



The effect of functional groups on the SO₂ adsorption on carbon surface I: A new insight into noncovalent interaction between SO₂ molecule and acidic oxygen-containing groups



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ARTICLE INFO

Article history:

Received 4 October 2015

Received in revised form

12 December 2015

Accepted 15 December 2015

Available online 17 December 2015

Keywords:

SO₂

Adsorption

DFT

Noncovalent interaction

ABSTRACT

For the aim to give a new insight into the interactions between SO₂ molecule and carbon surface and the effect of acidic oxygen-containing groups, density functional theory and noncovalent interaction analysis in terms of reduced density gradient were employed to investigate both the intensity and type of the interactions. The results indicate that the physisorption of SO₂ molecule mainly occurs on the basal plane of pure carbon surface due to van der Waals interactions, however, when acidic oxygen-containing groups were decorated on the carbon surface, they would facilitate SO₂ adsorption as a result of hydrogen bonding and dipole–dipole interactions. What's more, these groups could not affect the chemisorption of SO₂ remarkably, no matter they are near the adsorption sites or not. In addition, calculation results show that the interactions between SO₂ and acidic oxygen-containing groups are in physisorption nature, which challenges a long-held the viewpoint of irreversible chemisorption. Acidic oxygen-containing groups could boost the effective surface area of carbon by enhancing the physisorption on edge positions.

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1. Introduction

Desulphurization technology based on porous carbon materials has drawn great attention, since it has the advantages of less water consumption and multiple pollutant removal. The catalytic reaction on carbon surface consists of adsorption and oxidation into SO₃/H₂SO₄ of SO₂, in the presence of H₂O and O₂ [1–3]. Insight to the mechanism of SO₂ adsorption and oxidation is foundation of design and synthesis of high quality carbon materials for desulphurization, however, the mechanism is still an open question due to the complexity of carbon materials. Adsorption of SO₂ on carbon surface is the first step of catalytic reaction, so it should be the basis of the following oxidation reaction. Both chemisorption and physisorption, affected by pore structure and surface chemistry of carbon, are involved in the adsorption progress [3–5]. Due to its effect both on adsorption and oxidation of SO₂, the role of surface chemistry of carbon materials in the desulphurization progress was explored widely by researchers, but still did not reach a conclusion.

The chemical characteristics of carbons are mainly determined by unsaturated edge carbon atoms [6], delocalized π -electrons [7], and surface chemical heterogeneity [8]. Adsorption of SO₂

was reported to be related to acidic or basic character of functional groups on carbon surface [9–13]. Researchers reached an agreement on the promotion of basic groups, for instance, nitrogen-containing groups [14–17] and basic oxygen-containing groups [9–11]. However, the effect of acidic groups still seems contradictory according to previous study. Davini [9] reported that the amount of SO₂ adsorbed decreased with the acidic sites, titrated by diphenylguanidine, and carbon samples prepared through low temperature oxidation contained more acidic groups so as to adsorb less SO₂ [10]. Lisovskii [12] asserted that carbon samples treated by concentrated nitric acid, which is a method of introduction of a significant number of acidic oxygen-containing functionalities onto the carbon surface that mainly include carboxylic, lactone, and phenolic hydroxyl groups [8], adsorbed more SO₂ than those untreated ones, and there was an interaction of the sulfur dioxide with the acidic oxygenated surface groups produced during oxidation. Furthermore, the same research group concluded that SO₂ could be irreversibly adsorbed (chemisorption) on the surface as a result of interaction with the oxygen-containing groups that determined the acidic properties of the carbon [13]. Apparently, further investigations are still needed to gain an insight into the effect and mechanism of acidic oxygen-containing groups on sulfur dioxide adsorption.

Ab initio calculations can help to explore the reaction mechanism at the atom scale. Molecular orbital calculations at the

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B3LYP/6-31G(d)//HF/3-21G(d) level were employed for calculating the progress of SO₂ adsorption, oxidation and hydration by Yang and Yang [18], and they found all of three viable pathways took place on the zigzag edge sites, what's more, oxides (terminal O) on the surface could affect the reaction progress. Pliego et al. [19] investigated the SO₂ chemisorption process both on the surface and edges using pyrene and its dehydrogenated derivatives as models. They concluded that adsorption of SO₂ on basal plane was very unfavorable with a positive adsorption energies of 80–90 kcal/mol. However, to the authors' acknowledge, there is no any theory work of the effect of acidic oxides on SO₂ adsorption on carbon materials, which is indeed essential to clarify the conflicts or unsolved questions according to the previous experiments [9,10,12,13].

The objective of the present study is to discuss the effect of acidic oxygen-containing groups on chemi- or physisorption of SO₂ and the mechanism of the interactions among SO₂, acidic oxides, and carbon surface.

2. Calculation methods

Models shown in Fig. 1a–d were employed for physisorption calculations, and all the calculations were completed using ORCA software [20]. Geometry optimization and vibrational frequency at BLYP/def2-SVP level were carried out in consideration of basis set superposition error by means of geometrical correction [21]. Besides, dispersion correction [22] was taken into account, which proved crucial when calculating the interaction between gas molecule and carbon surface [23,24]. Density fitting approximation [25,26] was employed to accelerate the calculation without loss of accuracy. Single point energy of the optimized geometry was calculated at B3LYP/def2-QZVP level with dispersion correction, which was used for adsorption energy calculation. Adsorption energy E_{ad} is defined as:

$$E_{ad} = E_{\text{complex}} - (E_{\text{SO}_2} + E_{\text{surface}})$$

where E_{complex} , E_{SO_2} and E_{surface} represent the single point energies of the adsorption complex, the isolated molecule and the carbon surface, respectively.

Noncovalent interactions analysis by means of the reduced density gradient [27] was carried out in Multiwfn [28]. Since the analysis isn't sensitive to the accuracy of calculation level [27], wave functions from optimization tasks were used in noncovalent interactions analysis. The reduced density gradient isosurfaces ($s = 0.5$ au) are colored on a blue–green–red scale according to values of $\text{sign}(\lambda_2)\rho$, ranging from -0.04 to 0.02 au all through the paper. Large, negative values of $\text{sign}(\lambda_2)\rho$ are indicative of attractive interactions (such as dipole–dipole or hydrogen bonding); while if $\text{sign}(\lambda_2)\rho$ is large and positive, the interaction is nonbonding [27]. Values near zero indicate very weak, van der Waals interactions [27]. VMD software [29] was employed for all the drawing throughout the paper.

Chemisorption calculations were carried out by Gaussian03 [30] software, and density functional theory at B3LYP/6-31G (d, p) level was used for geometry optimization and vibrational frequency

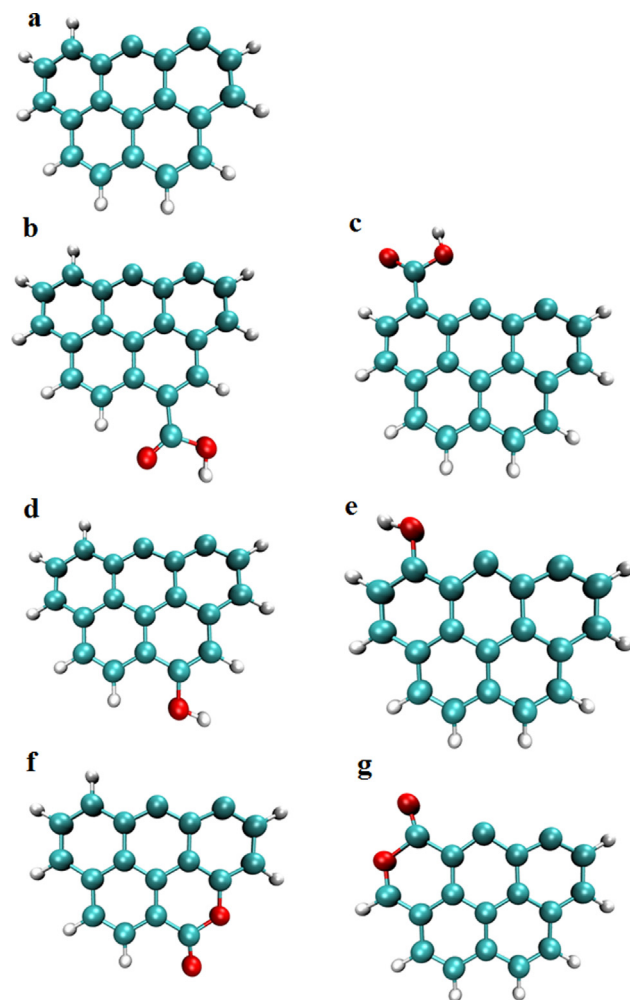


Fig. 2. Models of carbon surface for chemisorption calculation. The pristine carbon surface model without any oxygen-containing groups (a). Carbon surface with a carboxylic group far from (b) and near (c) the unsaturated carbon atoms. Carbon surface with a phenolic hydroxyl group far from (d) and near (e) the unsaturated carbon atoms. Carbon surface with a lactone group far from (f) and near (g) the unsaturated carbon atoms.

analysis; such combination has been evidenced efficient in many studies [18,19,31]. A cluster model was constructed in Fig. 2a–g, and similar models have been previously adopted for investigation of CO₂ [31] and SO₂ [18,19], which proved both reliable and computationally expedient.

3. Results and discussions

3.1. Physisorption

Density functional theory calculations and noncovalent interaction analysis were employed for investigating both SO₂ adsorption

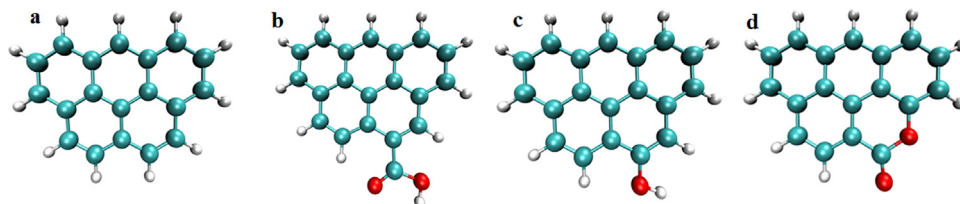


Fig. 1. Models of carbon surface for physisorption calculation. The pristine carbon surface model without any oxygen-containing groups (a). Carbon surface with a carboxylic group (b), a phenolic hydroxyl group (c), or a lactone group (d).

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