Chemical Physics Letters 629 (2015) 65–69

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Single layer hydrogenated graphyne membrane for selective hydrogen separation: A molecular dynamics simulation study

Mohammad Alaghemandi

Faculty of Mechanical Engineering, University of Paderborn, Warburger Str. 100, D-33098 Paderborn, Germany

ARTICLE INFO

Article history:
Received 9 January 2015
In final form 27 March 2015
Available online 20 April 2015

ABSTRACT

Using molecular dynamics simulations, we have investigated hydrogenated graphyne layers as molecular-sieving membranes. Hydrogenated α-graphyne layer with no defect indicated a complete separation capability for a mixture of H_2/CH_4. The separation selectivity for H_2/N_2 mixture was about 700 at room temperature using the same membrane. This value reduced by increasing the temperature. However, presence of defects in the membrane dramatically decreased the separation selectivity for both studied mixtures. Surprisingly, increasing the temperature enhanced the separation selectivity using the defected hydrogenated α-graphyne membrane. Hydrogenated γ-graphyne layer with no defect did not show any permeability effect for the studied gases.

1. Introduction

Different classes of materials such as polymers [1], zeolites [2,3], carbon [4], silica [5], and metal-organic-frameworks [6,7] have been shown for mixture separation. The separation process is normally based on difference in diffusion rate, selective adsorption, or molecular-sieving mechanisms. The thickness of the mentioned membranes is at minimum about 20 nm. Recently, Li et al. have reported an ultrathin membrane of graphene oxide (GO) with a thickness of about 1.8 nm [8]. Using GO membranes they could separate H_2/CO_2 and H_2/N_2 mixtures with separation selectivity of about 3400 and 900, respectively. They mentioned that the major transport pathway for the permeated molecules is the selective structural defects in the GO layers [8]. So increasing the membrane thickness exponentially reduces the permeance of small molecules like H_2. However, the transport channels for permeanced molecules are the structural defects within the membrane layer, and hence might be difficult to control, reproduce, and manipulate in comparison with a perfectly no-defect structure of a membrane with controllable pore size. Although the preparation and the properties measurement of purely single layer membranes with thickness less than 1 nm and without any defect are experimentally extreme difficult tasks, the theoretical investigations can go beyond the experimental difficulties for better understanding of the single atom thick membranes.

An interesting study of hydrogenated graphyne structures has been carried out recently by Koo et al. using first-principles calculations [9]. They have systemically studied the hydrogenated graphyne structures with different hydrogen concentration and compared the binding energies and the band-gaps. By looking at the optimized structure of the hydrogenated graphyne layers, one can observe tiny pores within the networks which are potentially useful for molecular-sieving applications. Since the graphyne layers are only one atom thick, the formed membranes potentially have the lowest friction for gas transport and hence a high flux. Here, in this study we investigate two different hydrogenated graphyne structures, hydrogenated α-graphyne with ratio of $C_1H_{0.75}$ and γ-graphyne with $C_1H_{0.5}$ proportion, as molecular-sieving candidates for separation H_2 molecules from H_2/CH_4 and H_2/N_2 mixtures; see Figure 1. Two type of membranes i.e. without defect and with defect are studied in this work.

2. Computational methods and simulation details

All molecular dynamics (MD) simulations have been performed using the LAMMPS software developed at Sandia National Laboratories [10]. The force field (FF) applied for the hydrogenated graphyne has been adopted by combining FF of the carbon nonotube/graphene [11–14] with the force field used for benzene/polystyrene [15]. The FF for gas molecules are taken from Refs. [16–18].

The simulation boxes consist of two parallel graphyne membranes with a distance of about 10 nm from each other and a 50:50 mixture of H_2/CH_4 or H_2/N_2. We use two membrane layers to

E-mail address: alagheh@mail.uni-paderborn.de

http://dx.doi.org/10.1016/j.cplett.2015.03.052
0009-2614/

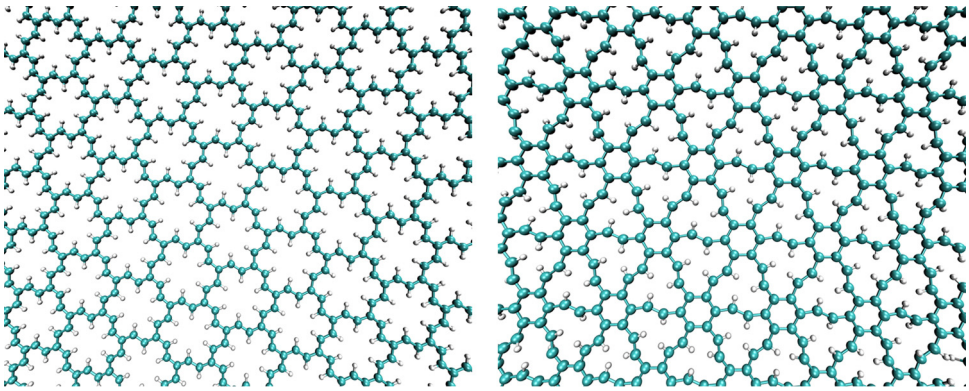

Figure 1. A snapshot of the hydrogenated graphyne layers, hydrogenated α-graphyne (left) and γ-graphyne (right).

enhance the statistics of the gas molecules cross the membrane. The two graphyne layers are located in far distance from each other to prevent any membrane-membrane interaction. The simulation box, as shown in Figure 2, has a size of 20.0 nm × 5.4 nm × 5.8 nm and the periodic boundary conditions PBC have been applied in all directions. The transmittable gas molecules can cross the membrane multi times and hence enough statistical data can be collected at the end of the simulation. To prevent any migration of the graphyne layers, one carbon atom at each corner of the membrane has been fixed. In the case of membrane with structural defect, we remove a central carbon atom with three carbon neighbors and convert those carbon neighbors to sp^3 type by adding additional hydrogen atoms. According to the chosen membrane size, the resulting defect density amounts to 3×10^4 in μm^2. For each of studied mixtures, three different amount of gas molecules have been loaded in the box, 100, 250, and 500 molecules of each components, to investigate any influence of number of gas molecules in our simulations.

In this study, the permeance of gas molecules is defined as the number of transferred molecules per time per cross sectional area divided by the gas pressure at each temperature. The separation selectivity is the ratio between the number of transferred hydrogen molecules and the second gas component in the mixture.

The MD simulations have been performed at constant temperature and volume. For the Nosé–Hoover thermostat [19] a coupling time of 1 ps has been used. The particle-particle particle-mesh (PPPM) method with a real space cutoff of 1.2 nm was used for evaluating the electrostatic interactions. A time step of 1 fs has been employed in all simulations.

3. Results and discussion

3.1. Hydrogenated graphyne membranes with no defect

To evaluate the membrane separation capability, we have calculated the permeance of each gas molecule of the binary gaseous mixtures through the membrane and hence the separation selectivity. Here, for each membrane type, two different mixtures of H_2/CH_4 and H_2/N_2 with 50:50 proportion of each component have been investigated and the separation selectivities have been measured.

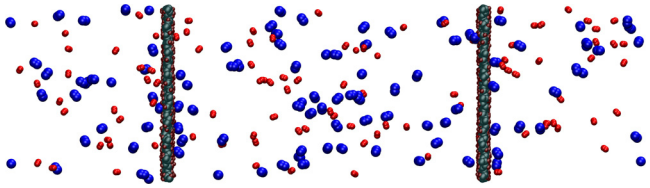

Figure 2. A snapshot of the simulation box of H_2/N_2 mixture with 100 molecules of each components. H_2 molecules are in red and N_2 in blue. The distance between two graphyne layers is about 10 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Simulations with hydrogenated γ-graphyne membrane have not shown any permeance for any of gas molecules even for H_2. Obviously, the size of the pores within the membrane are too small for any permeation. However, the calculations using hydrogenated α-graphyne membranes indicated a permeation for some molecules, so the separation selectivity could be measured for those; see Figure 3. As the figure shows, the permeance of H_2 is almost independent from the second component of the mixture, i.e. CH_4 or N_2, as well as the simulation temperature. Enhancing the number of molecules in the system slightly decreases the H_2 permeance value from about 270×10^{-5} for a system with 100 molecules of each component to 220×10^{-5} mol m^{-2} s^{-1} Pa^{-1} for one with 500 molecules at 300 K. This is due to the fact that the number of the second component with larger size and smaller penetration capability is also increased in the system and hence a smaller space for Hydrogen molecules is accessible to diffuse into the membrane and cross it. However, our simulations at different temperatures and mixtures loads did not show any permeance for CH_4 molecules; see the right hand side of Figure 3. This indicates that the separation selectivity for H_2/CH_4 mixtures using hydrogenated α-graphyne membrane is infinite. On the other hand, N_2 molecules can permeate into α-graphyne membrane. Their permeation enhances by increasing the temperature as a results of larger kinetic energy and higher probability to pass the potential barrier of crossing the membrane with close distance to the membranes atoms, see the left hand side of Figure 3. The separation selectivity for H_2/N_2 mixture decreases by increasing the temperature since the H_2 permeation is almost constant while of N_2 increases at higher temperatures. Because of low penetration of N_2, the statistical error at small molecule loads are higher, Figure 3(a). As Figure 3(e) with better statistics indicates, the separation selectivity reduces from 1160 to 597 at 280 and 380 K, respectively.

3.2. Hydrogenated graphyne membranes with defect

There is a high probability for existence of some defects in single layer hydrogenated graphyne membrane in practice, alike graphene and functionalized graphene [20,21]. One can imagine different types of structural defects caused by bond breaking or any other doping effect. Here, for simplicity, we restrict our investigation for only a structural defect caused by removing one central carbon atom surrounded by three other carbon atoms in α-graphyne membrane; see Figure 4. The carbon atoms of the created free arms converted to sp^3 carbon atoms and additional hydrogen atoms have been added. As Figure 4 shows, the defect site with flexible free arms has a larger pore size, however, the surrounding pores are shrunk.