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The structure and dipolar properties of CO_2 adsorbed in a porous glassy chalcogel: Insights from first-principles molecular dynamics

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ABSTRACT

A thorough understanding of the interactions of CO_2 with the hosting porous network is crucial for the design of new adsorbent materials with enhanced gas adsorption capacity and selectivity. In this paper, first-principles molecular dynamics simulations are performed to assess the interactions of CO_2 adsorbed in a nanoporous glassy chalcogenide (i.e. chalcogel) under relevant laboratory conditions. The structure and local organization of the confined CO_2 molecules are analyzed in terms of atomic density, orientational order parameter and pair correlation functions. Maximally localized Wannier functions are used to unravel the electronic structure, the local molecular dipole and the nature of the chemical bonding at the interface between CO_2 and the glassy surface. Our results provide a useful insight on the complex interplay between the chemical interactions competing at the buried interface made by the CO_2 molecules adsorbed in *g*-GeS_2 chalcogel.

1. Introduction

Finding innovative solutions towards a more sustainable and clean energy is a top priority of the global research agenda today [1–3]. The high costs associated with the current technologies employed in gas separation and purification processes, both implicated in several energy and environmental applications, motivates the seek of more efficient and cost-competitive sorbent materials able to separate carbon dioxide (CO_2). The separation of CO_2 from gas mixtures such as natural gas, biogas, and syngas is of crucial importance for the year-by-year growing production of hydrogen, estimated around 50 million tons per year worldwide [4]. Also, the increasing level of atmospheric CO_2, largely connected to the combustion of fossil fuels, is currently a very urgent environmental concern [5]. Among the few and yet viable strategies that can deal with the emission of CO_2 is carbon capture and storage via adsorption by means of porous solids. Many different porous materials have been investigated for the adsorption of CO_2 including metal-oxides [6–8], zeolites [9–12], porous carbon [13–16], and metal-organic frameworks (MOFs) [17, 18]. The ideal CO_2 sorbent material needs to show enhanced uptake capacity, high selectivity, easy recyclability, as well as very good structural stability. However, current sorbent materials fail to satisfy simultaneously all these requirements. Therefore, there is a need for new adsorbent materials with enhanced CO_2 adsorption performance. Recently, porous chalcogenides including chalcogels [19–21, 23] and zeolitic chalcogenides [24, 25] have attracted widespread attention in the field of CO_2 adsorption because of their high surface area and the soft Lewis base nature of chalcogen elements (S, Se, and Te) [26]. The polarizability of chalcogenide-based sorbents is thus much higher than that of metal-oxides and porous carbons, providing a strong affinity towards highly polarizable species, such as CO_2 [27–29]. However, despite the increasing interest in chalcogenide-based sorbents, the study of their adsorption properties is still at its infancy [30–33]. In a previous work, we resorted to Grand Canonical Monte Carlo simulations (GCMC) to identify the microscopic mechanisms of CO_2 adsorption in a prototypical chalcogel made of GeS_2 (*g*-GeS_2 hereafter) [34]. Those GCMC simulations allowed us to unravel the *g*-GeS_2 gas adsorption and separation properties via a study of the adsorption of N_2, CO_2, H_2, CH_4 and their mixtures. In the present work, first-principles molecular dynamics (FPMD) is the simulation protocol used to gain insights into the structure and dipolar properties of CO_2 adsorbed in a *g*-GeS_2 chalcogel. The effect of CO_2 content adsorbed inside the *g*-GeS_2 pore is accounted for by considering three systems, each one characterized by an increasing CO_2 partial pressure, on which GCMC simulations are performed. The article is organized as follows. In a first section, the atomic models of *g*-GeS_2 and CO_2 as well as the GCMC and FPMD methodologies are presented. In a second section, the FPMD trajectories are analyzed, and the structure and dipolar properties of the confined CO_2 are extracted and discussed. Then, we critically

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assess our results by invoking available experimental data before drawing a final set of conclusions.

2. Models and methodology

2.1. Porous GeS_2 model and GCMC simulations

In the present work we employed the realistic *g*-GeS_2 surface model previously optimized via FPMD [35, 36]. Such surface model was employed to produce *g*-GeS_2 slit-like nanopores for the study of the interactions between *g*-GeS_2 with both gas molecules [34] as well as ionic liquids [37]. The *g*-GeS_2 pore model used for the present study contains 480 atoms and has a surface area of $2.358 \times 2.358\,\mathrm{nm}^2$ with a pore width of 2.4 nm along the *z* direction. Following the same procedure employed in our previous work [34], we performed GCMC simulations of CO_2 adsorption in the *g*-GeS_2 pore by imposing a chemical potential and a finite temperature *T* (298 K) to an infinite reservoir of CO_2 molecules in equilibrium with the simulation box with constant volume *V*. The adsorption isotherm is obtained by the ensemble average of each number of CO_2 molecules as a function of the fugacity of the reservoir (the latter is determined from the chemical potential). For this work, the gas partial pressure *p* is assumed to be equal to the fugacity (i.e. ideal gas assumption). We model the CO_2 adsorption isotherm between the 0.01 and 125 bar (see Fig. 1). For the GCMC simulations, the rigid model by Harris and Yung [38] fitted to reproduce the experimental vapor-liquid equilibrium of bulk CO_2, was used in this work to describe the carbon dioxide molecule. The carbon–oxygen distance is assumed to be rigid and equal to 0.1149 nm, while the rigid O-C-O angle is set to 180°.

Each of the three atoms is a Lennard-Jones site which also carries a partial charge. All the interactions between the atoms of the CO_2 molecules and the Ge and S atoms of the chalcogel were calculated by considering the intermolecular energy $U_{ij}(\mathrm{r})$ between two sites (*i* and *j*) as the sum of a Coulombic contribution and a pairwise-additive Lennard Jones (LJ) 12–6 potential. In our simulations, the LJ cross interaction parameters (σ_{ij}, ϵ_{ij}) between unlike sites are calculated using the Lorentz-Berthelot mixing rules. The atomic partial charges on the Ge and S atoms of *g*-GeS_2 were derived using the charge equilibration method [39] in order to use a local charge distribution dependent on the local structural and chemical orders (i.e. atomic coordination). The dispersive interactions were neglected beyond a cutoff of 15 Å. The electrostatic interactions were computed using the Ewald summation technique (the parameters were chosen so that the relative accuracy in the Coulomb energy calculation is 10^{-5}). More details about the GCMC procedure and potential parameters employed in this study can be found in ref. [34].

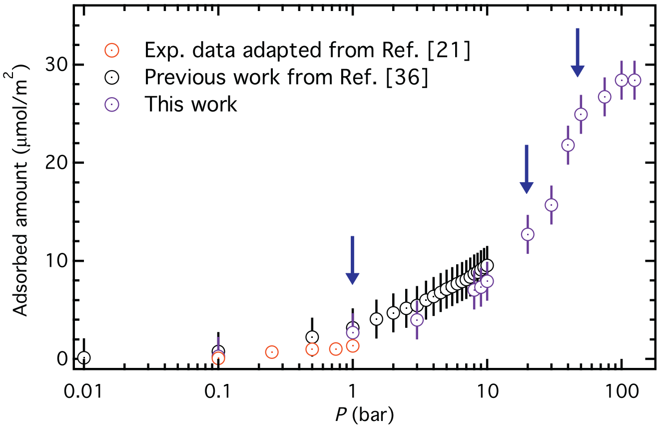

Fig. 1. CO_2 adsorption isotherm at 298 K in porous *g*-GeS_2 (purple circles). We also show the adsorption isotherm data obtained in our previous work on a model four time larger (black circles) and the experimental data obtained by Armatas et al. [21] for a chalcogel with S:Ge = 0.21 (orange circles). Note that the experimental adsorption data are normalized to the corrected Brunauer-Emmett-Teller (BET) [22] surface area (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. First-principles molecular dynamic simulations

For the FPMD simulations, the electronic structure is described within the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA) of Becke [40] for the exchange and Lee et al. [41] (BLYP) for the correlation energy, respectively. The valence electrons are treated explicitly and expanded on a plane wave basis set with a cutoff energy of 70 Ry. The sampling of the Brillouin zone is restricted to the Γ point and norm-conserving pseudopotentials account for the core-valence interaction. Empirical Grimme D2 dispersions for the van der Waals (vdW) interactions [42] are included for the long-range correlations not included in any GGA. In all canonical simulations, the ionic temperature is controlled with the Nosé-Hoover thermostat. A fictitious electron mass of 600 a.u. and a time step of $\Delta t = 0.1209$ fs were adopted to integrate the equations of motion. The FPMD simulations were performed within the Car-Parrinello formalism as implemented in the CPMD code [43]. This theoretical scheme has been extensively used and assessed on a wide range of glassy chalcogenides [44–46] and hybrid systems [47, 48] As inputs for the FPMD simulations, we employed three configurations obtained with GCMC simulation, corresponding to the systems obtained at $p_{CO_2} = 1$, 20 and 50 bar (531, 729 and 1011 total atoms with 17, 83, 177 CO_2 molecules, respectively). Fig. 2 shows typical configurations for the three systems. We initially performed a FPMD run applying a friction force (ion velocities scaled by a factor 0.98 at each step) in order to allow a first structural relaxation involving all atoms and optimize the models down to $T = 0$ K. The systems were then heated up to 298 K during ~0.75 ps keeping the *g*-GeS_2 atoms fixed at their atomic positions and allowing only the CO_2 molecules to move. Then, we equilibrated the systems at this finite temperature for ~2.5 ps, where for the last ~1.5 ps all the atoms were allowed to move. We used the last ~1 ps for the data production analysis.

3. Results and discussion

3.1. Simulated CO_2 adsorption isotherm

Fig. 1 shows the adsorption isotherm at 298 K for CO_2 obtained within the range of pressures from 0.01 to 125 bar. We also report in Fig. 1 the data simulated in our previous work with a system four times larger along the *xy* plane and the experimental data obtained by Armatas et al. [21] for a chalcogel with S:Ge = 0.21. Note that the experimental data are normalized to the corrected Brunauer-Emmett-Teller (BET) [22] surface area. It is appropriate to correct the BET surface to account for the overestimate of the true geometrical surface areas by about 25–30% [7, 50]. The data obtained confirm the behavior observed in the experiments of adsorption/condensation in solid nanopores [6, 7]. At low pressures, the amount of CO_2 adsorbed increases rapidly with pressure (note the logarithmic scale for the pressure values). Then, beyond adsorption of the first layer, the slope of the adsorption isotherm decreases once the pore gets filled. Then, the adsorbed amount increases in the multilayer adsorption regime until reaching the capillary condensation of CO_2 within the pore (~50–70 bar). The simulation pressure at which the pore gets filled is consistent with the CO_2 saturation pressure measured experimentally (64.5 bar at 298 K). The results obtained in this work are in agreement with those obtained previously on a larger system, thus ruling out any possible size effect. Within the statistical error bars, the new data along with the previous one are also in fair agreement with the available experimental data. This highlights the realistic nature of the employed

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