Molecular simulation study on the adsorption and separation of acidic gases in a model nanoporous carbon

Fatemeh Gholampour, Saeid Yeganegi *

Department of Physical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

HIGHLIGHTS

- The constricted carbon slit pore model is used for nanoporous carbons.
- Natural gas components adsorption and separations by slit pores are examined via GCMC.
- The constriction about the size of the guest molecules yields in the highest separations.
- The CO_2/CH_4 selectivities exceed experimental results of some activated carbons.
- The H_2S/CH_4 selectivities are lower than the results of some CNTs and zeolites.

GRAPHICAL ABSTRACT
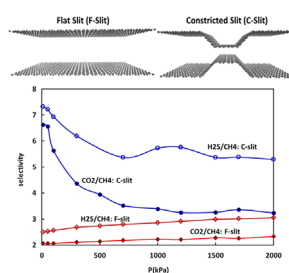
ABSTRACT

A constricted slit pore is constructed and examined as a model nanoporous carbon (NPC) for the adsorption of acidic gases (i.e., CO_2 and H_2S) as well as for the separation of binary H_2S/CH_4, CO_2/CH_4 and H_2S/CO_2 mixtures and ternary $CH_4/CO_2/H_2S$ mixture using GCMC simulations. The results show that the uptake values and heats of adsorption for pure gases at low pressures in the constricted slit models are larger than those in the simple slit. The obtained adsorption results for pure gases are in line with experimental values reported for NPCs. The adsorptive selectivities of the slit models are calculated for the binary and ternary mixtures. It is observed that the slit pore with the constriction width of about one molecular size of sorbate has the highest selectivity for the acidic gases and its calculated CO_2/CH_4 selectivity exceeds the experimental values of some activated carbons. The H_2S/CH_4 selectivities of the constricted slit models are lower than the simulation results of carbon nanotubes with comparable diameter. Our results indicate that the presence of the third component does not reveal any significant effect on the selectivities. Adsorbent performance indicator (API) is also calculated where the constricted slits show greater API values than that of an activated carbon (Takeda 5A). It is expected that the results of this work can be useful to guide the future experimental NPC synthesis efforts for their usage in natural gas purification.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The removal of acidic gases such as carbon dioxide and hydrogen sulfide is an important process in the natural gas (NG) industry. The presence of CO_2 leads to a decrease of the natural gas

* Corresponding author. Tel./fax: +98 112 5342350.
  E-mail address: yganegi@umz.ac.ir (S. Yeganegi).

calorific value and causes equipment and pipeline corrosion. Hydrogen sulfide (H_2S) is one of the most harmful and poisonous compounds that even in low concentration, causes pipes corrosion and clogs cryogenic equipment used for NG liquefaction (Tagliabue et al., 2012). The pipeline specification requires that the proportion of CO_2 and H_2S in the natural gas should be lower than 1% and 4 ppm, respectively (Chatterjee et al., 1997). The most common method for acid gas removal is liquid-phase chemical scrubbing with amines (Huang et al., 2003). However, this technology suffers a number of shortcomings, including high regeneration cost, toxicity, excessive corrosion, low absorption/desorption rate (Ma et al., 2009), loss of amine via oxidative degradation, and evaporation (Belmabkhout et al., 2011). Consequently, many researchers have been performing experiments and simulations to develop more effective technologies for natural gas sweetening (Mohamadalizadeh et al., 2011). Meanwhile, the gas separation using adsorbent is recognized to be an energy-efficient and technically feasible method. A good sorbent should have the desired properties such as large and reversible gas uptake, high gas selectivity, good chemical and thermal stability, and low cost. Various porous materials have been studied and reported as potential sorbents for the separation of CO_2 and/or H_2S from their mixtures with CH_4 (Belmabkhout et al., 2011, 2009; Crespo et al., 2008; Heymans et al., 2012; Wang et al., 2011), but each of them have some limitations for industrial scale usage. For example, zeolites have been studied as CO_2 adsorbents, while the separation ability is low, high temperature is required for regeneration, and adsorption capacity is strongly reduced by the presence of a small amount of water vapor (Eguchi et al., 2012). Metal organic frameworks (MOFs) have also shown high acid gas adsorption capacity, separation ability and unique structural flexibilities, while some of them are unstable under humid conditions. Accordingly, adsorption separation using porous materials has not yet been competitive with solvent extraction. If a good sorbent were developed, it would have the potential to replace solvent extraction in the natural gas industry. Nanoporous carbons (NPCs), because of their high thermal and chemical stability, predominately micro and mesoporous features and large specific surface area (Palmer and Gubbins, 2012), have been extensively studied as adsorbent materials for gas separations. In addition, industrial scale usage benefits from their low production cost, environmentally friendly nature (Chen et al., 2012) and low heat of adsorption; where the later results in low energy intensive regeneration operations and makes them practically friendly (Tagliabue et al., 2009).

Despite their present applications in many existing technologies (Tagliabue et al., 2009), the potential of NPCs has not been fully realized because of the absence of rational design principles to direct their experimental synthesis and application. Development of such guidelines requires a complete understanding of the correlations between their structural characteristics and assessing properties. It is here that molecular simulation methods could play an active role. These methods are needed for exploring the nanoscale phenomena such as adsorption, diffusion and chemical reactions that take place within the pores of NPC materials (Palmer and Gubbins, 2012; Palmer et al., 2011a). For crystalline materials such as zeolites and MOFs, using X-ray or neutron diffraction techniques their structure can be resolved, allowing for realistic models to be constructed for further study with simulation. But the heterogeneous nature of NPCs prevents fully characterizing their structural features by aforementioned experimental methods. Consequently, realistic structural models for these materials must be developed before their properties can be investigated by simulation methods (Palmer and Gubbins, 2012).

Over the last two decades, several structural models for NPCs have been proposed (Lim and Bhatia, 2011; Kumar et al., 2005; Pikunic et al., 2005; Arora and Sandler, 2007; Cai et al., 2008; Kumar and Rodriguez-Reinoso, 2012; Kowalczyk et al., 2010). Among them, the idealized carbon slit pore is the most simple

and traditional structural model that has been frequently used to study the characteristics of equilibrium adsorption as well as diffusion in porous carbon (Aukett et al., 1992; Sedigh et al., 1998; Wang and Johnson, 1999; Rzepka et al., 1998; Kowalczyk et al., 2005; Severson and Snurr, 2007; Mosher et al., 2013). However, this model is oversimplified, since it fails to account for pore connectivity or the highly disordered pore structure of many industrial carbons. Consequently, several authors have been trying to introduce modifications to the standard slit pore model, e.g. grafting energy sites onto the pore wall (Wongkoblap and Do, 2006), introducing energetically heterogeneity and geometrical corrugation (curved defective graphene sheets) (Jagiello and Olivier, 2013), etc. In our previous work (Yeganegi and Gholampour, 2013), we have shown that a constricted slit (C-slit) model, taking into account the variation of the pore width in NPCs in the simplest way, can better predict the adsorptive and diffusive properties of methane in NPCs compared to the common slit pore. In this work, the adsorption of pure CO_2 and H_2S and their separation from the mixture of $CH_4/CO_2/H_2S$ are examined by the C-slit model. To the best of our knowledge, sweetening of natural gas using slit models has not been studied so far. In what follows the details of model construction and simulation progress will be explained. Then, the results of the GCMC simulations related to the adsorption of pure gases to the pore models as well as the adsorptive separations of the binary and ternary mixtures of methane with the acidic gases (carbon dioxide and hydrogen sulfide) will be discussed and compared with the literature. Finally, from the industrial point of view, the parameter of "adsorbent performance indicator" (API) proposed by Wiersum et al. (2013), would be calculated for C-slit models.

2. Modeling and simulation details

2.1. Modeling

The detailed description of the slit models were reported in our pervious study (Yeganegi and Gholampour, 2013). The slit pore models were generated using ideal graphene sheets with unit cell dimensions of 30, 72 and 80 Å along the x-, y- and z-axis, respectively. The simple slit model, slit-0, is made of two graphene sheets in x–y plane with a pore width of 20 Å placed in the middle of the simulation box. To construct the C-slit models the graphene sheets were bent in 5 parts in the y direction. Fig. 1 shows the slit models studied in this work. The widths (the distance between the centers of the carbon atoms on the opposing pore walls) of the constricted parts were set as $H=5$, 7 and 9 Å where the relevant structures were referred as slit-1, -2 and -3, respectively. It is noted that the constriction widths were selected so that no guest molecule can pass the constriction region in slit-1 ($H=5$ Å) which is a representative of pore blockage, in the case of slit-2 only one layer of adsorbate molecules could be adsorbed in the constricted region ($H=7$ Å) and finally more than one molecule can be placed in vertical direction of constricted part of slit-3 (z direction in Fig. 1, $H=9$ Å). For each of the C-slit models the length of the flat and constricted regions along the y direction is 20 and 11.2 Å, respectively. The length of the intermediate region between the flat and constricted parts is 10.6, 9.19 and 7.77 Å for slits-1, -2 and -3, respectively. The pore width at the flat regions of C-slit models was kept constant at 20 Å.

The slit pores were fixed in space and only their interior surface was considered to be accessible for adsorbate. The size of simulation box in the z direction was chosen large enough to prevent the artifact interaction between the gas molecules in the adjacent unit cells (Ho et al., 2012; Nasrabadi and Foroutan, 2012). To avoid the adsorption of guest molecules to the external surface of the slit,