

COMPUTATIONAL MODELLING OF NANOPOROUS MATERIALS FOR SUSTAINABLE ENERGY AND ENVIRONMENTAL APPLICATIONS.**Ioannis Skarmoutsos^{1,2,3*}, Emmanuel Klontzas³, Emmanuel N. Koukaras², Guillaume Maurin¹**¹Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, Université de Montpellier, Place E. Bataillon, 34095 Montpellier Cedex 05, France²Institute of Chemical Engineering Sciences, Foundation of Research and Technology-Hellas (FORTH/ICE-HT), Stadiou Street, Platani, Patras, 26504, Greece³Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48, GR-116 35, Athens, Greece*(*iskarmoutsos@hotmail.com)***ABSTRACT**

The adsorptive separation and capture of CO₂ from natural and flue gases, as well as the separation of fluid SF₆-N₂ mixtures used in electrical power transmission applications, have been classified among the biggest challenges in chemical and environmental technology nowadays. At the same time, the rational design of nanoporous materials for processes requiring the capture and release of water, such as the screening of traces of water, the control of the humidity in the air and the delivery of drinking water in remote areas, has become another issue of crucial importance. In this context, our systematic computational molecular modelling studies on these topics will be presented and discussed. Particular attention will be paid to the behavior on the molecular-scale processes controlling the thermodynamic selectivity of the confined molecules in a variety of carbon-based and metal-organic framework nanoporous materials.

INTRODUCTION

Natural gas processing is a relatively complex industrial process designed to refine raw natural gas by separating impurities and undesired hydrocarbons in order to meet several specifications, mainly related to its heat content and flame temperature. Natural gas and biogas primarily consist of methane and to a lesser extent of carbon dioxide, hydrocarbons and hydrogen sulfide. It has been observed that the heat content of natural gas can be increased by reducing the amount of carbon dioxide. Therefore, the development of efficient methods to separate carbon dioxide from natural gas mixtures has become an issue of crucial importance over the last decade, in view also of the rapid decrease of fossil fuel resources^[1-3].

Owing to its high dielectric strength and arc-quenching properties, low toxicity and high stability, sulfur hexafluoride (SF₆) is the most widely used insulating and switching medium for electrical power transmission equipment and several other applications, especially under high voltage. However, SF₆ is a very potent greenhouse gas due to its very long atmospheric lifetime (3200 years) and its high efficiency as an infrared absorber. This gas shows one of the highest global warming potentials, 24000 times higher than CO₂ and it is amongst the main anthropogenic greenhouse gases. In this context, the Kyoto protocol aims to reduce its emission. Furthermore, SF₆ falls also under the European F-Gas regulation limiting its use in diverse fields. Therefore, there is a critical need to reduce the use of SF₆ as an insulator in high voltage and circuit breakers. The current alternative consists of considering a pressurized gas mixture, where a low content of SF₆ is mixed with ordinary gases such as N₂, CO₂ or air. It was demonstrated that when mixing SF₆ with N₂, the fluid mixture maintains the high dielectric strength of pure SF₆, even at high N₂ concentration. However, when mixing these two fluids the complexity of recovering and recycling SF₆ increases and this holds even more true when the amount of SF₆ in the mixture decreases. In this case, the development of efficient processes for the separation of SF₆/ N₂ mixtures is required^[4].

Over the last years the rational design of nanoporous materials for processes requiring the capture and release of water, such as the screening of traces of water, the control of the humidity in the air and the delivery of drinking water in remote areas, has also become an issue of crucial importance^[5]. In order to address the ongoing challenges in all the related technological, industrial and environmental applications, several criteria for developing high performing porous materials for water adsorption have been proposed. These criteria are mainly related to the condensation of water in the nanopores at low relative pressures, the uptake capacity and recyclability of the materials and their chemical stability in humid environments.

In order to reveal deeper insights into the molecular-scale mechanisms controlling the thermodynamic and dynamic adsorption selectivity of greenhouse gases and water in nanoporous materials, a detailed description of the intermolecular interactions is required. The use of a combination of quantum- and forcefield-based molecular simulations offers in principle such a possibility. These techniques have been shown to have high predictive capabilities of macroscopic properties of complex materials such as metal-organic frameworks (MOFs) and carbon-based nanoporous networks and have been employed in the present treatment.

The nanoporous materials under study in the present treatment were MOFs and a carbon-based nanoporous network. The MOFs under study were the recently reported ^[3] $[\text{Cu}(4,4'\text{-dipyridylacetylene})_2(\text{SiF}_6)]_n$, named as SIFSIX-2-Cu, and its interpenetrated polymorph isostructural to SIFSIX-2-Cu, named as SIFSIX-2-Cu-i. The SIFSIX-2-Cu MOF was reported as a one-dimensional square channel-like MOF with a pore dimension of 13.05 Å. The interpenetrated polymorph SIFSIX-2-Cu-i, is composed of double interpenetrated nets. The independent nets are staggered with respect to one another, significantly reducing the dimension of the one-dimensional square pore channels to 5.15 Å.

Carbon-based materials possess a superior structural stability to a wide range of processing conditions, keeping them in the race for commercial applications. Therefore, the key factor towards the rational design of carbon-based materials for storage and separation of gases is the development of novel architectures of large surface areas and pores. Such an approach could combine the superior stability and light framework of carbon-based materials with a larger surface area and high porosity, which is a missing requirement of carbon nanotubes. The carbon-based nanoporous materials under study in the present treatment was the three-dimensional (3D) porous nanotube network (PNN), consisting of interconnected (8,8) single-walled carbon nanotubes forming a 3D orthogonal network., with pore channels of about 11 Å ^[2]. Given very recent results from Maurin and coworkers ^[6], who report high compatibility and high affinity at the interface of MOF/functionalized GO composite materials, the findings presented herein might be also promising for flexible electronics applications in gas separation and gas sensors, through composite MOF / Molecularly Pillared Graphene composite.

COMPUTATIONAL METHODS

In order to build up a force field for the investigated MOFs, to be used in atomistic molecular dynamics and Monte Carlo studies, the atomic charges obtained by quantum density functional theory (DFT) calculations were used in combination with existing sigma and epsilon 12-6 Lennard-Jones (LJ) parameters from the literature ^[1,4]. In particular, LJ parameters from the DREIDING and the UFF force fields were assigned to the atoms of the organic and inorganic building blocks of the MOF, respectively ^[1,4]. In the case of the PNN, the C-C parameters for the Lennard-Jones interactions corresponding to the carbon atoms of the network also adopted by previous studies in the literature^[2]. Well-established all-atom rigid potential models for CO₂, CH₄, N₂, SF₆ ^[1,2,4] and water ^[7] were also employed in our studies.

The supercells of the investigated nanoporous materials used in the simulations are presented in Figure 1.

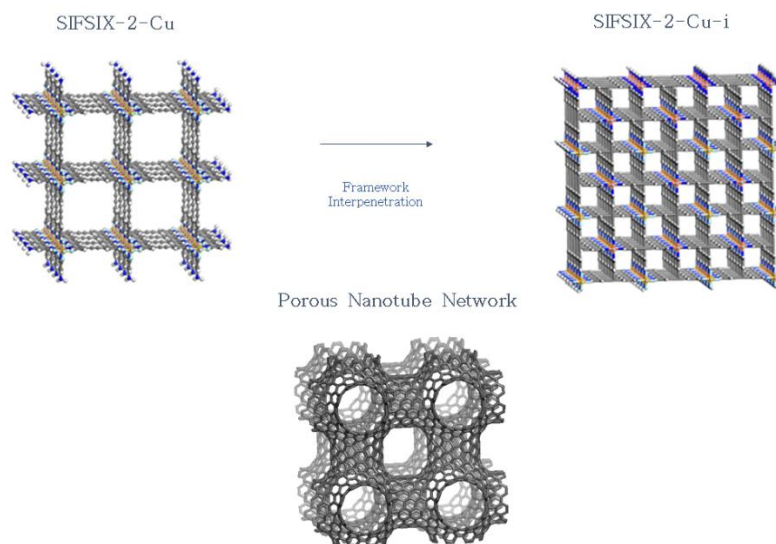


Figure 1. The structures of the employed supercells of the investigated nanomaterials, which were used in the Monte Carlo simulations in the present treatment.

Grand Canonical Monte Carlo (GCMC) simulations were then performed at 303 K and 1 bar in order to predict the binary mixture adsorption isotherms for equimolar CO_2 - CH_4 , CO_2 - N_2 and SF_6 - N_2 gas mixtures and for pure liquid ambient water at 298 K and 1 bar using the the Complex Adsorption and Diffusion Simulation Suite (CADSS) code [8]. The fugacities for each adsorbed species at the investigated thermodynamic conditions were calculated using the Peng-Robinson equation of state. For each simulated state point, 2×10^8 Monte Carlo steps were used for the equilibration and production runs, respectively. Several types of trial molecular moves were taken into account: translation or rotation, creation or deletion and exchange of molecular identity.

RESULTS AND DISCUSSION

The calculated uptakes of each constituent of the equimolar CO_2 - CH_4 and CO_2 - N_2 fluid mixtures in the SIFSIX-2-Cu-i material at 303 K and 1 bar are presented in Figure 2.

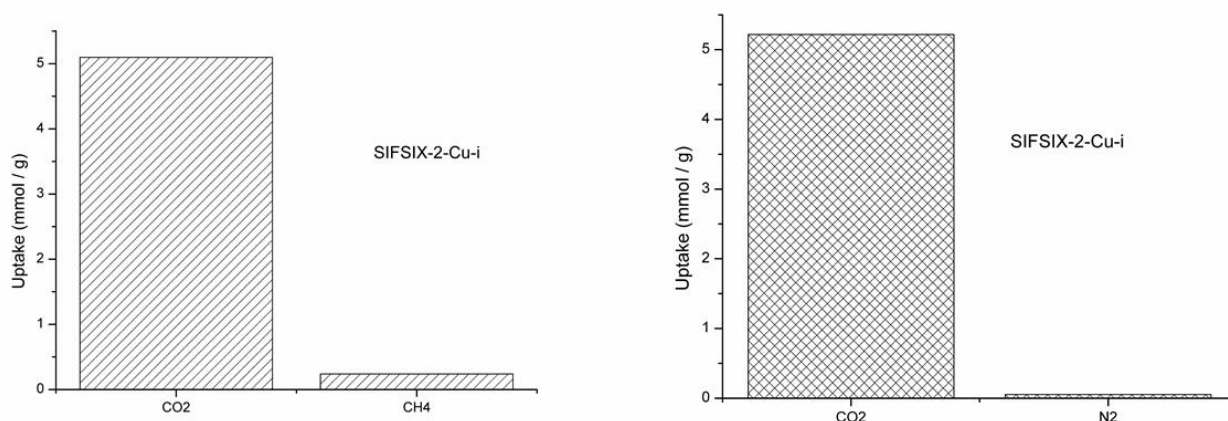


Figure 2. The calculated uptakes of CO_2 , CH_4 and N_2 for the SIFSIX-2-Cu-i material, corresponding to the equimolar CO_2 - CH_4 and CO_2 - N_2 bulk fluid mixtures at 303 K and 1 bar.

The calculated thermodynamic adsorption selectivity for the investigated CO₂-CH₄ and CO₂-N₂ equimolar mixtures in the case of the SIFSIX-2-Cu-i MOF has been estimated to be $S_{(CO_2/CH_4)} \approx 22$ ^[1] and $S_{(CO_2/N_2)} \approx 100$ at 303 K and 1 bar. The obtained values clearly indicate that the SIFSIX-2-Cu-i is very efficient for the separation of these fluid mixtures and the capture of CO₂, particularly in the case of the CO₂-N₂ ones.

The corresponding uptakes for the equimolar SF₆-N₂ mixtures are also presented in Figure 3.

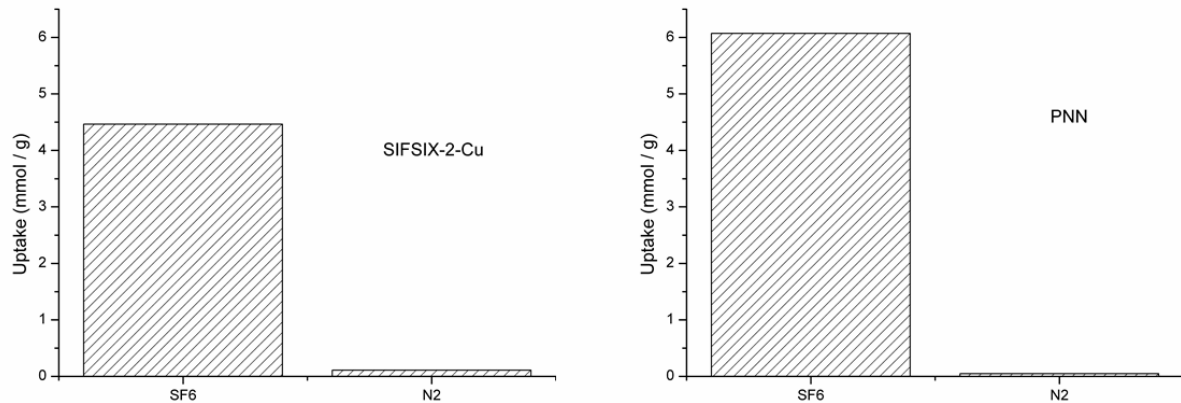


Figure 3. The calculated uptakes of SF₆ and N₂ for the SIFSIX-2-Cu and PNN materials, corresponding to the equimolar SF₆-N₂ bulk fluid mixture at 303 K and 1 bar.

The calculated thermodynamic adsorption selectivity for the investigated SF₆-N₂ equimolar mixtures at 303 K and 1 bar has been estimated to be $S_{(SF_6/N_2)} \approx 41$ ^[4] in the case of the SIFSIX-2-Cu MOF and $S_{(SF_6/N_2)} \approx 133$. The calculated uptakes and thermodynamic adsorption selectivity are amongst the highest reported so far in the literature, further confirming the efficiency of these materials for the separation of SF₆-N₂ fluid mixtures. It has also been found that the smaller pore dimensions of the SIFSIX-2-Cu-i interpenetrated network cause a molecular sieving effect, allowing only the adsorption of N₂. This finding clearly indicates that the control of the interpenetration in MOFs is an efficient way to tune their separation performances for strategic gas mixtures.

Finally, the capacity to adsorb water was investigated for the PNN carbon-based material. A typical snapshot of the Monte Carlo simulation, depicting the adsorbed water molecules in the nanopores of the PNN material is presented in Figure 4. The results obtained by the GCMC simulations revealed that the PNN material captures about 68% water by weight at 298 K and 1 bar, which is one of the highest values reported in the literature so far. Such a finding indicates that carbon-nanotube-based nanoporous networks could have potential applications in the adsorption-based water capture.

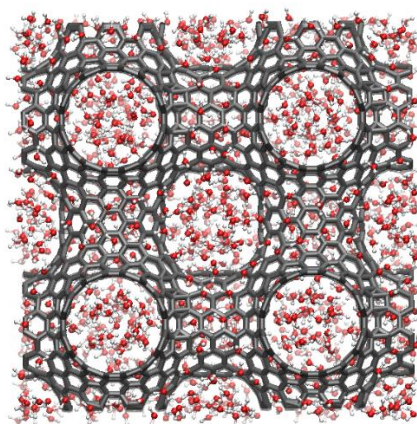


Figure 4. Typical snapshot depicting the structure of the adsorbed water molecules in the nanopores of the PNN material at 298 K and 1 bar.

CONCLUSIONS

A combination of quantum DFT calculations and classical, force field-based, Grand Canonical Monte Carlo (GCMC) simulations was employed in order to explore the separation and capture of CO₂ from natural and flue gases, the separation of fluid SF₆-N₂ mixtures and the capture of liquid water using several representative nanoporous materials. The results obtained have revealed the efficiency of the investigated metal-organic frameworks and carbon-nanotube porous networks for the above-mentioned applications. It was also revealed that the control of the interpenetration in MOFs is an efficient way to tune their separation performances for strategic gas mixtures, since it can cause molecular sieving effects. The present computational exploration paves the way towards the identification of adsorbents highly selective for these strategic fluid mixtures and liquid water.

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