameters for a pair of different interaction sites are calculated based on the Lorentz-Berthelot mixing rule. The potential energy of interaction between a gas molecule and the repulsive graphene layer is modeled with

$$\phi_{i\text{-graphene}} = \sum_i \sum_{j>i} \frac{4\epsilon\sigma^{12}}{r^{12}} \quad (2)$$

2.3. Simulation Methods

Constant-volume molecular dynamics (MD) simulations are performed using GROMACS 4.6.5 package [18]. The interaction of all molecules are truncated smoothly at 0.8655 nm using switching function that begin at 0.6655 nm. The equation of motion is solved using velocity-verlet algorithm, and

the temperature is maintained using Nose-Hoover thermostat. Each MD simulation consists of 5×10^6 steps that correspond to 10 ns.

Table 1. Pair-potential parameters for Z3D and MSM-Modified models for carbon dioxide, along with the graphene, methane, and MgO models used in the work. The electrostatic interaction parameter is denoted by an electrostatic charge q . The LJ 12-6 potential parameters are denoted by the σ that roughly describes the diameter of interaction site, and the ϵ that describe the depth of potential energy well.

Model	Site	q / e	$\sigma / 0.1 \text{ nm}$	$\epsilon / \text{kJ mol}^{-1}$
Z3D	C	+0.5888	2.7918	0.2398
	O	-0.2944	3.0000	0.6871
MSM-Modified	C	+0.66450	2.785	0.2411
	O	-0.33225	3.064	0.6901
Methane	C	0	3.758	1.2355
MgO	Mg	+2.000	2.377	0.0440
	O	-2.000	2.511	1.2827

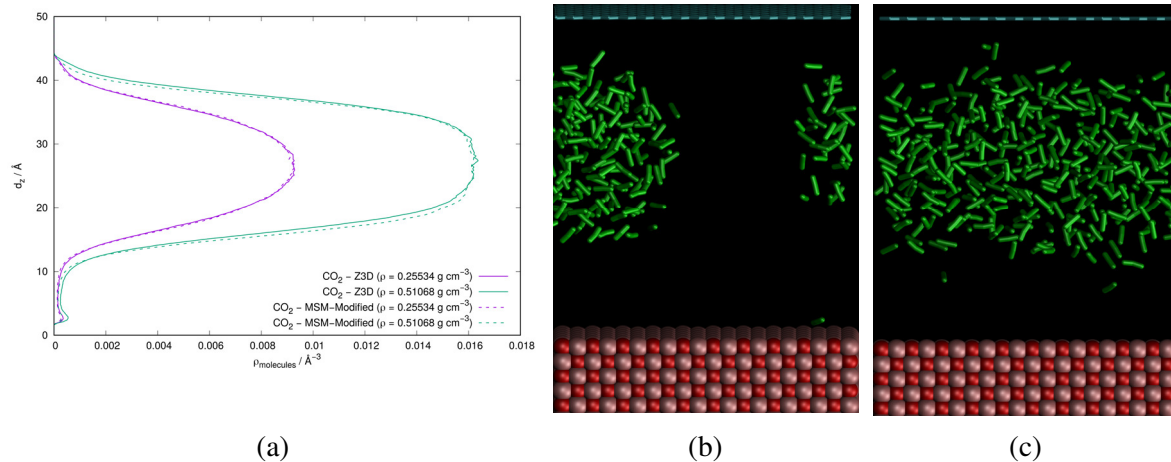


Figure 1. The axial density of carbon dioxide inside nano-confinement as a function of distance, d_z , from the surface of MgO at 100 °C (a); and the snapshot of simulation cell with carbon dioxide densities of $\rho = \rho_0$ (b) and $\rho = 2\rho_0$ (c).

3. Result and Discussion

The simulation results for the pure carbon dioxide system, at a high operating temperature of 100 oC and various densities, shows that no condensation of carbon dioxide on the surface of MgO is observed; instead, carbon dioxide condenses in form of a liquid-like spherical cluster, ignoring the adsorption preference to the MgO surface. Figure 1 shows the axial density of carbon dioxide as a function of distance from the MgO surface, and the snapshot of the simulation cell, which reveals the presence of carbon dioxide cluster located more than 1 nm away from the surface. The axial density profile also shows that the results are indifferent between two potential models that are employed. Considering the high operating temperature of 100 oC, the lack of carbon dioxide adsorption on the surface and the clustering formation in nano-confinement at a constant gas-density are reasonable. While the spherical cluster is observed for carbon dioxide system with the density of ρ_0 and $2\rho_0$, pure carbon dioxide at

high density of $4\rho_0$ forms a partial crystalline structure in this nano-confinement, as shown in Figure 2. The crystalline structure does not form at the area close to MgO surface, again; but the sharp peak at the bottom of the axial density profile in Figure 2a shows that an amorphous layer of carbon dioxide is formed on the surface of MgO under the condition of a high density. The visualization of simulation cell in Figure 2b and the trajectory analysis shows the coexistence of solid-liquid phase in this system. The phase transition can be observed from the evolution of potential energy arising from the carbon dioxide interactions that abruptly dropped during the course of simulation, as shown by Figure 2c.

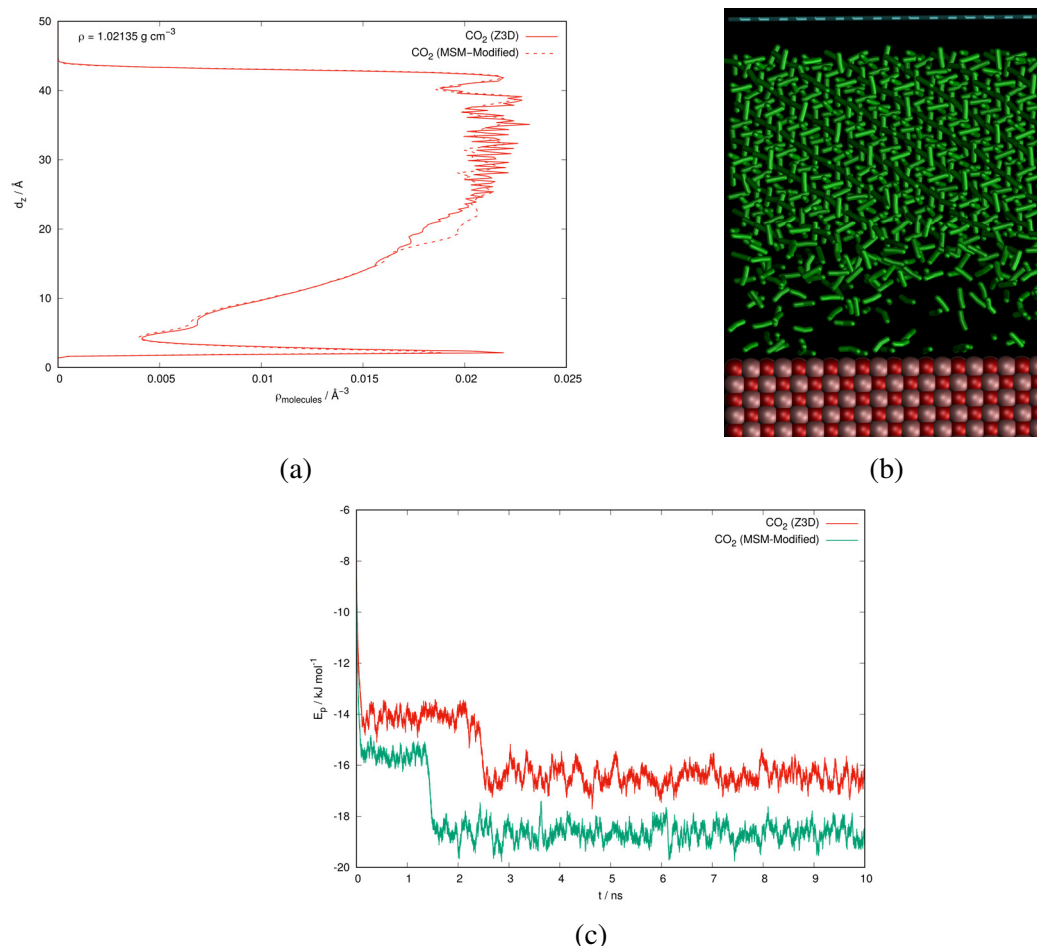


Figure 2. (a) Axial distribution function of a pure carbon dioxide with d_z is axial position measured from the surface of MgO. (b) Snapshot of MD simulation for a mixture of carbon dioxide (green) form like solid-liquid phase that coexistence. (c) The potential energy of carbon dioxide is suddenly decreased at certain times for both carbon dioxide models.

While the pure carbon dioxide is less likely condensed on the MgO surface at a high operating temperature, unless at a very high density of $4\rho_0$, the simulations of a mixture of carbon dioxide and methane in 1:1 composition with the total gas density of $2\rho_0$ shows that the presence of methane can drive the adsorption of carbon dioxide on MgO surface. Interestingly, the adsorbed carbon dioxide molecules is observed to form an ordered monolayer, which contrast to the pure carbon dioxide at a very high density. Figure 3a shows the axial density profile of carbon dioxide and methane as a function of axial distance from the MgO surface. The adsorbed carbon dioxide monolayer is indicated by the sharp peak near the MgO surface, whereas methane is distributed evenly in the container. The condensation of carbon dioxide on the MgO surface is followed by a significant change of the potential energy arisen from the interaction between carbon dioxide and MgO during the course of simulation, as shown in

Figure 3c and 3d. The sharp decrease of the potential energy in this case describes the strong interaction of carbon dioxide and MgO, which is not observed in the absence of methane. Note that the absence of gas adsorption on the graphene wall in this simulation is due to the method that purposely assigns the graphene to bear a repulsive behavior.

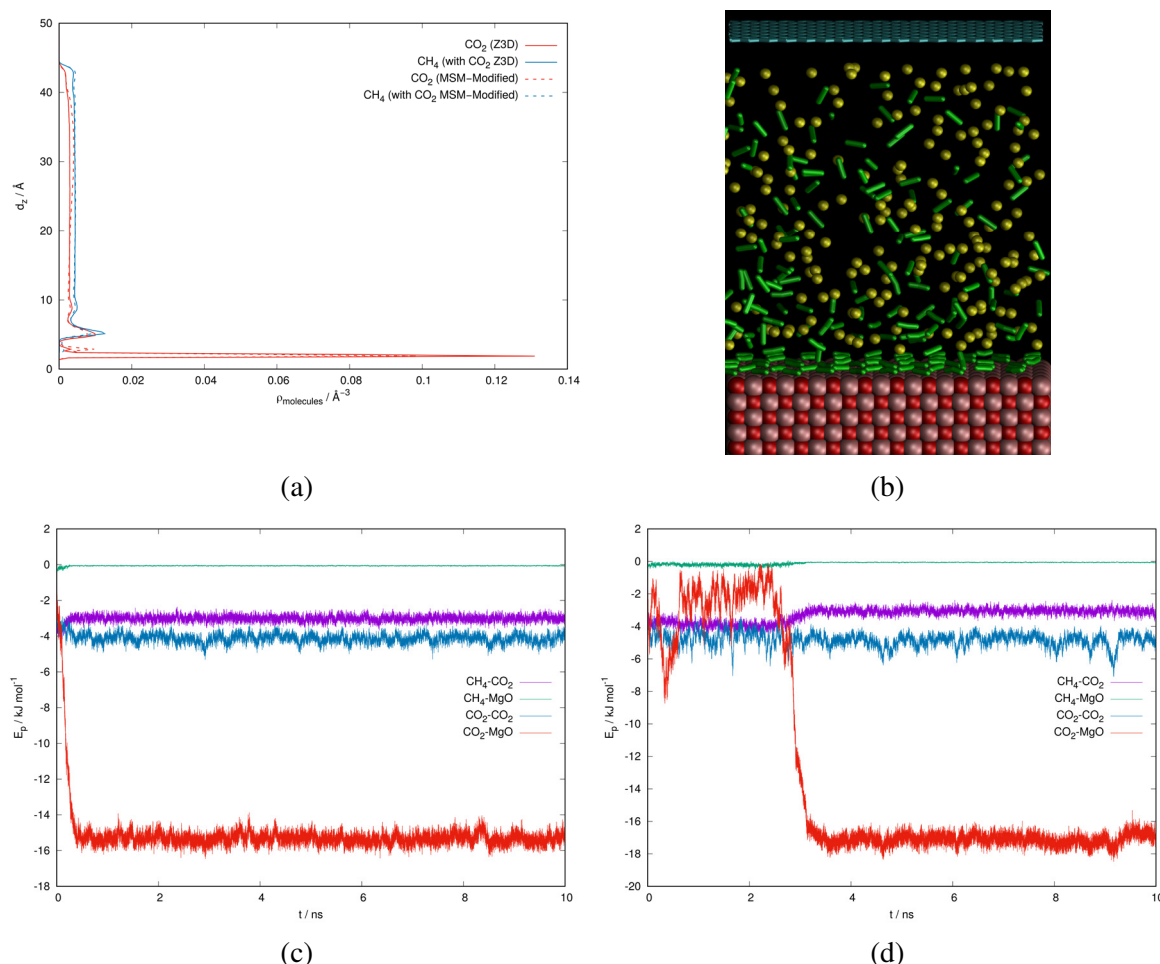


Figure 3. *Top:* (a) Axial distribution function of a mixture carbon dioxide and methane with d_z is axial position measured from the surface of MgO. (b) Snapshot of MD simulation for a mixture of carbon dioxide (green) and methane (yellow) with 1:1 mole ratio from an ordered single layer on the surface of MgO. *Bottom:* The potential energy arising from the interaction of carbon dioxide with the MgO surface and methane using carbon dioxide models: (c) Z3D and (d) MSM-Modified.

A quantitative insight on the structure of the ordered monolayer is obtained by analyzing the angular distribution of the adsorbed carbon dioxide molecules. Since carbon dioxide is modelled as a linear rigid rotor, the orientation of a carbon dioxide molecule can be represented by two angles: θ and φ . In particular, the φ angle describe the orientation of carbon dioxide on a plane that is parallel to the MgO surface. Figure 4 shows that the adsorbed carbon dioxide molecules are mainly oriented with φ angle is either $\pi/4$ (45°) or $3\pi/4$ (135°), indicating a zig-zag orientation. On the other hand, the θ angle that peaked on $\pi/2$ (90°) shows that the adsorbed carbon dioxide molecules have their principal axis aligned parallel to the MgO surface. The configuration of this monolayer is somewhat similar to the crystal structure of the bulk carbon dioxide [19]. An engineered solid surface whose atomic configuration promotes the ordered carbon dioxide alignment can thus be utilized to enhance the trapping of carbon dioxide in its mixture by the adsorption mean.

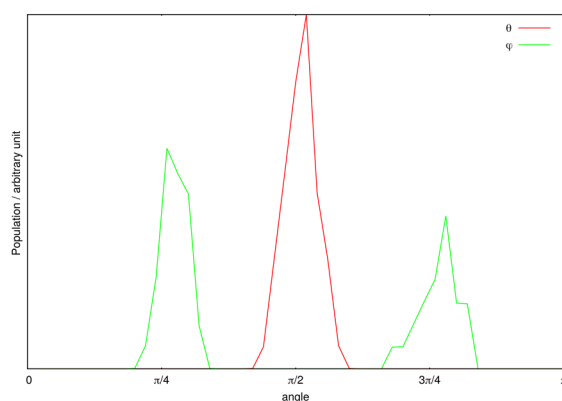


Figure 4. Angular distribution of carbon dioxide molecules that are adsorbed on the surface of MgO.

However, the observed adsorption behaviors as described above are seemed to be different with the case of MgO membrane with a cylindrical pore opening. In the latter case, there was no adsorption of carbon dioxide on the surface of MgO membrane under the presence of methane. As the methane permeated through the cylindrical pore opening and its number decreased, a condensation of carbon dioxide near the pore opening was observed and led to pore clogging that limit further permeation of gases [14]. Compared to their bulk counterpart, the behaviors of molecules are known to be different in nano-confinement due to the restriction in orientation and cluster formation caused by the limiting container's size and geometry [20, 21]. The presence of cylindrical pore opening whose diameter is narrow enough to sieve carbon dioxide provides another type of nano-confinement that raise another different behavior of carbon dioxide. The geometry of the reported cylindrical pore opening only allows carbon dioxide to enter the opening in a particular orientation and effectively act as a quasi-one dimensional tunnel. The fact that the adsorption of carbon dioxide was observed near the pore opening indeed shows that the condensation is triggered by the presence of the cylindrical opening in MgO membrane.

4. Conclusion

The MD simulations shows that low-density pure carbon dioxide system is less likely to condense on MgO surface. Instead, carbon dioxide forms a spherical cluster away from the MgO surface. At high density, pure carbon dioxide is observed to form a partial crystalline structure that coexist with the fluid phase. However, we found that the presence of methane induced carbon dioxide condensation on the MgO surface. The carbon dioxide forms a monolayer with ordered configuration that is similar to bulk carbon dioxide crystal. Such tendency can be used to design a surface material, particularly those with a large number of slit pores, whose atomic configuration promotes the carbon dioxide alignment in its monolayer thus enhance the carbon dioxide trapping. Furthermore, these different behaviors, compared to the case of MgO membrane with narrow pore opening, further emphasize the importance of understanding the effect of confinement size and geometry to the behavior of molecules.

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