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A molecular dynamics simulation study on separation selectivity of CO₂/CH₄ mixture in mesoporous carbons

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Abstract

The effect of surface charged defects in carbon mesoporous materials on adsorption selectivity for a CO₂/CH₄ gas mixture relevant to natural gas was studied by means of classical molecular dynamics (MD) simulation. The mole fraction of CO₂ was 0.1, T = 300K and the partial pressure of CO₂ was up to 40 bars. A graphite slit pore of 3.0 nm was taken as a model for mesoporous carbon. The localized charged defects within an electroneutral pore surface were found to increase the CO₂/CH₄ separation selectivity. In addition, such surface charges interact with CO₂ molecules only. The selectivity reduces with increasing pressures. Our model with a defect charge of 0.2 electron/atom can reproduce the selectivity CO₂/CH₄ of the experimental data reported in the literature. A perfect charge graphite model underestimates the adsorption selectivity of CO₂/CH₄. The results show that a very high selectivity around 25 can be achieved with a charged defect of 0.45 electron/atom. This suggests that controlling the charged defects on surface of carbon mesoporous can be used to enhance the CO₂/CH₄ separation for natural gas.

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1. Introduction

The separation of CO₂ from CH₄ is of primary importance in many industrial processes such as natural gas sweetening, biogas upgrading, and landfill gas purification [1]. Industrial technologies conventionally employed for this separation purpose include chemical absorption, pressure swing adsorption (PSA) and cryogenic separation [2]. Despite the maturity, these technologies usually involve substantially sophisticated equipment, energy-intensive operation and high investment cost. As an alternative, membrane separation technology has emerged and attracted increasing attention in CO₂ separation and capture research during the last decades, due to its high energy efficiency, simplicity in design and module construction and environmental compatibility [3]. Various membrane types for CO₂/CH₄ separation are available. Based on the membrane materials, they can be categorized in three major groups, which include (organic) polymeric membranes, inorganic membranes, and mixed matrix membranes. Inorganic membranes are more suitable for CO₂ separation under more severe conditions (higher temperatures and pressures) relevant for natural sweetening, when organic based membranes are not functional. However, a

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major drawback of these membranes is their substantially higher cost. Therefore, research and production of inexpensive membranes for CO₂/CH₄ separation is of great importance for the realization of carbon capture and sequestration technologies [4-7].

Recently, an experimental study on using inexpensive *mesoporous* carbon material for separation of CO₂ from CH₄ and N₂ was reported [8]. The tested material displayed very high adsorption capacity and selectivity for the gas mixtures. In another work, the importance of charged defects and charge distribution of carbon pore surfaces on the adsorption of CO₂ in *microporous* carbon was theoretically studied by means of Monte Carlo simulation [9]. It was reported that the surface heterogeneity changes the adsorbates' accumulation configuration by changing the geometry of the pore surface and the charge distribution of the surface. As the pore width decreases, the surface functionalities dictate the adsorption, and thus the surface functionalities play a more important role in increasing the CO₂ adsorption capacity. However, this information is currently not available in the open literature for mesoporous carbon material and therefore the study reported in this paper was carried out using molecular dynamics simulation method. The objective was to study the effect of localized surface charges on the adsorption and separation of the CO₂ and CH₄ gas mixture, relevant for natural gas. For this purpose, a gas mixture with the mole fractions of 10% CO₂ and 90% CH₄ was employed to simulate the chemical composition of natural gas. Molecular dynamics (MD) simulations are well suited to determine such properties surface charges can be varied in a controlled way. In the next section, we will introduce briefly the method and models used in MD simulations. We will show how important the surface charge is for CO₂ adsorption. The CO₂/CH₄ separation selectivity will also be demonstrated with varied pressure.

2. Method

2.1. Simulation method and model

In this work, LAMMPS package was employed for classical molecular dynamics (MD) simulations [10]. The simulated model was consisted of a graphite crystal and a mixture of CO₂ and CH₄ molecules. The mole fraction of CO₂ was 0.1 to mimic the composition of natural gas. The graphite structure was hexagonal, without any defect. The model system and was constructed from 10 sheets of graphene, containing 32000 carbon atoms. It is important to use a flexible and high number of graphene sheets to model graphite layers [11, 12]. Periodic boundary conditions in all directions were applied. The surface of graphite was 98x85 Å². In the *z* direction, there were two graphite regions, and the distance between them was equal to the pore width $W=3$ nm (Figure 1). The total surface charge was always kept neutral. One carbon atom in the graphite layer was positively charged, and surrounded by 3 negatively charged atoms. The distribution of charges around the positive atom was thus [C^{3δ+} - 3C^{δ-}], as pictured in Figure 1. A random amount, 30%, of the total atoms in the surface layer was charged positively or negatively in this manner. An average charged defect value was determined as the total absolute charge divided by the total number of atom (electron/atom). This simulation model can represent the charged defects inside carbon material. At each value of charged defects, ten systems with different total number *N* of molecules were established to simulate pressure of CO₂ up to 40 bars. All simulation was performed at temperature 300 K.

The initial configuration was constructed by randomly distributing the CO₂ and CH₄ molecules over the graphite surface. The system was stabilized during 2 ns by *NVT* runs with the Nosé-Hoover thermostat [13]. When a thermal equilibrium was established in the system, another 2 ns run were performed with micro-canonical ensemble conditions (*NVE*) to study the adsorption properties. The average values of temperature and pressure in the *NVE* simulations were within 1% of the expected values. In total, 4x10⁶ MD steps with a time step of 1fs was performed and this is sufficiently long to obtain good statistics and consistent trajectories.

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