



Adsorptive mercaptan removal of liquid phase using nanoporous graphene: Equilibrium, kinetic study and DFT calculations

Seyyed Salar Meshkat^a, Omid Tavakoli^{a,*}, Alimorad Rashidi^{b,*}, Mehdi D. Esrafil^c

^a School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11155/4563, Tehran, Iran

^b Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

^c Laboratory of Theoretical Chemistry, Department of Chemistry, University of Maragheh, P.O. Box: 5513864596, Maragheh, Iran

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ABSTRACT

This research investigated the adsorption of tertiary butyl mercaptan (TBM) from liquid phases by using nanoporous graphene. Nanoporous graphene synthesized through chemical vapor deposition method was characterized using Brunauer–Emmett–Teller method, transmission electron microscopy, field-emission scanning microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy techniques. The TBM adsorption equilibrium was investigated by using Langmuir, Freundlich, and Tempkin models. The obtained results were in good agreement with the Freundlich isotherm. The adsorption kinetics of this process was modeled by the pseudo-first-order, pseudo-second-order, and intraparticle models. The adsorption rate was obtained according to the pseudo-second-order model. The satisfactory results indicated that nanoporous graphene can be used as a good carbon nanostructure sorbent in mercaptan removal. The process reduced the sulfur content from 300 ppm to less than 10 ppm which was the standard level in environmental regulations. The capacity for TBM removal was achieved at 4.4 gr S/gr adsorbent. The desulfurization efficiency was revealed about 96.3% for nanoporous graphene at 298 K and 24 h. Moreover, density functional theory calculations were used to determine the stable configuration, adsorption energy, and electronic structure of different configurations of TBM adsorbed onto a graphene surface. TBM physically adsorbed onto the graphene surface with adsorption energies of approximately – 25 kJ/mol was indicated from DFT calculations.

1. Introduction

In oil industry-related studies, reducing sulfur content or producing sulfur-free products is desirable. These measures can prevent severe problems and provide fuels with increased efficiency for the transportation industry. Removal of sulfur compounds from fuel in the oil and sweetening gas industry has become an inevitable necessity. Extensive efforts have been exerted by research communities to determine an economical, convenient, and excellent substitute for hydrodesulfurization (HDS). Currently, HDS is used to remove sulfur compounds from oil refineries. However, this process requires high hydrogen pressure at high temperature, uses energy excessively, and consumes large amount of expensive hydrogen gas (Kim et al., 2006).

The adsorption process is a promising approach for ultra deep desulfurization because of its considerable potential to demercaptanize fuel to reach zero sulfur levels. Given its high selectivity, adsorption capacity, regenerability, and operation in safe mode, different adsorbent types may be used (Fakhri et al., 2017a; Fakhri, 2015; Gupta

et al., 2017a). Among the various methods, sulfur removal by the adsorption method is highly important. Several new desulfurization processes, such as adsorptive desulfurization, oxidative and extractive desulfurization, and biodesulfurization, are currently being developed to produce ultraclean fuel. The interactions between solute and adsorbent and the strong bands existing in confined nanospace are driving forces for the sulfur removal processes (Liua and Zhang, 2015).

To decrease the mercaptan content from fuels, many processes, such as adsorption, extraction, distillation, and oxidation, are considered (Gupta et al., 2018a, b, 2017b; Fakhri et al., 2017b). Among these methods, adsorptive desulfurization is the most suitable because of its simple operating conditions and cost effectiveness. The adsorption method is more acceptable than the hydro desulfurization process. With consideration of the energy consumption (Fakhri et al., 2018), the process can be performed at low temperature and pressure, and the aromatic mercaptan in fuels can be omitted in low levels by selecting the adsorptive desulfurization method. Nanoporous graphene has been considered the most suitable adsorbent in many research cases.

* Corresponding authors

E-mail addresses: otavakoli@ut.ac.ir (O. Tavakoli), rashidiam@ripi.ir (A. Rashidi).

Graphene is flat layers of carbon atoms tightly packed into a two dimensional (2D) honeycomb lattice, and it is a basic building block for carbonous materials of all other dimensionalities (Wu et al., 2013). Nanoporous material selectively adsorbs molecules on the basis of their size, configuration, and other physical characteristics. Activated carbon and zeolites are used typically to remove sulfur from hydrocarbon liquids (Pourmand et al., 2015; Wang et al., 2015a, b).

In the present research, the desulfurization properties of the inexpensive and simply synthesized nanoporous graphene were studied. Because of the high surface area and porosity of the nanoporous graphene, it was investigated for high adsorption capacity of tertiary butyl mercaptan (TBM) from the liquid mixture of n-heptane as a model fluid of gas condensate in liquid stream in lab scale. In this study, the adsorption isotherm and kinetics of TBM adsorption on nanoporous graphene were researched. Contact time, temperature, initial TBM concentration, and loading adsorbent mass were evaluated as adsorption parameter processes. It is the first time that the equilibrium characterization of the nanoporous graphene adsorption process is also investigated in mercaptan adsorption from the model fluid. In addition, density functional theory (DFT) calculations were conducted to investigate the possible adsorption configurations, corresponding adsorption energies, and electronic structures of the TBM molecule adsorbed over nano porous graphene. DFT calculation results were fitted the experimental section data exactly. The effect of the individual parameters and their interaction effects on TBM adsorption were determined and a DFT calculation of the process was developed. Nanoporous graphene has shown to be the best adsorbent in all optimized adsorption conditions.

2. Material and methods

2.1. Material

TBM (99%, Sigma-Aldrich) and n-heptane anhydrous (95%, Sigma-Aldrich) as model diesel fuel were purchased. Nanoporous graphene was synthesized through the chemical vapor deposition (CVD) method. In this method, methane was used as a carbon source in an electrical furnace consisting of a quartz tube reactor with a diameter of 50 mm and a length of 120 mm to grow graphene on a porous metal oxide nanocatalyst. Hydrogen was used as carrier gas, and the methane-to-hydrogen ratio was 4:1. A gas mixture was passed through a quartz tube for 10 min, and the furnace was heated to 900–1100 °C. To purify the nanoporous graphene, the product was stirred in HCl solution for about 16 h and washed with distillate water several times to obtain the neutral pH (Fakhri et al., 2017b). To characterize the prepared adsorbents, transmission electron microscopy (TEM), field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and Brunauer–Emmett–Teller (BET) techniques were used.

2.2. Characterization techniques

TEM images were used to detect the structure of the synthesized nanoporous graphene using a JEOL 1200 EXII microscope. FE-SEM images were obtained by utilizing a Tescan Mira3 device. Gold was used as a conductive material for sample coating. The surface area, pore volume, and pore size distribution were measured by nitrogen adsorption/desorption at 77 K by using an ASAP-2010 porosimeter (Micromeritics Corporation GA). The samples were degassed at 350 °C and 1.33–0.67 kPa overnight prior to the adsorption experiments. The pore-size distribution was evaluated from the adsorption isotherms by using the Barrett, Joyner, and Halenda algorithm (ASAP-2010) available as a built-in software from Micromeritics. XRD patterns were obtained by using the standard powder diffraction procedure carried out with a Philips diffractometer (PW- 1730) (Lump 3 u $\kappa\alpha$, $\lambda = 1.54 \text{ \AA}$) (Pourmand et al., 2015; Wang et al., 2015a). FT-IR was adopted to

study the variations in the surface chemical binding and structure within the frequency range of 4000–400 cm^{-1} .

2.3. Preparation of TBM solution

A standard n-heptane solution contains 1000 ppmw sulfur compound. This solution was prepared by accurate weighting of the TBM liquid amount. This standard solution was used to prepare the desired model condensation mercaptan for adsorption study. The total sulfur analysis instrument (TS-100) with a detection limit of 0.5 ppm was used to obtain the sulfur concentration of the final solution.

2.4. Adsorption experiments

A batch adsorption experiment was carried out in a 250 ml flask with graphene. Accordingly, 1 g of adsorbent was loaded in a 100 ml solution, which contained 1000 ppmw mercaptan. The bottle was transferred to a magnet stirrer shaken with 300 rpm at 25 °C for 24 h to reach the equilibrium point. To study the effects of the adsorbent mass load, contact time, TBM concentration, temperature, and adsorption isotherm and kinetics, 5 ml of each solution was sampled. In order to have accuracy in all data, each experiments was repeated three times and average data was showed the error less than $\pm 3\%$. The TBM concentration in each solution was determined by a total sulfur analyzer, which presented an uncertainty of less than $\pm 5\%$. The adsorbent capacity was calculated by Eq. (1):

$$q_e = \frac{C_0 - C_e * V}{m} \quad (1)$$

where q_e is the adsorbent capacity (mg S/g), C_0 is the initial concentration of adsorbate, C_e is the equilibrium concentration of adsorbate, V is the solution volume (ml), and m is the adsorbent mass loading (g).

2.5. Adsorption isotherms

Adsorbent capacity was investigated by using adsorption isotherms. The maximum mercaptan adsorption and equilibrium isotherm constants were determined by adsorption isotherms so that they were obtained at different concentrations. To determine the isotherm parameters, the linearized forms of the adsorption isotherm models were used (Gupta et al., 2017b; Fakhri et al., 2017b, 2018). These models (i.e., Freundlich, Langmuir, and Tempkin isotherms) are summarized in Table S1. In these models, q_e corresponds to the adsorption capacity at equilibrium in mg/g, and C_e is the TBM concentration in the solution at equilibrium in mg/l. In the Langmuir isotherm, Q_0 is the maximum monolayer adsorption capacity in mg/g, and b is the Langmuir constant. In the Freundlich model, K_F and n reflect the Freundlich parameter, where n indicates a measure of the heterogeneity of the adsorbent surface. In the Tempkin isotherm equation, A_T is the Tempkin isotherm constant in l/g, and B in J/mol is the Tempkin constant, which is related to the adsorption heat.

In the Langmuir model, the adsorption process is assumed to occur on a homogeneous surface by monolayer adsorption. However, the Freundlich model is described by an empirical model that considers the multilayer with reversible adsorption on a non-uniform distribution of the active site (Parab et al., 2006). Nevertheless, the Tempkin isotherm includes a factor that clearly describes the interaction between the adsorbate and adsorbent.

2.6. Adsorption kinetics

To obtain further understanding of the adsorption process, rate and rate-controlling step and the uptake rate of TBM were evaluated using different kinetics models (i.e., first-order, pseudo-second-order, and intraparticle models). The original equations for these three kinetic

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