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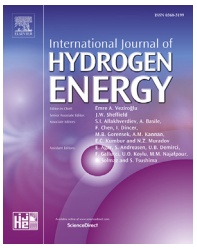

Grand canonical Monte Carlo and molecular dynamics simulations of the structural properties, diffusion and adsorption of hydrogen molecules through poly(benzimidazoles)/nanoparticle oxides composites

Abdollah Khosravanian [a], *Mostafa Dehghani* [b,*], *Mahdieh Pazirofteh* [c], *Morteza Asghari* [d], *Amir H. Mohammadi* [e,f], *Davood Shahsavari* [g]

[a] *Department of Petroleum and Chemical Engineering, Sharif University of Technology, Tehran, Iran*
[b] *Young Researchers and Elite Club, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[c] *Department of Chemical Engineering, Kermanshah University of Technology, Kermanshah, Iran*
[d] *Separation Processes Research Group (SPRG), Department of Engineering, University of Kashan, Kashan, Iran*
[e] *Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa*
[f] *Institut de Recherche en Genie Chimique et Petrolier (IRGCP), Paris Cedex, France*
[g] *Department of Mechanical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran*

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ABSTRACT

Comprehensive structural/molecular simulations have been undertaken to study the poly(benzimidazoles) (PBI) membrane combined with four different nano-oxide materials (ZnO, Al_2O_3, SiO_2 and TiO_2) for purification and production of hydrogen from natural gases. Composite membranes were built with different amounts of nano-oxide materials to investigate the influence of nano-oxide content on the PBI membrane performance. Several structural characterizations such as FFV, WAXD and also a thermal one (glass transition temperature) were done to study the structural properties of all simulated membrane cells. Moreover, MSD and adsorption isotherms tasks were used to estimate the diffusivity and solubility of hydrogen molecules through the latter mixed matrix membranes (MMMs), respectively. Permeability and permselectivity of H_2 penetrate molecules were also carefully calculated using the aforementioned penetrating factors (diffusivity and solubility). Results show a significant improvement in structural and transport properties by increasing the nanomaterials content, which could be due to the growth of penetration pathways through the membranes. Furthermore, membranes with SiO_2 yield the best results compared to other three nano-oxide fillers. H_2 gas yields the best results that help the storage and separation of this precious gas from other gas molecules, which present in natural gases. Compared to the previous studies and literature results, the current results are accurate and reliable to describe the structural and transport properties of PBI/nano-oxides composites.

* *Corresponding author*. Young Researchers and Elite Club, Science and Research Branch, Islamic Azad University, Tehran, Iran.
E-mail addresses: m.dehghani1990@gmail.com (M. Dehghani), shahsavari.davood@miau.ac.ir (D. Shahsavari).

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Introduction

Nowadays, the significance of purification and production of hydrogen (H_2) from natural gases has been dramatically raised due to the high price of H_2 and also its increasing need due to the vast applications of this gas such as using as an energy carrier or coolant, consumption in processes, usage in gas sensors, and also in semiconductor industries [1–4]. Separation and purification of gas molecules using membrane technology due to its brilliant, significant and pioneer features, operational flexibility, simple operating processes and low operating cost have made this technology as one of the best candidate for taking the place of the previous unclean and expensive processes [5–7]. Fossil fuels combustion in industries is one of the main sources of H_2 generation [8–10]. The synthesis of novel polymeric membranes with high selectivity and permeability has been done and studied extensively. However, the so-called trade-off between permeability (P) and selectivity (α) of gas molecules has remained as the chief concern for large-scale applications [11–13]. Robeson first developed the upper bound plots in 1991 and then revised it in 2008 which represented the trade-off behavior of permeability-selectivity and therefore, made a scientific basis to overcome the afore-mentioned issues [11,14].

The solution-diffusion mechanism theory is used for gas transport in most of the pressure-driven polymer membranes which consists of three main steps: sorption, diffusion, and desorption [15,16]. In the sorption, the gas molecules are absorbed on the surface of the polymer membrane, afterward and in the diffusion, gas molecules diffuse through the membrane by running through the cavities and finally in the desorption step, they are desorbed on the low-pressure side (permeate side) of the membranes [15,17]. From solution-diffusion theory, it can be seen that by increasing free volume of the membrane, permeability increases. On the other hand, the selectivity of the polymer membranes can be improved by decreasing the mobility of the chains and increasing the T_g (glass transition temperature) [18–20]. To achieve both higher permeability and selectivity, some modifications on the chain stiffness are required. Thus, in the past couple of decades, use of nanomaterials as filler in polymer membranes has become a major challenge to improve the later properties [21–23]. Choosing the polymer material for membranes is a challenging task and some factors should be considered carefully such as chemical stability and mechanical strength, low material cost, high separation and high flux efficiency, high thermal stability, plasticization resistant and engineering feasibility [24–28]. Based on the latter factors, PBI has been considered a good choice as it has high permeability and permselectivity, satisfactory thermal resistant, large free volume and non-hazardous property [29–31].

Using nanomaterials as filler and modifier agents such as zeolites, MOFs, carbon nanotubes and other organic and inorganic nanomaterials is one of the most promising and useful ways to achieve better permeability and rigidity [21,22,32]. Among these nanomaterials, nano-oxide materials are considered as the brilliant and pioneer modifiers which are widely used in gas separation industries [23,33,34]. These nano-oxides consist of a wide range of nanomaterials such as ZnO, Al_2O_3, SiO_2 and TiO_2.

In the past decades, molecular dynamics simulation (MD) has been applied to predict the behavior of systems in molecular scales [35–38]. Nowadays, by using MD simulation, transport behavior of molecules through the mixed matrix membranes (MMMs) and different aspects of these types of systems such as glass transition temperature (T_g), sorption and diffusion mechanism, free volume of the system and X-ray diffraction have been widely investigated [39–41]. To the best of our knowledge, MD study on the PBI membranes has been undertaken in diversity of applications, but there is no specific study on PBI/nano-oxide MMMs.

In the present study, MD and Monte Carlo (MC) simulations [42–44] have been used to investigate the structural and transport properties of PBI membranes with different nano-oxides (ZnO, Al_2O_3, SiO_2 and TiO_2). We have done a novel and comprehensive study on hydrogen storage and generation from natural gases by new designed PBI/nano-oxide membranes. The COMPASS force field was used to simulate all MMMs. The main aim of this study was to investigate the MMMs for H_2 separation and collection from a microscopic level. In particular, this study focuses on both separation properties (solubility, diffusivity, permeability and permselectivity) and structural properties (glass transition temperature (T_g), wide-angle X-ray diffraction (WAXD) and fractional free volume (FFV) of these particular membranes with nanomaterial contents of 0, 5, 10, 15 and 20 wt%; and its influence on the performance of simulated membranes. To ensure the reliability of the results, validation of the results with the literature data have been conducted. The flowchart of MD and MC simulations is presented in Fig. 1.

Theory and methods

Methods

COMPASS force field which is used for organic, and inorganic materials and polymers [45,46], has been used herein to simulate the PBI/nano-oxide MMMs and investigate H_2 separation, also to investigate structural properties of these membranes. COMPASS is an ab initio forcefield, whose structure is largely inherited from an earlier forcefield known as CFF. Most parameters were derived based on ab initio data. In general, the parameterization procedure can be divided into two phases: ab initio parameterization and empirical optimization. In the first phase, the parameterization was focused on partial charges and valence parameters. The atomic partial charges were derived using ab initio electrostatic potentials [47]. To ensure the transferability, a constrained Ensemble Streamflow Prediction (ESP) approach was used [48]. The valence parameters were derived using CFF ab initio parameterization techniques. The ab initio data used to determine the valence parameters included the total energies and the first and second derivatives of the total energies with respect to the Cartesian coordinates of the atoms. At this point, the Lennard-Jones 6–9 and other van der Waals parameters were set to initial values taken from the CFF forcefield [49].

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