Adsorption and Diffusion of CH_4, N_2 and their Mixture in MIL-101(Cr): A Molecular Simulation Study

Yimin Shao[1†], Shanshan Wang[2], Liangliang Huang[3], Shenghong Ju[4], Xianfeng Fan[1], Wei Li[1*]

[1]Institute for Materials and Processes, School of Engineering, University of Edinburgh, Edinburgh EH9 3FB, Scotland, UK
[2]College of Chemical Engineering, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing, Jiangsu 210037, P.R. China
[3]School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019, United States
[4]China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China

[†]Presenting Author: Y.Shao-20@sms.ed.ac.uk
[*]Corresponding Author: Wei.Li@ed.ac.uk

Abstract

A comprehensive quantitative grasp of methane (CH_4), nitrogen (N_2), and their mixture's adsorption and diffusion in MIL-101(Cr) is crucial for wide and important applications e.g. natural gas upgrading, coal-mine methane capturing. Previous studies often overlook the impact of gas molecular size and MIL-101 topology structure on adsorption, lacking quantitative assessment of primary and secondary adsorption sites. Additionally, understanding gas mixture adsorption mechanisms remains a research gap. To bridge this gap, we utilized Monte Carlo (GCMC) and molecular dynamics (MD) simulations for computing essential MIL-101 properties, encompassing adsorption isotherms, density profiles, self-diffusion coefficients, radial distribution function (RDF), and CH_4/N_2 selectivity. Our findings highlight the significance of the C=C double bond within MIL-101 for CH_4 and N_2 adsorption, with Cr and O atoms also exerting notable effects. Density distribution analysis reveals CH_4's preference for pentagonal windows, large and medium cages, while N_2 is evenly distributed along pentagonal and triangular window edges and small tetrahedral cages. Self-diffusion calculations suggest N_2's higher mobility within MIL-101 compared to CH_4. Moreover, our simulation results demonstrate that MIL-101 exhibits a higher affinity for CH_4 in the binary mixture, as evidenced by the calculated CH_4/N_2 selectivity. This investigation provides valuable microscopic insights into the adsorption and diffusion phenomena occurring in MIL-101, thereby contributing to a comprehensive understanding of its potential for selective capture of coal-mine methane.

Keywords

MIL-101, Methane, Adsorption, CH_4/N_2 selectivity, Molecular simulation

1 Introduction

Global warming, resulting from the escalating levels of greenhouse gases, represents an undeniable and urgent challenge in the twenty-first century [1]. Methane (CH_4), one of the six primary greenhouse gases regulated by the Kyoto Protocol, possesses a warming potential over 20 times greater than that of carbon dioxide (CO_2) [2]. Annual methane emissions from underground coal mines have exhibited a range of 2.03 to 2.87 billion cubic meters in recent decades [3]. Projections by the US Environmental Protection Agency forecast that global methane emissions from coal mines will surpass 784.3 MtCO2e by 2030 [4]. Consequently, the selective separation of CH_4 from N_2 in coal-mine methane holds immense significance and vitality. This separation process has the potential to not only yield valuable chemicals and fuels, leading to economic benefits but also contribute to the reduction of atmospheric greenhouse gas emissions, thereby aiding in the fight against global warming [5].

Extensive research has been conducted on conventional porous materials [5], including activated carbons, zeolites, and molecular sieves, to evaluate their effectiveness in separating CH_4/N_2 mixtures. However, the challenge of achieving high CH_4/N_2 selectivity remains unresolved. To address this issue, it is imperative to explore novel types of porous materials. Metal-organic frameworks (MOFs) have emerged as promising candidates for selective gas separations due to their tunable pore size and chemistry [5]. MIL-101(Cr) possesses an exceptionally high specific surface area, large pore size, significant pore volume, superior separation selectivity, ease of regeneration, and excellent thermal, chemical, and water stability [6].

While numerous experimental studies investigated the adsorption of individual N_2 and CH_4 gases using various MIL-101 modifications [7], few theoretical studies have been conducted to investigate this area. Additionally, limited experimental and theoretical research has been conducted on the utilization of MIL-101 for the adsorption and separation of CH_4/N_2 mixtures.

In this study, the primary objective is to employ grand canonical GCMC and MD simulation methods to gain a comprehensive understanding of the influence of structural variations in the MIL-101 framework on the adsorption and diffusion of CH_4 and N_2 gases within its pores.

2 Methodology

The work is divided into two parts: the analysis of the single-component system and the analysis of the two-component system. Before the analysis in Parts 1 and 2, for single-component gases, it is necessary to verify the reliability of the simulation and validate the force filed through the adsorption isotherm and isosteric heat. In the case of the two-component system, the reliability of the simulation is assessed by analyzing the selectivity of CH_4/N_2, which enables a more comprehensive investigation of the adsorption and diffusion behaviors. The analysis primarily utilizes three methods attained from RASPA2 and LAMMPS [8]: density distribution profile, self-diffusion coefficients, and RDF. By elucidating the mass transport characteristics of CH_4 in MIL-101 with varying N_2 concentrations at the atomic level, this study provides valuable theoretical insights for the separation of CH_4/N_2 mixtures using MIL-101(Cr).

3 Results

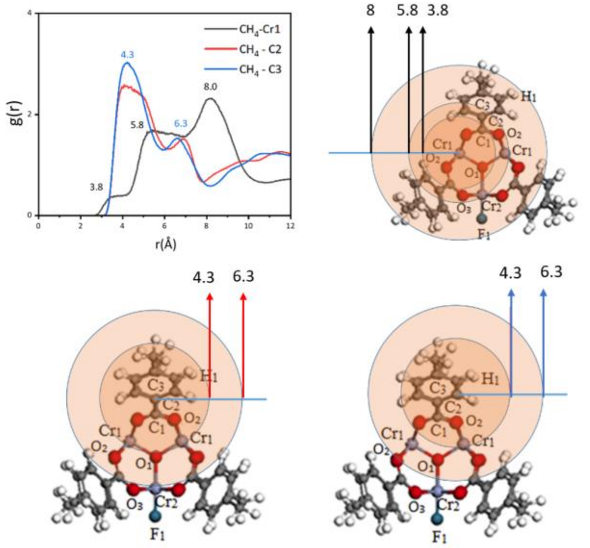

Fig. 1 RDF of CH4 around Cr1 atom and C3 atom.

In Fig.1, the RDF curve for Cr1 displays three distinct peaks at around 3.8 Å, 5.8 Å, and 8 Å. The highest peak, situated at 8 Å, indicates CH_4 accumulation near Cr1, influenced by C2 and C3 (C=C) atoms facilitating interactions. The 5.8 Å peak shows lower CH_4 density due to steric hindrance near C2/C3, limiting interaction. Nearby atoms and arrangement affect CH_4 accessibility and binding. The 3.8 Å peak results from O2, O1, and Cr1, favorably impacting CH_4 adsorption. These reveal the C=C bond's pivotal role in CH_4 adsorption.

In Fig. 1, peaks at ~4.3 Å and 6.3 Å in C2 and C3 curves are observed. The ~4.3 Å peak signifies CH_4 adsorption near the C=C bond, a vital interaction site. A smaller peak around 6.3 Å stems from Cr-O interaction, leading to less CH_4 adsorption. Notably, the C3 curve's 4.3 Å peak surpasses C2, attributed to reduced steric hindrance, enabling denser adsorption. These insights elucidate specific CH_4 adsorption sites and the C=C bond's and metal's role in MIL-101's CH_4 adsorption.

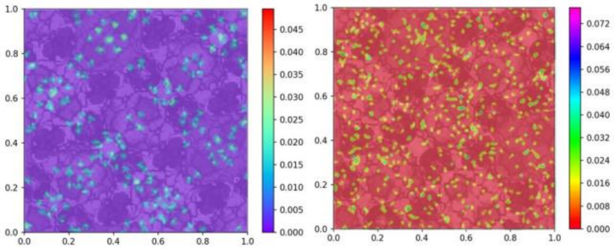

Fig. 2 2D Density distribution of binary mixture with 200 CH_4 (left) and 600 N_2 (right) molecules.

The 2D density distribution profiles in Fig. 2 shows that CH_4 molecules preferentially occupy pentagonal windows, large and medium cages, with the highest density observed at the edges of the pentagonal window connecting the large and medium cages. Similarly, N_2 molecules exhibit a relatively uniform distribution along the edges of pentagonal and triangular windows, as well as in the small cages of the tetrahedron. Additionally, the analysis of 2D density distribution profiles for binary mixtures reveals that the overall distribution of CH_4 molecules remains largely unaffected by an increase in the number of N_2 molecules.

4 Concluding remarks

1. CH_4 and N_2 adsorption depends on C=C bond (major) and Cr, O atoms (secondary).
2. Gas diffusion is influenced mainly by pore size and molecular diameter.
3. CH_4 prefers occupying large and medium cages, rarely entering the small cage.
4. N_2 evenly distributes in medium, large cages, and small tetrahedron cages.

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