CrossMark

Molecular simulation and experimental characterization of the nanoporous structures of coal and gas shale

Mahnaz Firouzi [a], Erik C. Rupp [a], Corey W. Liu [b], Jennifer Wilcox [a,*]

[a] Department of Energy Resources Engineering, Stanford University, Stanford, CA 94305-2220, USA
[b] Stanford Magnetic Resonance Laboratory, School of Medicine, Stanford University, Stanford, CA 94305-2220, USA

ARTICLE INFO

ABSTRACT

Characterization of coal and shale is required to obtain pore size distribution (PSD) in order to create realistic models to design efficient strategies for carbon capture and sequestration (CCS) at full scale. Proton nuclear magnetic resonance (NMR) cryoporometry and low-pressure gas adsorption isothermal experiments, conducted with N_2 at 77 K over a P/P_0 range of 10^{-7} to 0.995, were carried out to determine the PSD and total pore volumes to provide insight into the development of realistic simulation models for the organic matter comprising coal and gas shale rock. The PSDs determined on the reference materials (SiliaFlash F60 and Vycor 7930) show a reasonable agreement between low-pressure gas adsorption and NMR cryoporometry showing complementarity of the two independent techniques. The PSDs of coal and shale samples were determined with low-pressure gas adsorption isothermal experiments, but were unable to be measured by NMR cryoporometry. This is likely due to a combined size and pore surface chemistry effect that prevents the water from condensing in the pores, such that when the sample is heated there is no distinction based upon melting or phase change. Molecular modeling is carried out to create the pore structure network in which the transport and adsorption predictions are based. The three-dimensional (3D) pore network, representative of porous carbon-based materials, has been generated atomistically using the Voronoi tessellation method. A comparison of the computed PSD using this method was made to the measured PSD using isothermal low-pressure gas adsorption isothermal experiments on coal and gas shale samples. Applications of this work will lead to the development of more realistic 3-D models from which enhanced understanding of gas adsorption and transport for enhanced methane recovery and CO_2 storage applications can be developed.

1. Introduction

The effect of increasing atmospheric CO_2 concentration on climate change is recognized as one of the most important environmental concerns (IPCC, 2007; White et al., 2005). Carbon capture and sequestration is one strategy that could potentially mitigate gigatons (Gt) of CO_2 emissions per year; however, technical and policy obstacles have thus far hindered wide-scale deployment of this strategy (Wilcox, 2012). To design efficient and reliable strategies for either carbon capture or sequestration at the full-scale, one needs to understand the chemical and physical properties of CO_2 and its interaction with its local surroundings at the molecular-scale. To investigate these properties, characterization studies need to be carried out alongside theoretical modeling efforts. Integration of theory and experiments will allow for the relevant physics at the molecular-level to be revealed. Determining the transport of CO_2 within the model systems can be used to understand the complex pore matrices of coal and gas shale that are important to determining their potential for CO_2 storage.

Coals and gas shale rocks are structural and chemical heterogeneous porous materials with porosity and PSDs varying throughout. For instance, a three dimensional chemical representation of a coal macromolecule based on data from physiochemical analyses was developed by Faulon et al. (1993). Pores in coal vary in size from microns to angstroms in dimension and cleat-fractures. A significant proportion of their total open pore volume is located in micropores of less than 20 Å pore size (Sharkey and McCartney, 1981; Wang et al., 2007). The pore size is classified into three pores: macropores which are larger than 500 Å, mesopores which are between 20 and 500 Å, micropores which are less than 20 Å (IUPAC, 1972). Quantifying PSD, pore connectivity and porosity is desirable to determine the difference between how gases such as methane and CO_2 are stored and permeate in the coal seams and shale formations (White et al., 2005). Hence, there is great interest in methods for measuring PSD and characterization of the porous structures previously discussed, which is the focus of this work from both theory and experiment.

Transport and adsorption properties of CO_2 and methane in the organic matrix of coal and gas shale rocks are strongly influenced, and sometimes even dominated by the morphology of their structure, which consist of the connectivity of pores, and their sizes, shapes and

surface characteristics. The main source of heterogeneity for coal and shale rock is the complicated porous structure that cannot be represented by a single pore, as it contains pores of different shapes and sizes, including straight and tortuous pathways, and contracting and diverging channels. When such single pores are connected, they form pore networks. The realistic simulation of porous materials addresses two prominent aspects, namely, the modeling of the solid material itself and the generation of its pore structure including pore-size distribution and pore-network connectivity. The most direct route towards addressing both of these aspects is through the atomistic simulation of these materials. To properly address the representation of the morphology of these complicated structures, in the present work we describe an efficient molecular pore-network model for porous materials, and particularly of carbon-based materials with a pore space that contains pores of irregular shapes and sizes that follow a certain PSD. The pore networks are generated by the Voronoi tessellation of a solid material composed of millions to hundreds of thousands of atoms, and by designating a fraction of the Voronoi polyhedra as the pores. The pore space of many natural porous materials, ranging from biological materials, wood, and foam (Gibson and Ashby, 1997; Unger et al., 1988), to sandstone and other types of rock (Sahimi, 1995), can be well represented by Voronoi-type structures. The model allows for the investigation of the effect of the morphology on the pore space, i.e., its PSD and pore connectivity, on the adsorption and transport of methane and CO_2 for capture and storage applications (Firouzi and Wilcox, 2012, 2013).

Techniques to determine pore size distributions include small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) (Radlinski et al., 2004) and ^{129}Xe NMR (Terskikh et al., 1993). In this study, we utilize proton NMR cryoporometry and low-pressure gas adsorption isothermal experiments to characterize the porous structure of two reference materials, lignite coal and gas shale. NMR cryoporometry detects the pore-size-dependent shift of the melting and/or freezing points of pore imbibed materials (Hansen et al., 1996; Petrov and Furó, 2006; Strange et al., 1993). For detection, NMR cryoprometry exploits the substantial difference between solid and liquid NMR signals. In the gas adsorption experiments, isotherms were developed using N_2 as the probe gas with a Quantachrome Autosorb iQ$_2$ instrument. The isotherms were then analyzed to determine the PSD and total micro- and mesopore volumes of the coal and gas shale samples.

In the first part of this work, the molecular pore network simulation employed to model the carbon-based porous structure of coals and gas shales is described. Next, the NMR cryoporometry and gas adsorption techniques used to characterize the porous structure of reference materials and coal and gas shale are explained. The results are presented and analyzed in the final part.

2. Molecular porous structure model

The molecular pore network is generated based on geometric considerations alone and the chemical and energetic details of creating the pores are ignored. In this method, we begin with a 3-D cell of carbon atoms with a structure corresponding to graphite so that the number density of carbon atoms is 114 nm^{-3} and the spacing between the adjacent graphene layers in the z- direction is 0.335 nm. Periodic boundary conditions were employed in all directions. The details of the system size are elucidated in the results and discussion section. The graphite cell is then tessellated through the insertion of a given number of Poisson points at random positions inside the simulation cell, each of which is used for constructing a 3-D Voronoi polyhedron, such that every point inside each polyhedron is closer to its own Poisson point than to any other Poisson point. The pore space is then generated by fixing the desired porosity and selecting a number of polyhedra, that can be chosen randomly or by first sorting and listing the polyhedra in the cell according to their sizes from smallest to largest (or vice versa), in such a way that their total volume fraction equals the desired porosity. The polyhedra, so chosen, are then designated as the pores by

removing the carbon atoms comprising them, as well as those that are connected to only one neighboring carbon atom (the dangling atoms, i.e., connected to only one other atom), since it is impossible to have such atoms connected to the internal surface of the pores. Also, removal of the dangling atoms gives rise to pore surface roughness at the molecular level, which is expected to exist in any real pore (Firouzi and Wilcox, 2012; Rajabbeigi et al., 2009a,b; Xu et al., 2000a). The remaining carbon atoms constitute the solid matrix, while the pore space consists of interconnected pores of various shapes and sizes. We should note that the influence of heteroatoms is not included in this work. The equivalent radius size of each polyhedron is taken to be the radius of a sphere that has the same volume as the polyhedron.

If the pore polyhedra are selected at random, then, assuming that the size of the simulation cell is large enough, their size distribution will always be Gaussian, regardless of the porosity or even the size of the initial graphite cell. The 3-D graphite pore networks with desired porosities can be generated using this model. In addition, any desired average pore size can be fixed by varying the number of Poisson points inside the initial graphite cell. Clearly, the larger the number of Poisson points, the smaller the average pore size. The pore space generated by these models is a molecular-scale pore network and, unlike the traditional pore networks that are used in the simulation of flow and transport in microporous media, this allows for the interaction of the fluid molecules with the atoms in the structure. Moreover, the Voronoi algorithm has great flexibility in terms of constructing disordered pore networks with many variations in the sizes and shapes of the polyhedra. The algorithm can be modified to generate pore polyhedra with a great variety of shapes, from completely random to very regular shapes (Cromwell, 1997).

The Voronoi network has been previously utilized as a prototype of irregular networks to study transport in disordered composites (Jerauld et al., 1984a,b; Sahimi and Tsotsis, 1997), and the statistics of Voronoi tessellations have been used in the past to characterize the porosity distribution in porous materials (Dominguez and Rivera, 2002; Firouzi and Wilcox, 2012, 2013; Ghassemzadeh et al., 2000; Rivera and Dominguez, 2003; Xu et al., 2000a, 2001). The Voronoi structure has also been used in the past for modeling of polymer membrane and adsorption processes. The atomistic Voronoi structure has been developed to model carbon membranes to study the transport and adsorption of gases, including the existence of an optimal pore structure for maximum gas separation (Xu et al., 2000a). The Voronoi model has also been utilized to compute the adsorption isotherms of N_2 in three distinct silicon-carbide (SiC) membranes at 77 K, and transport and separation of H_2/CO_2 and H_2/CH_4 mixtures and found reasonable agreement with experimental data (Rajabbeigi et al., 2009a,b). In addition, previous studies included a comparison of the computed PSD for the model Carbon Molecular Sieve Membrane (CMSM) using the Voronoi tessellation to the experimentally measured PSD of a typical CMSM (Xu et al., 2000b), which are in reasonable agreement (Firouzi, 2005).

3. Characterization experiments

Reference materials used were a silica gel, SiliaFlash F60 (SiliCycle, Inc., Canada) of 230–400 mesh particle size and 60 Å pore size, and an open-cell porous glass, Vycor 7930 (Corning, Inc., New York) of 30–100 mesh particle size and 40 to 200 Å pore diameter. The coal sample used in the studies is a wet, lignite sample from North Dakota, United States. The shale sample is from the Eagle Ford shale formation from southeast Texas, United States. The formation is characterized as a "black" or organic-rich shale.

The SiliaFlash F60 and Vycor 7930 reference materials were used as provided. The lignite and shale samples were prepared by grinding a representative sample (0.1 to 0.2 g) in a chalcedony mortar and pestle and sieved through a 45-mesh (Tyler equivalent) screen so the entire