

Sequestration of carbon dioxide in coal: Energetics and bonding from first-principles calculations



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ABSTRACT

Sequestration of CO₂ in unmineable coalbeds is one of the attractive ways being investigated to reduce the CO₂ concentration in the atmosphere. Extensive experimental studies have demonstrated that storage of CO₂ molecules in coal seam involves both chemisorption and physisorption, but the underlying mechanism at the atomic scale has remained elusive. We report results of first-principles density-functional-theory calculations for the interaction between molecular CO₂ and coal. The calculations show that chemisorption of CO₂ in defective coal is possible, and CO₂ can form chemical bonding with defective coal, particularly at the defects involving carbon and hydrogen vacancies and epoxy functional groups. On the other hand, formation of chemical bonding of CO₂ with defect-free coal network is unlikely.

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1. Introduction

Anthropogenic carbon dioxide (CO₂), mostly released from combustion of fossil fuel including oil, gas, and coal, is considered as the major cause of global warming [1–5]. Therefore, the concentration of CO₂ in the atmosphere becomes a great concern. One of the promising approaches to reduce CO₂ concentration is CO₂ Capture and Sequestration (CCS), which is a technology to capture CO₂ produced during the combustion prior to emission to the atmosphere and then sequester it in underground geological formations, such as depleted oil or gas reservoirs, deep saline aquifers and unmineable coal seams [6–11]. CO₂ Capture and Sequestration (CCS) in unmineable coal seams is one of the more attractive ways to mitigate the concentration of atmospheric CO₂ whereas the cost of sequestration can be partially offset by the enhanced coalbed methane recovery [9,12]. The injected CO₂, being a preferentially adsorbed gas in coal and thus a competitor with methane (CH₄) [13,14] for the adsorption site, enhances desorption of CH₄.

The experimental work has established that injection of CO₂ molecules into coal (particularly under high pressure) results in swelling of coal [15–17]. It has been suggested that it is a consequence of both physisorption (reversible process, in which no

chemical bonds are formed, and both the adsorbate and adsorbent return to their initial state after the pressure is released) and chemisorption (irreversible process) of CO₂ in coal after injecting CO₂ into coal [18–20]. A number of experimental studies have shown that the swollen coal due to CO₂ adsorption returns to its original dimensions after the gas is removed, even after multiple exposure [16,21–24], suggesting the sorption process is physical and reversible. However, other experimental investigations have provided indirect evidence on structural rearrangements of coal [25–31], which indicates that chemical reaction may occur. The faster diffusion rate of CO₂ into coal for second exposure and the difference of the in situ recorded acoustic emission between the first and subsequent cycle of CO₂ adsorption have been reported, and these results imply that structure rearrangement of coal may occur during the first exposure to CO₂ [27,28]. Abrupt reduction of exotherm studied by differential scanning calorimetry in the two successive exposures of coal to CO₂ and the small angle neutron scattering results applied on coal at high-pressure CO₂ environment also indicate that coal may undergo a physical structure change during the interaction between coal and CO₂ [29,31]. It has been suggested that the structural changes observed in experiments may be understood by considering the gas dissolution process in polymer as CO₂ molecules diffused in the coal matrix behave like a plasticizer, which facilitates the change of macromolecular structure or intermolecular bonding [32].

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Theoretically, the adsorption capacity and adsorbate microstructure of CO₂ in carbon slit pores were investigated using Grand Canonical Monte Carlo (GCMC) simulations and graphite-based models [33,34]. Adsorption isotherms into graphitic surfaces with [35–38] and without [39] embedded functional groups were generated via GCMC simulations. Classical molecular dynamics simulations with the use of a general bituminous coal model were also performed to study the CO₂ adsorption behavior in coal including adsorption capacity [40] and distribution [41]. Quantum-mechanical calculations for the binding energies of CO₂ adsorbed on graphite surfaces with oxygen-containing groups were determined by using DMol³ module in Material Studio [42]. The gas adsorption energy after introducing native point defects in graphene-derived materials were determined using the plane-wave Quantum-ESPRESSO code [43]. It was found that chemisorption energy of CO₂ on the monovacancy site in graphite is 1.43 eV after overcoming energy barrier of ~1 eV by forming a “lactone complex” [44], while the chemisorption of CO₂ in the monovacancy site in graphene occurs with an energy released of ~1.72 eV and energy barrier of 0.80 eV [45].

However, all of the previous first-principles quantum-mechanical calculations involved graphene/graphite-based models, which may not well represent the coal network. Consideration of structural and chemical heterogeneities of coal with different functionalized groups involved in the interaction between CO₂ and the coal network was lacking.

Here, we report results of first-principles quantum-mechanical calculations for the interaction between CO₂ molecules and coal – with the use of a model that may well represent the coal network. A key result is that chemisorption can occur when CO₂ is near the defect sites of the coal network including the sites of H vacancies, C vacancies, and the epoxy functionalized structures. On the other hand, chemisorption does not occur at any sites of the defect-free coal network.

2. Model and method

Coal is a heterogeneous material with a three-dimensionally cross-linked macromolecular structure and a wide range of highly reactive chemical functional groups [46]. Molecular level representations for coal were previously established [47]. In particular, Castro-Marciano et al. proposed a model that contains 728 segments with over 50,000 atoms to represent the complex coal [48]. Currently, first-principles quantum-mechanical calculations for such large systems are formidable. However, the interaction of CO₂ with coal is essentially determined by the local structure. We therefore chose a typical segment, shown in Fig. 1, as our initial model to represent a local structure of the coal network that is defect-free. Given the periodic boundary conditions, the interaction between the periodic structures in each direction has to be minimized while keeping the computational efficiency, therefore, a vacuum region has been chosen to be 8 Å (including the vacuum in both sides of the structure) after a number of test calculations with the size of the vacuum region varying from 6 Å to 10 Å. The chosen segment contains 96 atoms (51 carbon atoms, 39 hydrogen atoms, 4 oxygen atoms, 1 nitrogen atom, and 1 sulfur atom). The model is composed of a normalized elemental composition of C₁₀₀-H_{76.5}O_{7.8}N_{2.0}S_{2.0}, which is close to the experimental composition of C₁₀₀H_{77.3}O_{9.3}N_{1.5}S_{1.2} on a dry, mineral-matter-free (dmmf) basis [48,49]. As shown in Fig. 1, a sulfur atom (S) and two oxygen atoms (O2 and O3) form bridges connecting four different portions. Each portion has a C–H structure with C-rings. The –OH group of the left portion in Fig. 1b is bonded to a C-ring while the O atom of the right portion is inside of a C-ring. The N atom, which is located in the lower portion, is inside the 6-atom ring that is composed of

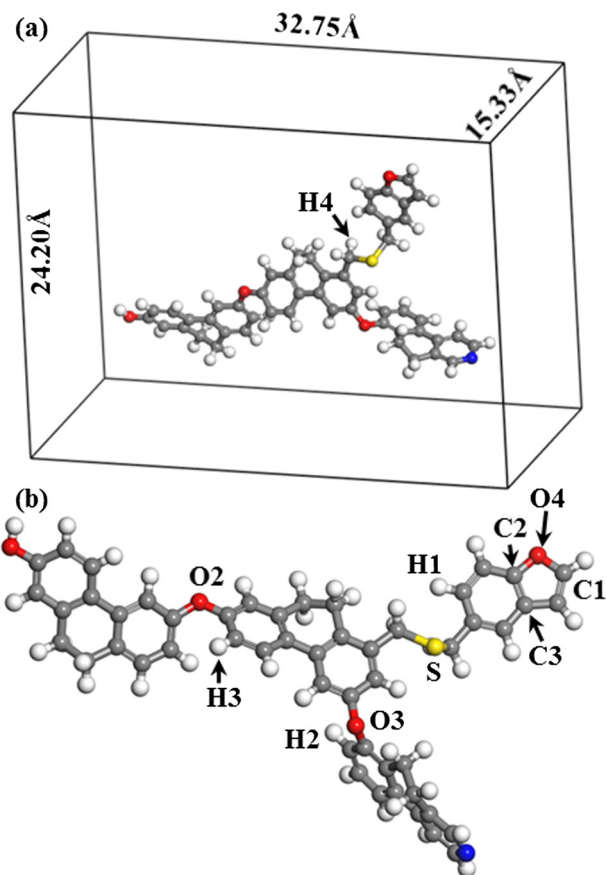


Fig. 1. (a) Schematic of the supercell used to represent an ideal (defect-free) local structure of coal. (b) Close-up configuration of the segment of coal included in the supercell. The C, H, O, N, and S atoms are represented by spheres with colors of grey, white, red, blue, and yellow, respectively. The specific hydrogen sites (H1–H4), carbon sites (C1–C3), oxygen sites (O2–O4), and sulfur site (S) are also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the N atom (N) and five C atoms. The coal segment was placed into a supercell (repeated unit cell), as shown in Fig. 1a. The configuration was fully relaxed, and the obtained configuration represents an ideal local structure of coal.

The first-principles calculations were performed with density-functional theory (DFT), using the projector augmented wave (PAW) method and a plane wave basis set [50–55]. The results reported in this paper were obtained using Vienna Ab-Initio Simulation Package (VASP) [51–53]. The exchange-correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE) [56]. For structure optimizations, all atoms were allowed to relax until the force on each atom was smaller than 0.05 eV/Å. A plane-wave energy cut-off of 400 eV was used in all calculations. The optimized reaction pathways and the corresponding activation energies of possible chemical reactions were determined with climbing nudged elastic band method [57–59]. The calculations were conducted with one special *k* point in the Brillouin zone of the supercell, the Γ point. The adsorption energy of a CO₂ molecule was calculated as [60–62]

$$E_{ads} = E_{coal+CO_2} - E_{coal} - E_{CO_2}$$

where $E_{coal+CO_2}$, E_{coal} , and E_{CO_2} are the total energies of the adsorbed system, the coal network (adsorbent), and the isolated CO₂ molecule (adsorbate), respectively.

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