



The function of poly aromatic nuclei structure for adsorption of vanadyl/nickel etioporphyrin on asphaltene/graphene

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ABSTRACT

Adsorption behaviors of metal porphyrins on graphene were studied by investigating adsorption kinetics, thermodynamics and density functional theoretical calculation. The interactions between poly aromatic nuclei structure of graphene and metal porphyrins were confirmed by XPS, TEM analysis and adsorption results, which account for adsorption of metal porphyrins. As the poly aromatic nuclei structure is the main structure of asphaltene, it also acted as active sites for adsorption of metal porphyrins. The differences of adsorption results between graphene and asphaltene indicated that the aliphatic side chains and other structures of asphaltene also have influence on adsorption process. Furthermore, chemical and physical adsorptions were also confirmed during the adsorption process of porphyrins on graphene.

1. Introduction

The metal elements in the crude oil, which bring adverse impact on petroleum processing, could be removed by the solvent deasphalting technology [1–4]. Unfortunately, several metals, especially nickel and vanadium porphyrins, are hard to be fully removed to produce qualified deasphalted oil [5]. Investigations have confirmed that Vanadyl octaethylporphyrin (VO-OEP) and Nickel octaethylporphyrin (Ni-OEP) could be adsorbed onto asphaltene, which means that enhancing the interactions between metal porphyrins and asphaltene may increase the removal efficiency of the metals [6,7]. However, the verification of the interactions seem to be particularly problematic, as asphaltene has very complex structures, such as polyaromatic nuclei, aliphatic side chains, heteroatoms, naphthenic rings, etc. Proper model compounds with simple structure, such as graphene or modified graphene, may make the investigation much easier.

As a new member of carbon-based materials, graphene is composed of a monolayer of carbon atoms packed into a dense honeycomb crystal structure [8–12]. It exhibits great promise for potential applications in many technological aspects such as field-effect transistors [13], solar cells [14], sensors [15], and adsorbent. The structure of graphene and asphaltene are provided in Fig. 1. It can be seen that the graphene has the same poly aromatic nuclei structure as the asphaltene, but without heteroatoms and aliphatic side chains. Adsorption of metal porphyrins by graphene could be attributed to its poly aromatic nuclei structure. Therefore, adsorption results by graphene could be used to better

understand the function of poly aromatic nuclei of asphaltene.

Density functional theoretical (DFT) is widely used in the calculation of the interactions between chemical molecules and graphene or graphene derivative [16–18]. Calculation results compared with experiments can provide more detail for studying of the adsorption process, and always used for further understanding of the adsorption mechanism. Krasheninnikov et al. studied transition metal atoms embedded graphene using DFT and confirmed the relationship between the structure and its magnetism [19]. López-Corral et al. investigated preferential adsorption geometry, adsorption sites and binding energy for H₂ adsorption on Pd-decorated graphene. They deduced that the adsorption mechanism involved dissociation of H₂ molecule and binding of atomic hydrogen and the graphene surface [20].

In this work, adsorption of vanadyl or nickel etioporphyrin on graphene was studied. Adsorption kinetics and thermodynamics were performed. The results were compared with that of asphaltene to discover the function of poly aromatic nuclei structure. In addition, the binding energy between porphyrin and graphene in pentane was computed by DFT for further understanding of the adsorption mechanism.

2. Experimental and theory

2.1. Materials

Graphene nanoplatelets are obtained from Nanjing XFNANO Corp.,

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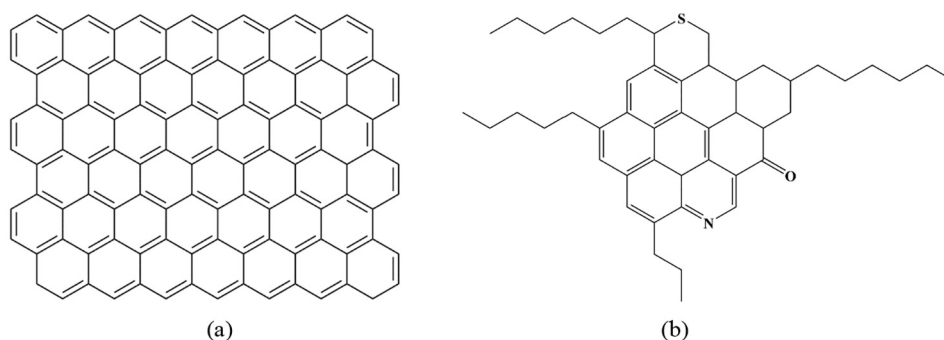


Fig. 1. The structure of graphene and unit structure model of asphaltene.

Table 1
Properties of graphene nanoplatelets.

Graphene nanoplatelets					
Appearance	A black and grey powder	Electrical conductivity	8000–10,000 S/m	Specific surface area	40–60 m ² /g
Carbon content	> 99.5%	Water content	< 0.5 wt%	Diameter	0.5–20 μm
Bulk density	~0.30 g/mL	Density	~2.25 g/cm ³	Thickness	5–25 nm
Tensile strength	5 GPa	Residual impurities	< 0.5 wt%		

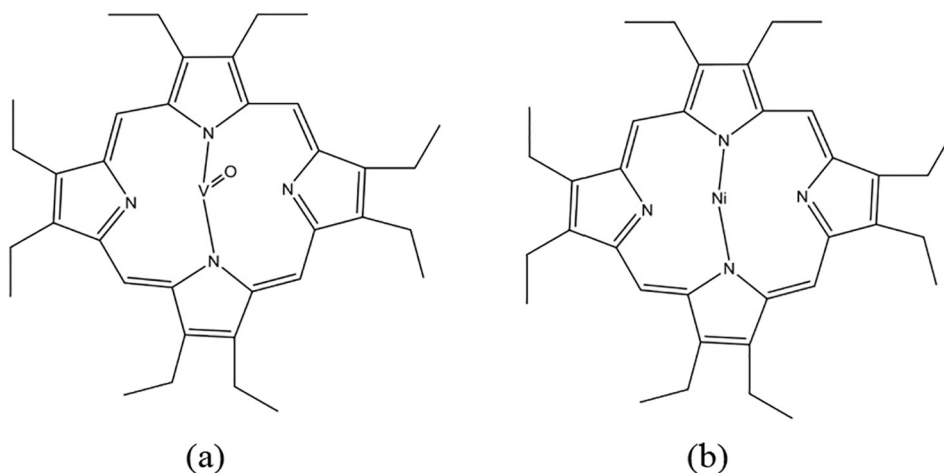


Fig. 2. Structure of vanadyl/nickel porphyrins: (a) VO-OEP; (b) Ni-OEP.

Ltd. Graphene nanoplatelets are the stack of multi-layer graphene sheets including platelet morphology. The properties of them are shown in Table 1. Their layered structures are as same as graphite crystal. VO-OEP and Ni-OEP have structural similarity with vanadyl/nickel etio-porphyrin (ETIO). The structure of VO-OEP/Ni-OEP is shown in Fig. 2 (VO-OEP: C₃₆H₄₄N₄OV, 599.71, Purity > 99%, Fig. 2(a), J&K Scientific Ltd.; Ni-OEP: C₃₆H₄₄N₄Ni, 591.45, Purity > 99%, Fig. 2(b), J&K Scientific Ltd). The other chemicals were provided by Beijing Chemical Works.

2.2. Adsorption test

The equilibrium adsorption experiments had been undertaken to assess the adsorption efficiency of VO-OEP or Ni-OEP on graphene. For adsorption kinetic tests, accurately weighted graphene were continuously oscillated with 3.5 mL of pentane solution of porphyrin at constant temperature. Adsorption parameters such as temperature, initial porphyrin concentration, and graphene dosage were varied to study their influence on the adsorption process. For equilibrium isotherm tests, 0.015 g of graphene were mixed with 20 mL of pentane solution (4–12 μg/mL). The mixture was vibrated for 48 h in a constant temperature vibrator at different temperatures (15, 20, and 25 °C). The

other detailed experimental procedures can be found in our previous study [6].

2.3. Theoretical models

The experimental data were analyzed by four kinetic models which were the pseudo-first-order [21–23], pseudo-second-order [24–26], Elovich [27–29], and diffusion kinetic models [30–32] in Table 2.

The equilibrium data were analyzed by the Langmuir and Freundlich isotherm equations [33–35].

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (1)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (2)$$

where C_e is the equilibrium concentration (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F and $1/n$ are the Freundlich constants.

Thermodynamic parameters like standard free energy (ΔG° , kJ·mol⁻¹), enthalpy (ΔH° , kJ·mol⁻¹), and entropy (ΔS° , kJ/mol·K) were calculated from the following equations to understand the adsorption

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