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Improvement of methane storage in nitrogen, boron and lithium doped pillared graphene: A hybrid molecular simulation

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ABSTRACT

The aim of this study is to investigate the storage capacity of methane on the doped pillared graphene using molecular simulation. To this end, a pillared graphene containing two parallel graphene sheets with two vertical carbon nanotubes as holders was selected. This carbon structure was doped using nitrogen, boron and lithium atoms to enhance the gas storage capacity. A hybrid molecular simulation - a combination of molecular dynamics and grand canonical Monte Carlo simulation - was applied to simulate the storage capacity of adsorbent. The results showed that in all systems, doping could enhance the storage capacity of pillared graphene in comparison to pure structure. This improvement was more significant for lithium doped structures while the enhancement of methane storage capacity was estimated 28% higher than that of pristine pillared graphene. In all systems, the storage capacity improvement could be reinforced by increasing the doping percentage of dopant atoms, but this difference was more noticeable for the lithium doped structure. Furthermore, lithium doped pillared graphenes at all levels of dopant and nitrogen doped structures with high doping values (equal or greater than18.5%) were shown to meet the recent target set by U.S. Department of Energy for methane storage capacity.

1. Introduction

Natural gas is a homogenous mixture of various hydrocarbons, especially methane (Solar et al., 2010), that can be used as a renewable and clean source of energy (Guan et al., 2008; Kowalczyk et al., 2006; Sudibandriyo, 2011; Wang et al., 2011). The use of natural gas that is abundant in nature as a vehicular fuel can have environmental and economic advantages (Cavenati et al., 2004; Vicente and Albesa, 2011), most notably the reduction of CO, CO_2, SO_X and NO_X emissions, which is achieved by consuming natural gas rather than gasoline (Candelaria et al., 2012; Mason et al., 2014). One challenging problem with respect to the natural gas usage is its maintenance conditions. Two common methods of natural gas usage are compressed natural gas (CNG) and liquid natural gas (LNG) with both facing challenges in terms of storage and safety conditions. Recently, as an alternative to CNG and LNG, adsorbed natural gas (ANG) has been proposed in porous media at ambient pressure and moderate temperature (Candelaria et al., 2012; Mason et al., 2014; Rasoolzadeh et al., 2008). The main challenge in ANG storage is the selection of the best material as adsorbent. In this regard, a good candidate is porous material, mainly carbon nanostructures, which can uptake natural gas, specifically methane, through physisorption (Candelaria et al., 2012; Zollo and Gala, 2012). A number of the proposed and applicable nano and nano carbon structures in this area include kerogen (Sui and Yao, 2016), activated carbon (Giraldo and Moreno-Piraján, 2011; Heller and Zoback, 2014; Ning et al., 2012; Wang et al., 2010), carbon nanotube (Monemtabary et al., 2013; Rasoolzadeh et al., 2008; Zhang and Wang, 2002), graphene (Candelaria et al., 2012; Chen et al., 2012; Mosher et al., 2013; Zhao and Meng, 2013) and carbon nanoscrolls (Peng et al., 2010). Carbon-based structures are favorable materials for gas storage due to several features like high surface area, thermal and chemical stability, regulated and vigorous porosity, light weight, great quantity and ease of synthesis for industrial scale (Gadipelli and Guo, 2015; Thallapally et al., 2007).

In addition to the common graphene-based material discussed above, a new nanostructure material known as pillared graphene has been suggested for gas storage (Dimitrakakis et al., 2008). This new material is characterized by features such as stable and light weight structure, high volume and high capacity of gas uptake

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(Dimitrakakis et al., 2008; Froudakis, 2011; Hassani et al., 2015). Pillared graphene is composed of two parallel graphene sheets with single-wall carbon nanotubes inserted between two sheets in a vertical position. Graphene sheet is a two-dimensional carbon structure with excellent thermal and mechanical properties (Bai and Shen, 2012; Singh et al., 2011). Also, single-wall carbon nanotube of medium length has high permeability for methane caused by its small diameter, high curvature and lower surface resistance (Chen and Sholl, 2006; Newsome and Sholl, 2006; Skoulidas et al., 2002).

Indeed, a combination of graphene and nanotube can provide a new structure with improved properties. There is a paucity of experimental and theoretical researches on pillared graphene. Theoretical studies were initiated by Georgios and his colleagues in 2008. They studied hydrogen storage in the pillared graphene using grand canonical Monte Carlo (GCMC) simulations (Dimitrakakis et al., 2008). In 2012, molecular dynamic (MD) simulation was applied to examine the effect of geometrical structure, pressure and temperature on the hydrogen storage capacity of pillared graphene. The results showed that hydrogen storage capacity could be enhanced by applying high pressure, low temperature and greater interlayer distance between the graphene sheets (Wu et al., 2012a). Furthermore, our previous study showed that methane adsorption capacity could be enhanced by using pillared graphene instead of graphene sheets for methane storage (Hassani et al., 2015). In addition to the theoretical research, practical researches in the field of pillared graphene synthesis were done. For the first time, pillared graphene was fabricated by combining the surface catalysis and in situ vapor-liquid-solid mechanism (Paul et al., 2010). Then, this structure was constructed by pyrolysis procedure for direct growing aligned carbon nanotubes between graphitic layers (Du et al., 2011). Covalently bonded graphene-single wall carbon nanotube, were grown through chemical vapor deposition (CVD) method in 2012 (Zhu et al., 2012). Also, in 2014 in situ growth of three dimensional carbon nanotubes (CNTs) on graphene oxide by CVD were applied for raising pillared graphene (Kamaliya et al., 2014).

An efficient method of improving the intrinsic properties of carboneous adsorbents such as electronic structure is doping carbon nanostructure with heteroatoms (Fujimoto and Saito, 2015; Rao et al., 2014). Lithium, nitrogen and boron atoms are good alternatives for doping purpose (Chen et al., 2012; Lee et al., 2014; Liu et al., 2009; Panchakarla et al., 2010; Rao et al., 2014, Hassani et al., 2016b). Lithium doping can enhance the strength of interactions between adsorbent and adsorbate, which can increase the adsorption capacity. This is due to enhancement of London dispersion forces and induced dipole moment (Lan et al., 2009). Also, the substitution of nitrogen and boron atoms in the grapheme structure can help tuning electronic structure and change physicochemical and other intrinsic properties of graphene sheets. The inclusion of nitrogen and boron in carbon nano-structures can increase the enthalpy of adsorption. Boron and nitrogen atoms foster the chemical activation energy of inert carbon nanomaterials surface which heightens the extra electronic states around the Fermi level (Ewels et al., 2007; Stadie, 2013). The chemical reactivity of nitrogen doped graphene is higher than the pure graphene sheet, which is due to the facile excitation of electron from valence bands to conduction bands (Wu et al., 2012b). Also, boron and nitrogen doping can lead to physical adsorption of gases such as methane (Liu et al., 2013).

There are a number of theoretical studies on methane adsorption in lithium doped carbon nanostructure. In 2008, the storage capacity of methane in pure and Li doped 3D covalent organic frameworks (COFs) was examined in combination of grand canonical Monte Carlo and first-principles calculation. The results showed a strong affinity between Li cations and methane molecules. Additionally, the findings confirmed that London dispersion forces and induced dipole moment interfere in the binding of methane to the substrate. This improves the storage capacity of methane nearly twice as much as the pristine adsorbent at low pressure and temperature (Lan et al., 2009). In another study, in 2012, the effect of Li doping on multilayer graphene nanostructures (MGNs) for methane storage and biogas separation was examined using DFT and GCMC methods. Results showed that Li doping increased the strength of adsorption of methane molecules on graphene sheets (Chen et al., 2012). In a similar simulation study, in 2012, Li doped covalent organic framework was applied for diffusion and separation of hydrogen and methane. The results of simulation indicated that the affinity of Li atoms to gas molecules influenced the gas adsorption and separation (Yang and Cao, 2012). By the same token, another study, in 2010, applied the same method to the hydrogen uptake in low pressure and temperature for lithium doped pillared graphene oxide, which could meet DOE target for hydrogen storage (Tylianakis et al., 2010). In 2015, the methane adsorption in nitrogen doped graphene sheets was also investigated using Vienna Ab Initio simulation method. The results showed that adding nitrogen to the graphene structure could stimulate the methane uptake capacity (Wang et al., 2015). In another study, nitrogen atoms were added to SWCNT structure as dopant. Simulation results indicated that incorporating nitrogen atoms increased the adsorption energy of adsorbents for methane storage (Denis, 2008). A review of the literature suggests a paucity of specific studies on gas storage inside boron doped graphene or pillared graphene sheets. The existing studies reveal that boron doping can lead to the physical adsorption of gases such as methane (Liu et al., 2013).

To the best knowledge of the authors, based on literature review, there is not any molecular simulation via GCMC or MD simulation for methane storage characteristics in the doped pillared graphene (including graphene sheets and CNT). To overcome this deficiency the effect of lithium, nitrogen and boron doping of pillared graphene on methane adsorption was examined theoretically in this study. For this purpose, hybrid molecular simulation based on Grand Canonical Monte Carlo (GCMC) and molecular dynamics simulation methods were applied. Methane adsorption isotherm curves were calculated for all considered structures in the pressure range of 1–44 bars. The results were compared with pure pillared graphene structure to examine the performance of new proposed carbon structures.

2. Computational details

2.1. System configuration

Methane adsorption on the pillared graphene was simulated by the hybrid molecular dynamics-grand canonical Monte Carlo method. In the first step, the simulation was performed on the pure pillared graphene structure. The geometry of this structure was adopted from our previous study due to its methane adsorption optimality (Hassani et al., 2015). In that study, the features of the optimum structure for the pillared graphene was reported in form of pillared graphene with a 1.2 nm distance between two parallel graphene sheets and two carbon nanotubes with a diameter of 0.938 nm. Although, graphene is an amorphous structure and has turbostratic nature, but there are many limitations in simulation studies for constructing the real structure. Refer to previous studies related to graphene sheets (Chen et al., 2012) and pillared graphene (Wu et al., 2012a), the uniform structure was selected for further studies.

In the next step, the optimum structure was doped by lithium,