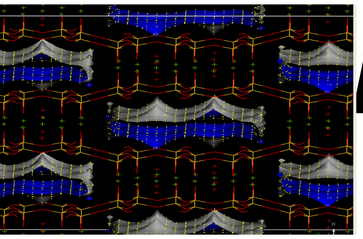
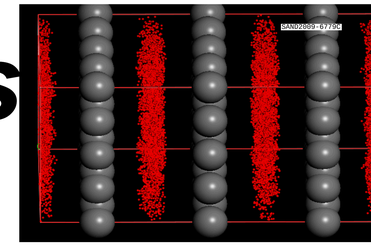


Molecular Modeling Gas Adsorbents

Phillip Pohl, Yifeng Wang, Yongliang Xiong and Kathleen Holt-Larese, Sandia National Laboratories

Al_2O_3 , Sepiolite, Zeolites, Activated Carbons and Kr, I_2



Why?

Separation of radioactive gases is important in many proposed nuclear fuel cycles

Gas separation can be done via cryogenic, membrane, adsorption or other chemical processes

Adsorption of gases by zeolites and activated carbons has been shown to be the most economically viable choice in many cases

Computer simulation of molecular adsorption and sieving has been carried out successfully in the past decade to assist in product development.

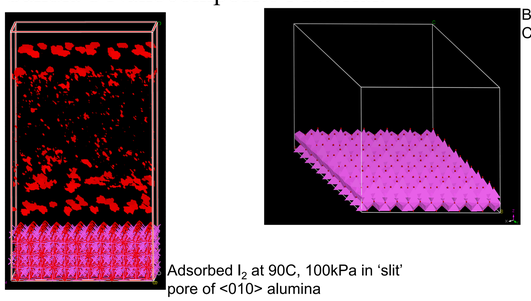
How? GCMC

we conducted Grand Canonical Monte Carlo (GCMC) computer simulations of Kr, Xe, and I_2 on different molecular models of materials under evaluation. The adsorbate model I_2, because of the large atomic radii of iodine and its ability to become polarized, used force-field parameters that mimic this molecular phenomenon. Lennard-Jones 6-12 parameters were used for I_2 (s = 2.376 Å; e = 35.56 kcal/mol) however the individual iodine atoms of I_2 were artificially charged ($d^{\pm}$ = ±0.366 e) such that molecular neutrality was maintained but a dipole established. The result is a sorption analyte which accounts for the molecular polarization of I_2 when it interacts with another atom or surface. Kr, Ar, and Xe were simulated as L-J 6-12 spheres.

Various models of potential adsorbents were developed and tested using the GCMC approach over expected operating conditions.

Alumina Models

The nanoporous alumina model was created by exposing a γ-alumina (Al_2O_3) <111> surface to the adsorbing iodine. The pore size was assumed to be a slit between two parallel surfaces as shown below. The coordinate perpendicular to the planar walls was changed from 1.5 to 4 nm to simulate different pore sized alumina. The <101> surface was also treated in a similar way. These model 'pores' of alumina should compare with Sandia's Nanocomposite Material.

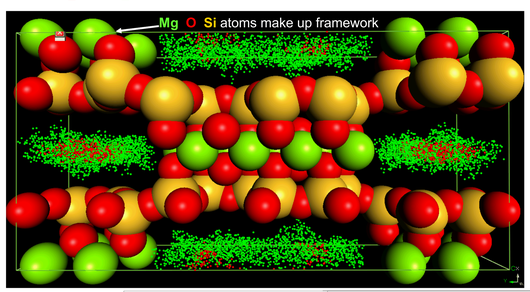


Adsorbed I_2 at 90C, 100kPa in 'slit' pore of <010> alumina

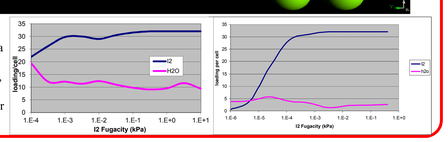
Sepiolite

Sepiolite is a clay mineral, a complex magnesium silicate, a typical formula for which is $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, but the number of crystalwater molecules can vary from 2 to 12.

H_2O / I_2 sorption sites: perspective View



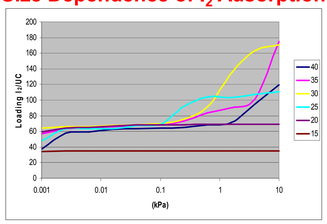
Effect of water/humidity on I_2 adsorption. 100 kPa (left) and 10kPa H_2O. Total I_2 adsorbed is same, but low pressure adsorption more for lower humidity.



NanoPorous Alumina

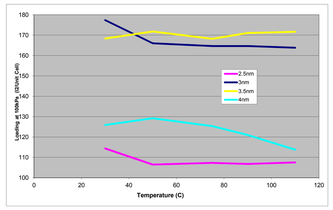
Pore Size Dependence of I_2 Adsorption

The GCMC adsorption simulation of I_2 is shown at right. The models labeled 30 and 25nm suggest an optimum pore size for adsorption of low presssure iodine.



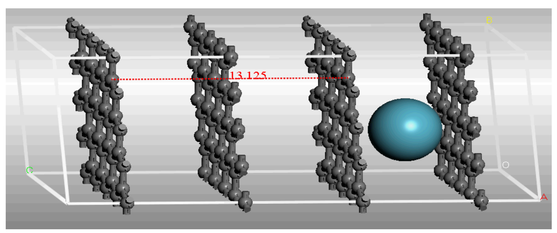
Temperature Dependence of I_2 Adsorption

The different pore sized alumina models were tested at different temperatures to verify experimental results. The GCMC adsorption simulation of I_2 could not corroborate the rise found in the sorption experiments with increasing temperature from 75C to 90C. The smaller size pore simulations should be carried out to for more Monte Carlo steps.

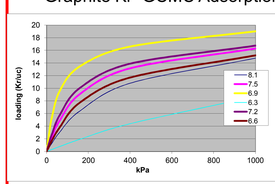


Graphite Results

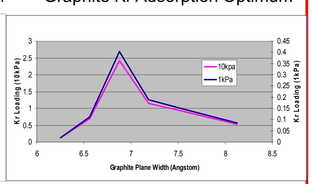
Graphite models were studied to simulate the adsorption onto various activated carbons. The primary surface feature in these materials is a graphite wall.



Graphite Kr GCMC Adsorption



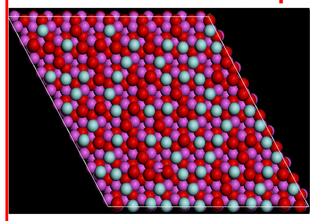
Graphite Kr Adsorption Optimum



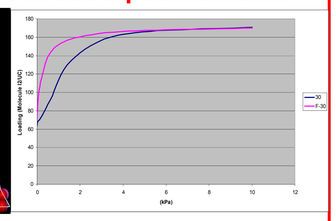
An optimum pore size of 7 Å is suggested by GCMC simulations for Kr adsorption.

Fluorination

Does Fluorination improve adsorption & how?



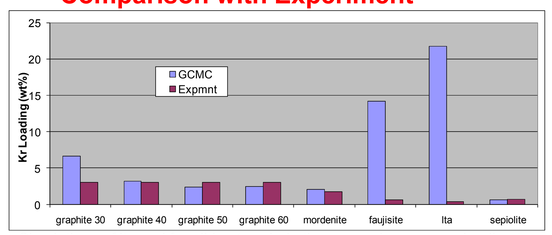
Plane view of 60% fluorinated alumina surface. Turquoise balls are F, Red = O and Magenta = Al.



GCMC adsorption onto fluorinated alumina models.

60% of the alumina model surface oxygens were replaced with F atoms. The resultant porous solid model is shown on left, where the turquoise balls are F atoms. Simulating adsorption onto the new fluorinated surface is shown right, where the fluorinated surface has enhanced the attraction of I_2 to the solid as was found experimentally. Understanding why and what an optimum might be would be next steps.

Comparison with Experiment



Simulations of lta and fau did not exclude the porous inner cages leading to greater adsorption predicted.

Conclusions

Molecular Dynamics techniques are applicable to adsorbate investigation with different adsorbents.

Explicit exact conditions are unnecessary during adsorption simulation but intermolecular potentials are very important.

An adsorption model should be used to understand the affects of humidity, temperature and adatoms.

Another question to investigate is whether there is a way to design adsorbents to remove gases selectively.

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