

Design of new porous materials for natural gas storage

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Abstract – We propose a new IRMOF material that should be more efficient for natural gas storage than all the IRMOFs already synthesized. These results are based upon the adsorption isotherms of the methane gas within the pores of materials using the *Grand Canonical* Monte Carlo method.

The natural gas is mainly stored in pressure vessels at 204 atm, which demands an expensive multistage compression. An alternative that reduces the costs and risks of that process is to store the natural gas as an adsorbed phase within a solid porous material, because the interactions of the gas molecules with the material allows a compression at lower pressures. Zeolites are typical examples of solid porous materials used for this application. We propose in this work new porous materials with even higher capacity for natural gas storage called Isorecticular Metal-Organic Frameworks (IRMOFs)¹⁻⁴. The IRMOFs consists of an isorecticular framework with a cubic lattice with tetrahedral Zn₄O clusters at the cube vertices and organic dicarboxylate aromatic linkers between the vertices. Therefore, each Zn₄O is connected to six linkers with an octahedral symmetry. IRMOFs are very versatile materials, since the organic linkers can be easily modified and/or functionalized.

We performed *Grand Canonical* Monte Carlo simulations⁵ to calculate the adsorption isotherms of the methane within the IRMOF-6 (the most efficient synthesized IRMOF for natural gas storage), IRMOF-992 and IRMOF-993 (two new IRMOFs proposed in the literature⁵) and IRMOF-t and IRMOF-e (two new IRMOFs proposed in this work). We used the BIG_MAC⁵ program with the IRMOF structures kept rigid under periodic boundary conditions with the P³M method to treat the electrostatic long range interactions. The methane-methane and methane-IRMOF atoms interactions were represented by the Lennard-Jones potential with the OPLS force field. The OPLS parameters reproduced the adsorption isotherm of the IRMOF-6 properly, so no additional parameterization was performed. We performed the simulations at 298 K with 100 equilibration and 10000 acquisition MC cycles for each pressure, neglecting the interactions between pairs at distances larger than 1.25 nm for the IRMOF-6, IRMOF-992, IRMOF-993 and IRMOF-t and than 1.05 nm for the IRMOF-e.

The simulated adsorption isotherms suggests that the IRMOF-t proposed in this work is most efficient for natural gas storage than all the IRMOFs proposed or synthesized previously in the literature¹⁻⁵ and this porous material would probably also be highly efficient for the hydrogen storage. Therefore, we strongly recommend the synthesis of the IRMOF-t to corroborate these results, especially because the synthesis of IRMOFs is a procedure already well established. It is important to remark that we also investigated the importance of the conformational changes of the IRMOFs linkers in the adsorption isotherms.

Finally, this work exemplifies how the computational materials can guide the understanding of chemical processes related to the natural gas technology, saving time and effort of the experimental procedures.

References

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