A Chemometric Study of Methane Adsorption in Model MOFs

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Abstract – Metal-organic frameworks (MOFs) are potential materials for adsorption, gas separation and catalysis. One class of these materials, namely, isoreticular MOFs (IRMOFs) has an inorganic Zn_4O cluster at the corners of a cubic structure coordinated to dipotic organic linkers. The interactions between the IRMOF and methane molecules were described by the Lennard-Jones potential, which depends upon two parameters: σ (average particle size) and ε (depth of the potential well). These parameters are determinant for the adsorption isotherm and since which interaction site has two parameters a chemometric analysis is needed. We performed a factorial design experiment yielding a total of 68 simulations. The analysis showed that the σ parameters are the most important variable indicating that there is a strong dependence with the attractive potential. Then we propose one material MOF-T2 that is constituted with the same inorganic part than MOF-T1 but we modify the linker which should produce a better material for methane adsorption.

Alternative energy sources are becoming very important for the world energy matrix mainly due to environmental concerns. Natural gas, which is a mixture of many volatile hydrocarbons with methane as the major component (~90%) is an interesting option because of its lower environmental impact. However, the process for obtaining, transporting and distributing liquid natural gas to be used as fuel has a high cost, which hinders its use [1]. In order to minimize these costs, the use of efficient adsorvents can drastically reduce the pressure storage and increase safety issues. As a result, many research groups are actively searching for new, more efficient and low cost adsorvents. For this purpose, computational methods can be quite useful for screening potential adsorvents from a large set of systems, leading to combinatorial computational materials. However, the adsorption isotherms obtained from computer simulation methods, such as Grand-Canonical Monte Carlo (GCMC), are very dependent upon the interaction potential used. So, for screening, design and quantitative work it is necessary to have appropriate interaction potentials. To our knowledge, the effects of the interaction potential parameters on the adsorption isotherms have not been elucidated. Thus, the main goal of this work is to provide qualitative and quantitative relationships between the interaction potential parameters and the adsorption isotherms, so that new or improved potentials can be developed.

We have chosen a new IRMOF-T1 based upon the 1,2,4,5-tetrazine-3,6-dicarboxylate proposed in a previous work performed in our laboratory [2], since it has the largest calculated adsorbed amount (181 cm^3 $(CH_4)/cm^3$). The adsorption isotherms were calculated with the GCMC method implemented in the Big_Mac program. The interactions between the IRMOF-T1 model and the methane molecules were described by the Lennard-Jones potential, which depends upon two parameters: σ (average particle size) and ε (depth of the potential well). The IRMOF-T1 has four types of atoms: Zn, O, N and C; and the methane molecules are described by the united atoms approach, that is, they are described by only one set of $\{\sigma, \varepsilon\}$ parameters. We have used standard UFF and OPLS parameters for these atoms, and for the fractional factorial design $2^{(8-2)}$ we changed the values of these parameters in ±20%. A total of 68 experiments (GCMC simulations) were performed, with four of them used to yield the degrees of freedom for the error [3].

The factorial analysis showed that the zinc parameters do not have any significant effects on the adsorption isotherm. Indeed, the most influential are the σ parameters of C, N, O and CH_4, with the oxygen being the most important one. In this way we notice that the choice of a force field is very important for a good description of the system. Based on these results we proposed another IRMOF-T2 where the linkers are 1,2,4,5-tetrazine-3,6-biscarbodithiolate, that is, the oxygen atoms in the carboxylate groups are replaced by sulfur, since it has a larger σ value and has a larger methane adsorption than the IRMOF-T1.
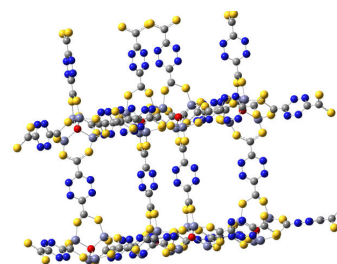

Figure 1. Structure of the new IRMOF-T2 (yellow = S, blue = N, red = O).

References
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