An Adsorption Study of NO on Graphene and Graphene Oxides

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Abstract. The adsorption and oxidation of NO over GP and GOs experiment was performed in a fixed bed double tube type reactor. The experimental data showed the GOs added can enhance the adsorption and oxidation. The further DFT calculations found that the adsorption energy of NO₂ is greater about 4 times than NO. The adsorption distance are with the trend of oxidation degree increase order GP < HOGP < OGP, but the adsorption energy of HOGP is bigger than OGP. The charge transfer show the NO’s role changed from an acceptor on the GP surface to a donor on the OGP surface. It indicates increasing levels of covalency.

Introduction

It is urgent to find a practical method for the treatment of NOx in energy, manufacturing and chemical industry’s green development in China. Since the NO₂ can be removed easily by water scrubbing, scientific and technical personnel have been developing many NOx control methods, among them, catalytic oxidation of NO into NO₂ over active carbonaceous [1, 2] has been studied and regarded as one of feasible technical route. But its conversion efficiency is still unsatisfactory to apply in industry extensively. Very recently, graphene (GP), a single layer of carbon atoms arranged in hexagonal structure, has attracted considerable interest due to its unique structure [3]. The graphene and graphene oxides (GOs) are widely employed as supports or catalysts in environmental protection area. The GOs not only acts as the oxidant in the reaction, but also as the catalyst to catalyze the reaction of SO₂ and O₂ to form SO₃. Similarly, it is very interesting to investigate how the NO was oxidized to NO₂ over the GP and GOs surface and new ways are being explored to improve the efficiency of oxidation of NO at a house temperature. Firstly, in this paper we experimentally study the adsorption and oxidation of NO molecules on GP and GOs. The density functional theory (DFT) calculations were performed to explain the observations quantitatively. Depending on them, we propose that using negative oxide ion maybe increase the oxidation of NO on the surface of GOs.

Experiment

Materials: the commercial expandable graphite purchased from Qingdao Nanshu-Hongda Graphite Products Co., Ltd. The graphene slurry purchased from the Sixth Element (Changzhou) Materials Technology Co., Ltd. The other chemicals materials unless specifically noted were purchased from Tianjin Chemical Reagent Co., Ltd.

Preparation of GOs: the expandable graphite was firstly placed into a 1050°C Muffle furnace with nitrogen protection to produce the expanded graphite. Depending on the Hummers method [4], the following processes in laboratory were made to prepare GOs from the expanded graphite. Under ice-water bath, potassium permanganate (30g) and the concentrated sulfuric acid (98%, 300mL) were initially stirred until being homogeneous. Then, with continuous stirring, the expanded graphite (10g) was added to the mixture until a uniform deep green liquid paste was formed. Then the ice-water bath was removed. The stirring continued until the product formed (around 3hours) at room temperature with a large volumetric expansion. Deionized water (850ml) was added, and rapid stirring was restarted to prevent effervescing. Next, the vessel was placed into a 90°C water
bath, and after 1 hour, a homogeneous suspension was obtained which was brown in color. Deionized water (1500ml) was added again, standing for over 10 hours and then removed the clean liquid on the top of it. Unload the product into the dialysis bag and put in ultrapure water for 1 week, during the time, change the ultrapure water every day until the PH value closed to 7.

Preparation of experimental sample: the GP and the GO/GP samples were prepared by impregnation method using graphene slurry, graphene oxides, and glass fiber. The glass fiber will act as the carrier to support the GP or GO/GP to obtain a fine structure. Two samples of 2g glass fiber were firstly marinated into soapy water for 20 min, then washed, dried and weighted. The aqueous solution GO/GP was obtained by mixing 1g GOs dry powder, 10g GP slurry, and 50ml deionized water by ultrasonic treatment for 30 minutes. The samples of glass fiber were dipped for 2 hours into the GP slurry and GO/GP aqueous solution respectively, and then dried under 110°C.

Figure 1 shows the NO adsorption and oxidation experimental system. The gas components were based on the power station boiler flue gas with 5% O2 concentration, and they were passed into the mixing chamber to generate the required simulate flue gas. The flow of each gas was controlled by the mass flow controllers; and the total flow controlled at the rate of 1 L/min was monitored by a pre-calibrated rotameter.

Figure 2 shows the concentration of NO and NO2 in reactor outlet tested by a flue gas analyzer. For conciseness, the adsorption configuration of NO or NO2 on graphene are denoted as NO@GP and NO2@GP; NO or NO2 on GOs and GP slurry are denoted as NO@GO/GP and NO2@GO/GP. The green line and blue line in Figure 2 indicates the mixing gas concentration of NO and NO2 from mixing camber, 416 mg/m3 and 112 mg/m3, respectively. Because the reaction: 
$$2NO + O_2 \rightarrow 2NO_2$$
the process of volume decreasing, we can find the green line is below the curve of NO@GP and NO@GO/GP; initially, The NO2@GP and NO2@GO/GP are lower than the NO2 line (blue line), as time goes on, it exceeds the NO2 line with a slow increasing trend; from the beginning to the end, the concentration of NO is higher than the NO line (green line) and keeps stable, which means a oxidation of NO is taking place.

Compared to the curve interval of NO@GP and NO@GO/GP with NO2@GP and NO2@GO/GP, we can find out: (1) During the experiment, the curves are keeping stable but the concentration of NO(NO2)@GO/GP sample is below the NO(NO2)@GP; (2) At beginning of the experiment, the gap of NO2@GP and NO2@GO/GP curve is large which narrows in the later. All that above maybe indicates that the adding of GOs will enhance the capacity of adsorption and oxidation. The following computer simulations of quantum-chemical calculation will contribute to reveal the phenomenon and help us to understand the state of reaction in atom level.

Modeling and Computational Details
The adsorption of nitrogen oxides on GP and GO were studied with the density functional theory (DFT). The calculations were performed with Materials Studio, a product of Accelrys Software Inc. The full geometry optimizations, energy calculations were carried out by the DMol3 module. In all
electron calculations, the density functional theory of the GGA with the exchange–correlation potential parameterized by PBE and the double numerical plus d-function basis set were adopted. In order to reduce the interaction between NO or NO2 molecules, the periodic supercell of 4×4 graphene unit cells composed of 32 carbon atoms was used to simulate the adsorption. The supercell was extended to up and down for 15 Å to avoid the interference between adjacent graphene layers. The Monkhorst–Pack grid parameters were sampled with a 5×5×1 k-points. In geometry optimization, the whole configuration was allowed to relax until all the force components on any atom were less than 2×10⁻³ Ha/Å.

A hydroxyl group or epoxy group was grafted onto the graphene substrate to fabricate graphene oxides. Adsorption Locator module can find the low energy adsorption sites on the all kinds of substrates. For conciseness, the adsorption configuration of NO(NO2) on GP with hydroxyl group is denoted as NO(NO2)@HO GP, and NO(NO2) on GP with epoxy group is denoted as NO(NO2)@OGP. It is critically important to perform geometry optimizations of the adsorbate structures using COMPASS in the Forcefield module. The pre-work will ensure that the energy results returned to the Adsorption Locator are accurate.

Since the energy of the substrate is not calculated in an Adsorption Locator running. The Adsorption Locator results of module files (NO@GP, NO@HOGP, NO@OGP, NO2@GP, NO2@HOGP, NO2@OGP) was used as the input file by the DMol3 module to calculate the total energy $E_{\text{tot}}$ and adsorption energy $E_{\text{ads}}$. The adsorption energy $E_{\text{ads}}$ is defined as:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{mol}} - E_{\text{sub}}$$  \hspace{1cm} (1)

Where $E_{\text{tot}}$, $E_{\text{mol}}$, and $E_{\text{sub}}$ are the total energies of the adsorption complex, the isolated molecule and the GP or GO substrates, respectively.

The Mulliken population analysis and the other electronic properties of the optimized structures were obtained by the CASTEP module. This module applies to the first-principles plane-wave pseudopotential code for quantum mechanics-based simulation of solid-state materials. In the energy calculation, it uses the ultrasoft pseudopotentials for the ion–electron interactions and the generalized gradient approximation (GGA) with a Perdew Burke Ernzerh (PBE) exchange and correlation functional. A plane-wave basis set with a cutoff energy of 350 eV was employed in calculation.

**Results and Discussions**

**Geometric characteristics:** We first investigated the adopted locations of NO or NO2 on GP and the GO as the substrate. As the adsorption of NO on pristine graphene is weak physisorption [16], the orientation for the adsorption of NO molecule on GP surface has little effects on the adsorption energy. However, whether it leads to any differences on its adsorption on graphene oxides is still unknown. The Adsorption Locator module will help us to explore the proper places on the substrate’s surface.

Figure 3. (a) NO adsorbed on the graphene (NO@GP); (b) NO2 adsorbed on the graphene (NO2@GP); (c) NO adsorbed on the graphene with hydroxyl group (NO@HOGP); (d) NO2 adsorbed on the graphene with epoxy group (NO@OGP).
adsorbed on the graphene with hydroxyl group (NO2@HOGP). (e) NO adsorbed on the graphene with epoxy group (NO@OGP); (f) NO2 adsorbed on the graphene with epoxy group (NO2@OGP).

Simulated annealing task was employed by Adsorption Locator module. A low energy adsorption site is identified by carrying out a Monte Carlo search. This process is repeated to identify energy minima. The configuration results in FIG 3 showed that the NO and NO2 molecules are almost parallel to the substrate surface.

Adsorption Locator module calculated that the distance of NO from GP surface in NO@GP configuration is 3.2531 Å, NO@HOGP configuration is 3.2976 Å and NO@OGP configuration is 3.3543 Å. All of them are longer than 2.67 Å in Ref. [5], but shorter than 3.76 Å in Ref. [6]. It indicates that the results are acceptable. Compared to the results of the calculations, the distance of NO to the different surfaces is increased in the order NO@GP< NO@HOGP <NO@OGP. In other words, the distance of NO from different surfaces increase consistently with the oxidation degree order GP < HOGP< OGP. The increase trend on distance of NO2 from the surfaces is similar.

Adsorption energy: In table 1, the adsorption energies of configurations are given by Adsorption Locator. We can find out that the graphene oxides could enhances the adsorption energy in different degrees. The adsorption energy of NO/OGP is 0.0989 kcal/mol which is lower than that of NO/HOGP. With the same trend, the adsorption energy of NO2/OGP is 0.465 kcal/mol which is lower NO2/HOGP. Since the energy of the substrate is not calculated in an Adsorption Locator module, the Dmol3 allow us further to investigate the adsorption with the effect of deformation of GP.

On the base of the configuration provided by Adsorption Locator module, the Dmol3 module calculated the adsorption energy with function (1) in table 2. With the similarly trend of Adsorption Locator module gave, the adsorption energy of the GOs to NO2 in the calculation are more than 4 times to NO.

Charge transfer: When the adsorbate, NO or NO2, molecule located on GP/GOs surfaces, the charge transfer between them was calculated with Mulliken population analysis and listed in Table 3. The values of atomic bond population for the bonds between the N-O atoms can be used as a measure of bond strength [2]. Compared to the Mulliken population of the isolated NO and NO2 molecule, the little change means the adsorption is in the state of physisorption.

The overlap population may be used to assess the covalent or ionic nature of a bond. A value of zero indicates a perfectly ionic bond, while values greater than zero indicate increasing levels of covalency [7]. On a further observation in table 3, the electrons are transferred from graphene surface to adsorbed NO molecule with quite a small value of 0.01e at NO@GP configuration. When epoxy group is introduced, the direction of charge transfer is reversed; 0.04e electrons are transferred from NO to OGP surface. NO’s role changed from an acceptor to a donor and electrons are transferred to OGP surface.

Summary
The adsorption and oxidation of NO over GP and GOs experiment was performed in a fixed bed double tube type reactor. The experimental data showed the GOs added can decrease the concentration NO and NO2 in outlet, that means the GOs can enhance the oxidation of NO and the adsorption of NO2. In order to further understand the process of conversion of NO to NO2, The adsorption and oxidation of NO on GP and GOs have been investigated with DFT calculations. It is found that the adsorption energy of NO2 is greater about 4 times than NO on GP or GOs surfaces by Dmol3 module calculation. The adsorption distance of all 6 kinds configuration are with the trend of oxidation degree increase order GP < HOGP< OGP, but the adsorption energy of HOGP is bigger than OGP substrate. The charge transfer show the NO’s role changed from an acceptor on the GP surface to a donor on the OGP surface. It indicates increasing levels of covalency.
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References


