

Surface properties of amorphous nanoporous GeS₂

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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, CO₂ 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 (CO₂) 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 new 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 GeS₂ (*g*-GeS₂, *g* standing hereafter for glass). GCMC simulations are employed to investigate the adsorption of nitrogen (N₂), for characterization purposes, carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄) and their mixture in *g*-GeS₂ pores. Here we used a realistic model *g*-GeS₂ 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*-GeS₂ 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*-GeS₂ 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 GeS₂ surface contains 480 atoms and has a size of $2.358 \times 2.358 \times 2.358$ nm³ 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 2×2 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 $4.716 \times 4.716 \times 1.20$ nm³ vac-

uum slab in between the facing chalcogenide surfaces. To build a hydrogenated g -GeS₂ 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 ~ 2.3 SH/nm². 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 -GeS₂ 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.[9], [10] The DFT calculations were performed with the CPMD code.[11] Computational details can be found in Ref. 6. Nitrogen was described using the model of Potoff and Siepmann (TraPPE forcefield).[12] The rigid model by Harris and Yung,[13] which has been fitted to reproduce the experimental vapor-liquid equilibrium and dynamical properties of bulk CO₂, was used in this work to describe the carbon dioxide molecule. Molecular H₂ and CH₄ 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 (N₂, CO₂, CH₄, and H₂) 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 (ϵ and σ) 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 -GeS₂ were derived using the Qeq method.[16] 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 (σ_{ij} , ϵ_{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

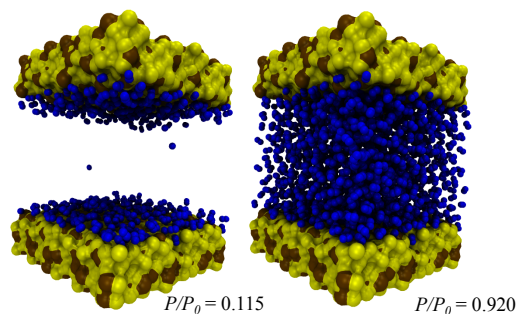


Figure 1: (Color online) Typical molecular configurations for nitrogen in the bare chalcogenide pore with $H = 3.6$ nm: 0.115 P/P_0 (left) and 0.920 P/P_0 (right). The ochre and yellow spheres are the Ge and S atoms of the chalcogenide surfaces, respectively. The blue spheres are the nitrogen molecules.

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.[7] 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 coadsorption 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 μ_S on each species ($S = \text{N}_2, \text{CO}_2, \text{CH}_4, \text{and H}_2$) at temperature T .

3 RESULTS AND DISCUSSION

The structural and electronic properties of the bare g -GeS₂ surface are reported in our previous study.[7] The g -GeS₂ surface shows a slightly lower chemical order with respect to bulk g -GeS₂, [6] although it shows a similar main tetrahedral structural motif. To characterize the sample further, here, N₂ adsorption at 77 K is performed by means of GCMC simulations. N₂ 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 -GeS₂ 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 N₂ within the pore. The condensation pressure is $\sim 0.67 P/P_0$. The data obtained conform to the experimen-

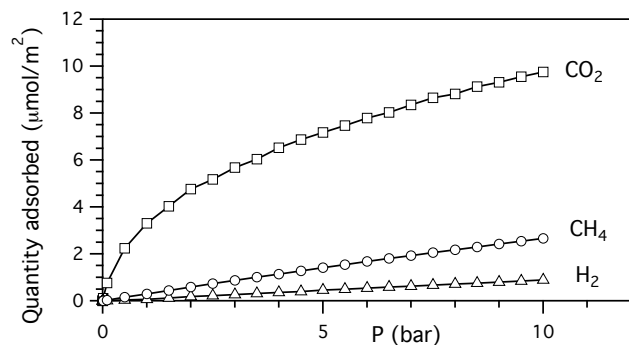


Figure 2: CO₂ (cubes), CH₄ (circles), and H₂ (triangles) adsorption isotherms for bare *g*-GeS₂ at 298 K. The data are shown for the pore with $H = 3.6$.

tal behavior for adsorption/condensation obtained by Kanatzidis et al.[4] Independently of the pore width the surface of *g*-GeS₂ nanopores is covered with a homogeneous film at the onset of capillary condensation. A discontinuous transition between the partially filled and completely filled configurations occurs when the adsorbed film becomes unstable, in line with the experimental data. Figure 1 shows typical molecular configurations of nitrogen adsorbed at different pressures upon adsorption in the nanopore with $H = 3.6$ nm. At low pressure ($\sim 0.115 P/P_0$) the chalcogenide surface is covered with a homogeneous film of N₂. At $\sim 0.920 P/P_0$ the *g*-GeS₂ nanopore is completely filled. The hydrogenated *g*-GeS₂ nanopores show similar trend for all the pore widths (data not shown). The only appreciable difference is a lower adsorption ($\sim -5\%$) of N₂ at the low pressure ($< 0.02 P/P_0$). This result can be attributed to a weaker interaction between N₂ molecules and the hydrogen atoms of the surface with respect to the sulfur atoms. This result shows that a small variation (intended as contamination or functionalization) of the surface chemistry of *g*-GeS₂ causes an effect on the adsorption properties.

All the CO₂, CH₄ and H₂ adsorption isotherms in this work were simulated at 298 K in order to investigate gas adsorption at a temperature of practical interest. Figure 2 shows the adsorption isotherm for CO₂, CH₄, and H₂ in the bare *g*-GeS₂ nanopores with $H = 3.6$ nm. For CO₂ the adsorption amount increases rapidly with increasing the pressure and then the slope decreases as the pores get filled. For CH₄ and H₂, the adsorption amount increases almost linearly with the pressure. The adsorption isotherms for CO₂, CH₄ and H₂ of *g*-GeS₂ indicate a significantly higher affinity for CO₂ compared with CH₄ and H₂. The stronger affinity CO₂ for the *g*-GeS₂ surface can be ascribed to the favorable interactions between quadrupole of CO₂ (here represented by the partial charges attributed to the oxygen and car-

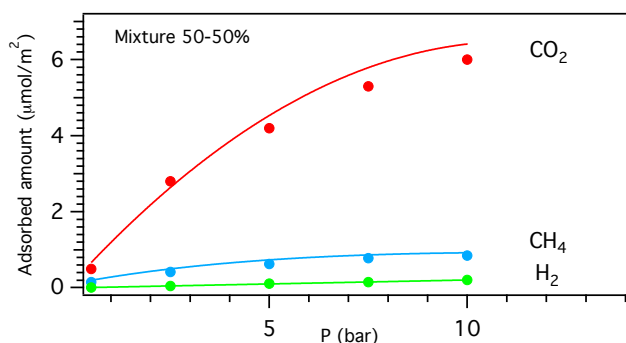


Figure 3: (Color online) Simulated coadsorption of CO₂/CH₄ and CO₂/H₂ at 298 K. The bulk composition of the CO₂-CH₄(H₂) mixture are 50-50%. The solid lines are predictions obtained from the simulated adsorption isotherms obtained by the IAST theory (see text).

bon atoms) and the *g*-GeS₂ surface atoms. For CO₂, the adsorbed amount does not differ significantly with increasing the pore width. In contrast, a small increase with increasing the pore width can be noted for CH₄. For H₂, this effect is significant. This result can be ascribed to the stronger affinity of CO₂ for the *g*-GeS₂ surface in comparison to CH₄ and H₂. The almost perfect linearity of the adsorbed content with increasing the pressure for H₂ suggests a very weak interaction with the *g*-GeS₂ surface. This observation is in accordance with the fact that H₂ content increases almost linearly with increasing the pore volume; the H₂ adsorbed content in *g*-GeS₂ nanopores corresponds to the content in equilibrium with the gas phase at a given pressure and temperature. For CH₄ an intermediate behavior can be noted; only a small effect of the pore width on the CH₄ 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:Ge₉ ~ 1.9 . 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 CO₂ due to the polarizable nature of S. As for the case of N₂ adsorption, CO₂, CH₄, and H₂ adsorption isotherms for the hydrogenated nanopores indicate an overall decrease on gas adsorption with respect to the bare *g*-GeS₂ nanopores. In particular, the decreases in gas adsorption are $\sim 12\%$, $\sim 11\%$, and $\sim 7\%$ for CO₂, CH₄, and H₂, respectively. These values indicate that the interaction between the adsorbates and the surface hydrogen atoms is weaker than with the sulfur atom of *g*-GeS₂. This effect is more pronounced for the gas adsorption of CO₂ and CH₄ than of H₂. This result is consistent with the fact that the

interaction of CO₂ with the *g*-GeS₂ surface is stronger than those of CH₄ and H₂, thus is more affected by the presence of hydrogen atoms on the *g*-GeS₂ surface. We also performed GCMC simulations of the coadsorption of CO₂/CH₄ and CO₂/H₂ mixtures in the bare *g*-GeS₂ nanopore with width $H = 3.6$ nm. Figure 3 shows the simulated coadsorption isotherms. The bulk molar composition of CO₂/CH₄ and CO₂/H₂ mixtures studied in this work is 50-50%. The maximum adsorbed contents of CO₂ at $P = 10$ bar and $T = 298$ K is $5.9 \mu\text{mol}/\text{m}^2$ for CO₂. For CO₂/H₂ mixtures the maximum adsorbed amounts of CO₂ at the same P and T is $6.0 \mu\text{mol}/\text{m}^2$ 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 (N₂, CO₂, CH₄, and H₂) adsorption in *g*-GeS₂ nanopores are reported and discussed. Thanks to the realistic quality of the *g*-GeS₂ 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*-GeS₂ by means of N₂ adsorption at 77 K shows the typical behavior observed in the experiments of adsorption/condensation in solid nanopores. We found a N₂ 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*-GeS₂ nanopore models investigated in this work. By investigating the adsorption isotherms of *g*-GeS₂ nanopores for CO₂, CH₄, and H₂, a stronger interaction for CO₂ with the *g*-GeS₂ surface is highlighted with respect to CH₄ and H₂. H₂ shows a very weak affinity with the *g*-GeS₂ surface, thanks to which the H₂ adsorption increases linearly as a function of the pore width for higher pressures. The simulations of the adsorption of CO₂/CH₄ and CO₂/H₂ mixtures show a relevant selective adsorption of CO₂ over CH₄ and H₂. 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 N₂ adsorption at 77 K at low pressure and a small decrease in the ad-

sorption at 298 K for CO₂ over both CH₄ and H₂.

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*-GeS₂ nanopores. The present work shows how glassy porous chalcogenide represent a valuable material for gas separation, especially for the CO₂/H₂ mixture.

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