

## Adsorption and Catalysis within Porous Materials: A Computational Approach

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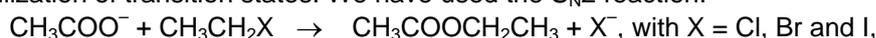
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**Abstract** – We proposed new metal-organic frameworks (MOFs) porous materials for natural gas storage, for organocatalysis and for adsorption of organosulfur compounds in fuels. These proposed materials are based upon molecular modeling with quantum chemical combined with molecular mechanics methods and upon computer simulation Monte Carlo 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. Due to their high surface area, crystalline structure and versatility (easiness to perform changes in the organic linkers), metal-organic frameworks (MOFs) and their isoreticular (IRMOFs) class are potential materials for gas storage applications, for adsorption of organosulfur contaminants in fuels and as catalysts for organic reactions. Indeed, MOFs and IRMOFs can have an almost endless variety of structures and functional groups, leading to the possibility of rational design of 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.

As organocatalyst we have proposed the IRMOF-OH, which has the linker 2,5-bis(hydroxymethyl) terephthalate. This linker contains two groups  $-CH_2OH$  per benzene ring and can perform organocatalysis by hydrogen bond stabilization of transition states. We have used the  $S_N2$  reaction:



as a model to establish the catalytic performance and to tune the substituents in the benzene ring to improve catalysis. Preliminary results with AM1 method showed that for  $X = Cl$  the reaction within the IRMOF-OH cavity has an activation energy ( $\sim 100 \text{ kJ mol}^{-1}$ ) significantly lower than the reaction in gas phase ( $\sim 140 \text{ kJ mol}^{-1}$ ). The reaction energy profile is illustrated in Figure 1.

The adsorption isotherms obtained from computer simulation methods, such as Grand-Canonical Monte Carlo (GCMC), are very dependent upon the interaction potential used. For adsorption of methane in IRMOFs this potential is usually described by a Lennard-Jones type function with two parameters:  $\sigma$  (average particle size) and  $\varepsilon$  (depth of the potential well) for each interaction site. We have used the IRMOF-T1 based upon the 1,2,4,5-tetrazine-3,6-dicarboxylate proposed in a previous work performed in our laboratory as a model to perform a chemometric analysis using a fractional factorial design  $2^{(8-2)}$  for the parameters ( $\pm 20\%$ ).

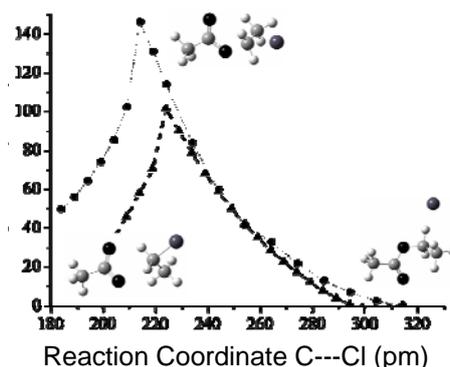
A total of 68 experiments (GCMC simulations) were performed and we found that the zinc parameters do not have any significant effects on the adsorption isotherm. Indeed, the most influential are the  $\sigma$  parameters of C, N, O and  $CH_4$ , with the oxygen being the most important one.

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  $\sigma$  value and has a larger methane adsorption than the IRMOF-T1. This new IRMOF-T2 is quite promising for adsorption of natural gas.

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

For adsorption of organosulfur compounds we proposed a new ionic MOF that has exchangeable cation to improve performance.

These and other results shall be shown in greater details in the presentation.



**Figure 1.** Relative energy ( $\text{kJ mol}^{-1}$ ) for the reaction coordinate C---Cl. Circles correspond to the reaction in gas phase and triangles to the reaction within IRMOF-OH.

