

Computer Simulation of the Natural Gas Adsorption on New Metal-Organic Frameworks (MOFs) Porous Materials

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Abstract – We proposed new metal-organic frameworks (MOFs) porous materials that could be more efficient for natural gas storage than most porous materials available. These results are based upon the adsorption isotherms of the methane gas and hydrocarbon gas mixtures within the pores of these materials obtained by *Grand Canonical Monte Carlo* (GCMC) method.

The recently developed new class of nano- and meso-porous materials based upon metal-organic frameworks (MOFs), that keep their porosity and crystalline structure, has caused significant changes in the field of gas storage, gas separation, catalysis and chemistry in confined spaces. The design of new materials is needed to eliminate some problems in the storage of natural gas, such as high pressure (over 182 atm), which entails high costs and risks. Adsorption/desorption of natural gas on porous solid material can reduce or eliminate this problem. Due to their high surface area, crystalline structure and versatility (easiness to perform changes in the organic linkers), metal-organic frameworks (MOFs) and their isorecticular (IRMOFs) class are potential materials for gas storage applications. Indeed, MOFs and IRMOFs can have an almost endless variety of structures and functional groups, leading to the possibility of rational design of sorbent materials tailored for the specific applications. IRMOFs have Zn_4O cluster building units (inorganic or metal part) at the corners of a cubic structure, which are connected by ditopic organic linkers such as (substituted) benzene-1,4-dicarboxylate, naphthalene-2,6-dicarboxylate, biphenyl-4,4'-dicarboxylate, 1,5a¹-dihydropyrene-2,7-dicarboxylate, triphenyl-4,4'-dicarboxylate, etc.

We performed *Grand Canonical Monte Carlo* (GCMC) computer simulations to obtain the absolute adsorption isotherms of the methane within the IRMOF-1 (used as reference), IRMOF-6 (which is regarded as a safe and cost-effective pressure limit), IRMOF-992 and IRMOF-993 (proposed in the literature) and the new IRMOF-tetrazine and IRMOF-C≡C. The MuSic program was used, with the MOF structures kept rigid and the methane molecules considered as single pseudo-atoms (united atoms approximation) described by a Lennard-Jones potential. The intermolecular interactions were described by the UFF force field and periodic boundary conditions were employed to avoid surface effects.

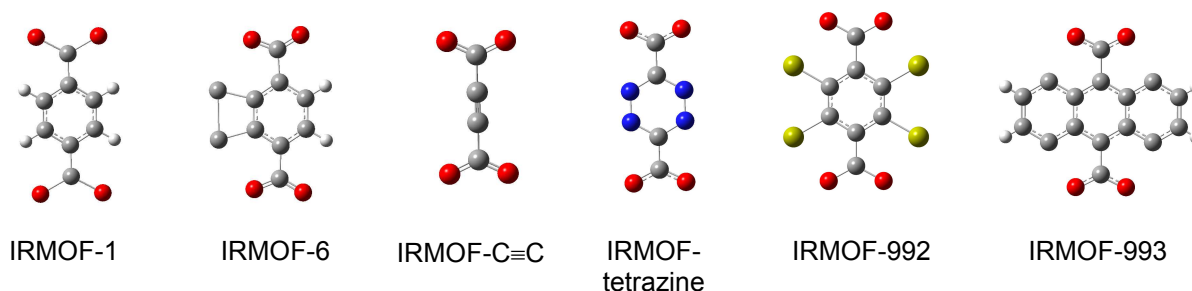


Figure 1: Some linkers of IRMOFs. Notation: red atoms are oxygen, gray atoms are carbon, blue atoms are nitrogen, green atoms are bromide and white atoms are hydrogen.

The simulated absolute adsorption isotherms are in disagreement with the experimental isotherms, since the latter are excess quantities. We are testing two approaches to determine the excess adsorption isotherms from the GCMC simulations. A better agreement with the experimental data is obtained; however, there appears to be necessary to modify the interaction potentials in order to obtain quantitative predictions. It should be noted that one of the approaches needs the state equation for the adsorbate (gas) and, thus it is inadequate to treat adsorption gas mixtures. Also, IRMOF-992 and IRMOF-993 have bulky ortho substituents and thus have perpendicular conformation of the benzene ring with respect to the carboxylate groups. This conformation leads to a significant decrease of the adsorption, and thus the results available in the literature need to be revised.