Surface properties of amorphous nanoporous GeS$_2$

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ABSTRACT

In this work molecular simulations are used to probe the gas adsorption properties of amorphous chalcogenide nanopores. A realistic atom-scale model, derived by first-principles calculations, of glassy chalcogenide surface is considered for the present study. Nitrogen adsorption and condensation at 77 K in pores of different widths are simulated for characterization purposes. The adsorption of carbon dioxide, methane, hydrogen, and their mixtures is investigated at 298 K. Analysis of the adsorption data shows nice agreement with the prediction of obtained using the Ideal Adsorbed Solution Theory. A detailed comparison with experimental literature data is also proposed and discussed. We also address the effect of the surface chemistry on the gas adsorption by studying both bare and hydrogenated chalcogenide surfaces. We show here that porous glassy chalcogenide exhibits highly selective gas adsorption properties and can strongly discriminate among gases on the basis of their interaction with the chalcogenide surface.

Keywords: glasses, porous chalcogenide, molecular simulation, gas separation, CO$_2$ capture

1 INTRODUCTION

Gas separation and purification have the potential to play a relevant role in creating large-scale changes to the mix of energy sources currently used by our global society (i.e., hydrogen purification).[1] The challenge of developing effective separation and purification technologies that have much smaller energy footprints is greater for carbon dioxide (CO$_2$) than for other gases.

Porous materials, such as gels, thanks to their properties based on high surface area and adsorption capacities are relevant to efficient gas separations and therefore critical to energy utilization and emerging clean energy technology.[2] Porous materials, typically made of metal oxides, carbon, or metal-organic frameworks (MOF), have recently been expanded to include the emerging chalcogenide materials called chalcogels.[3],[4] Chalcogels feature random amorphous networks similar to those of amorphous silica. Because of the soft nature of chalcogen elements (S, Se, and Te), the polarizability of the internal surface of chalcogels is much higher than those of metal oxides and porous carbons and therefore provides an entirely new medium through which to study separation of gases. Molecular simulations have proven to be an efficient technique to investigate the physics of gas adsorption on solid surfaces. In particular, Grand Canonical Monte Carlo simulations (GCMC) have proven to be a suitable technique to achieve an atom-scale understanding of the physical phenomena involved during adsorption of various gas on porous silica and carbon, in nice agreement with both experiment and theory.[5]

The present work aims at looking at the gas adsorption properties of a porous material made of glassy GeS$_2$ (g-GeS$_2$, g standing hereafter for glass). GCMC simulations are employed to investigate the adsorption of nitrogen (N$_2$), for characterization purposes, carbon dioxide (CO$_2$), hydrogen (H$_2$), methane (CH$_4$) and their mixture in g-GeS$_2$ pores. Here we used a realistic model g-GeS$_2$ surface recently developed by means of first-principles calculations from a bulk model.[6],[7] We also investigate the effect of surface chemistry by considering both bare and hydrogenated g-GeS$_2$ surfaces. The study of a hydrogenated chalcogenide, as film or porous material, is relevant to its final application.[8]

2 METHOD AND COMPUTATIONAL DETAILS

Two models of porous chalcogenide have been used in this work: a bare and a hydrogenated chalcogenide. The model of bare g-GeS$_2$ was obtained by means of first-principles molecular dynamics. Details of the procedure used can be found in Ref. 6 and 7. This realistic model of GeS$_2$ surface contains 480 atoms and has a size of 2.358 $\times$ 2.358 $\times$ 2.358 nm$^3$ with 1.2 nm along the z direction of free volume on the top and the bottom. The bare chalcogenide pore was obtained as follows: by applying periodic boundary conditions along the three directions (x, y, z) the model is characterized by two (different) opposite surfaces replicated infinitely along the x and y axes. This system was replicated $2 \times 2$ times along the xy plane. Note that the width of our pores (H) is defined as the distance between the mean positions of the S and Ge of each facing (along the z axes) surface. A nanopore with width $H = 3.6$ nm was obtained by inserting 4.716 $\times$ 4.716 $\times$ 1.20 nm$^3$ vac-
uum slab in between the facing chalcogenide surfaces. To build a hydrogenated $g$-GeS$_2$ surface, the undercoordinated (with less than two neighbors) S atoms located at a distance $< 0.5$ nm from the surface were saturated by hydrogen atoms. In so doing, the final thiol surface density is $\sim 2.3$ SH/nm$^2$. The Ge-S-H and S-S-H angles were obtained by DFT calculations performed for several sub-units (Ge$_x$S$_y$ clusters of $< 20$ atoms) taken from the original $g$-GeS$_2$ surface model. The electronic structure was described using the DFT theory with the BLYP functional in the frame of generalized gradient approximation for the exchange and correlation parts of the total energy. The DFT calculations were performed with the CPMD code. Computational details can be found in Ref. Nitrogen was described using the model of Potoff and Siepmann (TraPPE forcefield). The rigid model by Harris and Yung, which has been fitted to reproduce the experimental vapor-liquid equilibrium and dynamical properties of bulk CO$_2$, was used in this work to describe the carbon dioxide molecule. Molecular H$_2$ and CH$_4$ are treated as single spherical particles. In our simulations, the methane and hydrogen molecules are simply described as a single Lennard-Jones sphere. All the interactions between the atoms of the adsorbate molecules (N$_2$, CO$_2$, CH$_4$, and H$_2$) and the Ge, S, H atoms were calculated by considering the intermolecular energy as the sum of the Coulombic and dispersion interactions with a repulsive short-range contribution. The Ge, S and H atoms of the chalcogenide models are described as Lennard-Jones spheres with parameters ($\epsilon$ and $\sigma$) from Ref. 14 and 15 for Ge and S plus a set of electrostatic charges. Following our previous work, the atomic partial charges on the Ge and S atoms of $g$-GeS$_2$ were derived using the Qeq method. In this method, the atomic Ge and S partial charges are derived as a function of their local coordination (for details see Ref. 7). For the hydrogenated surface, the potential parameters and partial charge for the H atoms were taken from Ref. 15. The intermolecular interaction energy between various sites in adsorbates and chalcogenide atoms are calculated through a Coulombic electrostatic contribution and a pairwise-additive Lennard Jones (LJ) 12-6 potential. In our simulations, the LJ cross interaction parameters ($\sigma_{ij}$, $\epsilon_{ij}$) between unlike sites are calculated using the Lorentz-Berthelot mixing rules. Periodic boundary conditions were used in the simulations. The dispersive interactions were neglected past a cutoff of 15 Å. The electrostatic interactions were computed using the Ewald summation technique to correct for the finite size of the simulation box (the parameters were chosen so that the accuracy is $10^{-5}$). The potential form used in this work reproduces a surface charge distribution dependent on the local environment for Ge and S atoms. This charge assignment is particularly suitable for the present study because it describes the charge distribution as a function of the chemical order, which for the case of glassy chalcogenides can differ discretely from the perfect chemical order. We performed GCMC simulations of nitrogen adsorption at 77 K (for characterization purposes) as well as carbon dioxide, methane, and hydrogen at 298 K in bare and hydrogenated chalcogenides. We also considered the adsorption of carbon dioxide-methane and carbon dioxide-hydrogen mixtures with bulk compositions of 50-50%. The GCMC technique is a stochastic method that simulates a system having a constant volume $V$ (the pore with the adsorbed phase) in equilibrium with an infinite reservoir of molecules imposing its chemical potential $\mu_S$ on each species ($S = N_2$, CO$_2$, CH$_4$, and H$_2$) at temperature $T$.

### 3 RESULTS AND DISCUSSION

The structural and electronic properties of the bare $g$-GeS$_2$ surface are reported in our previous study. The $g$-GeS$_2$ surface shows a slightly lower chemical order with respect to bulk $g$-GeS$_2$, although it shows a similar main tetrahedral structural motif. To characterize the sample further, here, $N_2$ adsorption at 77 K is performed by means of GCMC simulations. $N_2$ adsorption is a widely used technique to characterize the surface area and porosity of materials. We studied the adsorption isotherms for bare and hydrogenated $g$-GeS$_2$ nanopores with several widths. Here we discuss the results obtained for nanopores with $H = 3.6$ nm. The data obtained conform to the typical behavior observed in the experiments of adsorption/condensation in solid nanopores; the adsorbed content increases continuously in the multilayer adsorption regime until a jump occurs because of capillary condensation of the $N_2$ within the pore. The condensation pressures is $\sim 0.67 \ P/\ P_0$. The data obtained conform to the experimen-
tions between quadrupole of CO$_2$ the partial charges attributed to the oxygen and car-
g$\rm{^{12}C}$ with CH$_4$ indicate a significantly higher affinity for CO$_2$ compared to CH$_4$. The stronger affinity CO$_2$ for the g-GeS$_2$ surface can be ascribed to the favorable interactions between quadrupole of CO$_2$ (here represented by the partial charges attributed to the oxygen and carbon atoms) and the g-GeS$_2$ surface atoms. For CO$_2$, the adsorbed amount does not differ significantly with increasing the the pore width. In contrast, a small increase with increasing the pore width can be noted for CH$_4$. For H$_2$, this effect is significant. This result can be ascribed to the stronger affinity of CO$_2$ for the g-GeS$_2$ surface in comparison to CH$_4$ and H$_2$. The almost perfect linearity of the adsorbed content with increasing the pressure for H$_2$ suggests a weak interaction with the g-GeS$_2$ surface. This observation is in accordance with the fact that H$_2$ content increases almost linearly with increasing the pore volume; the H$_2$ adsorbed content in g-GeS$_2$ nanopores corresponds to the content in equilibrium with the gas phase at a given pressure and temperature. For CH$_4$ an intermediate behavior can be noted; only a small effect of the pore width on the CH$_4$ adsorbed content can be noted with increasing the pressure. Overall, the simulated data conform qualitatively to the experimental isotherms obtained by Kanatzidis et al.[4] for a chalcogel with S:Ge$_{378}$.

The differences between our simulated results and the experimental data can be ascribed to the different S:Ge ratio, where the higher S content of our model could explain the higher adsorption of CO$_2$ due to the polarizable nature of S. As for the case of N$_2$ adsorption, CO$_2$, CH$_4$, and H$_2$ adsorption isotherms for the hydrogenated nanopores indicate an overall decrease on gas adsorption with respect to the bare g-GeS$_2$ nanopores. In particular, the decreases in gas adsorption are $\sim$12%, $\sim$11%, and $\sim$7% for CO$_2$, CH$_4$, and H$_2$, respectively. These values indicate that the interaction between the adsorbates and the surface hydrogen atoms is weaker than with the sulfur atom of g-GeS$_2$. This effect is more pronounced for the gas adsorption of CO$_2$ and CH$_4$ than of H$_2$. This result is consistent with the fact that the
interaction of CO$_2$ with the g-GeS$_2$ surface is stronger than those of CH$_4$ and H$_2$, thus is more affected by the presence of hydrogen atoms on the g-GeS$_2$ surface. We also performed GCMC simulations of the coadsorption of CO$_2$/CH$_4$ and CO$_2$/H$_2$ mixtures in the bare g-GeS$_2$ nanopore with width $H = 3.6$ nm. Figure 3 shows the simulated coadsorption isotherms. The bulk molar composition of CO$_2$/CH$_4$ and CO$_2$/H$_2$ mixtures studied in this work is 50-50%. The maximum adsorbed contents of CO$_2$ at $P = 10$ bar and $T = 298$ K is 5.9 $\mu$mol/m$^2$ for CO$_2$. For CO$_2$/H$_2$ mixtures the maximum adsorbed amounts of CO$_2$ at the same $P$ and $T$ is 6.0 $\mu$mol/m$^2$ for the same bulk composition. We show also in Figure 2 the predictions obtained using the ideal adsorbed solution theory (IAST)[17], which is widely used to predict the adsorption of mixtures from the data of the pure components. IAST assumes that the adsorbed mixture is an ideal solution. The GCMC simulations and the predicted theoretical values are in good agreement. The discrepancy between the simulated and predicted data can be ascribed to the fact that the IAST does not take into account adsorbate-adsorbate interaction in the adsorbed phase.

4 Conclusions

GCMC simulations of gas (N$_2$, CO$_2$, CH$_4$, and H$_2$) adsorption in g-GeS$_2$ nanopores are reported and discussed. Thanks to the realistic quality of the g-GeS$_2$ model used in this work, we are able to compare the adsorption properties simulated in this work with experimental data from literature. The characterization of the adsorption properties of g-GeS$_2$ by means of N$_2$ adsorption at 77 K shows the typical behavior observed in the experiments of adsorption/condensation in solid nanopores. We found a N$_2$ condensation pressure in nice agreement with the GeS-based chalcogel synthesized the group of Kanatzidis for a similar pore size. This result further proves the realistic quality (in terms of surface structure and charge distribution) of the g-GeS$_2$ nanopore models investigated in this work. By investigating the adsorption isotherms of g-GeS$_2$ nanopores for CO$_2$, CH$_4$, and H$_2$, a stronger interaction for CO$_2$ with the g-GeS$_2$ surface is highlighted with respect to CH$_4$ and H$_2$. H$_2$ shows a very weak affinity with the g-GeS$_2$ surface, thanks to which the H$_2$ adsorption increases linearly as a function of the pore width for higher pressures. The simulations of the adsorption of CO$_2$/CH$_4$ and CO$_2$/H$_2$ mixtures show a relevant selective adsorption of CO$_2$ over CH$_4$ and H$_2$. The results obtained are well described by the ideal adsorption solution theory. We also addressed the study of the effect of the surface chemistry by studying the adsorption in hydrogenated chalcogenide nanopores. The hydrogenation of chalcogenide surfaces causes a small decrease of N$_2$ adsorption at 77 K at low pressure and a small decrease in the adsorption at 298 K for CO$_2$ over both CH$_4$ and H$_2$.

While further work is needed to clarify the gas adsorption on chalcogenide pores with different shape and surface chemistry, the results above help better understanding the interactions between adsorbates and g-GeS$_2$ nanopores. The present work shows how glassy porous chalcogenide represent a valuable material for gas separation, especially for the CO$_2$/H$_2$ mixture.

REFERENCES