On the nature of the interaction between H_2 and Metal-Organic Frameworks.

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Introduction

The onboard hydrogen storage for mobile applications has been a challenging subject over the past years. An alternative would be to store hydrogen in low-weight solids. H_2 may be stored in solids by two principal mechanisms: chemisorption of hydrogen atoms (e.g. metal hydrides, aminoboranes, etc.), and physisorption of hydrogen molecules in nanoporous, e.g. carbon-based, materials. As H_2 is a neutral molecule with a small polarizability, the two main contributions to the adsorption energy are weak London (dispersion) interactions and electrostatic interactions with multipoles at H_2 induced by the polarity of the host system. The dispersion interaction depends on the polarizability of H_2 and of the host material, and on the distance between them. Good storage media should have high polarizability and a large surface area with a pore size of ~0.6 nm.[1] The class of light, highly porous carbon materials belongs to this group, and hydrogen storage capacities have already been discussed for graphitic (sp^2) carbon structures and more advanced materials. Among the family of highly porous materials, metal-organic frameworks (MOFs, see Figure 1), have recently been proposed as one of the most promising materials with these properties.

The aim of this work is to contribute to a better understanding of the fundamental interactions of H_2 with MOFs on the basis of high-level quantum chemical calculations. A major problem to be solved is to attribute the nature of H_2-MOF interactions to London dispersion and to electrostatic interactions. We have chosen the most widely investigated IRMOF-1 as a benchmark system.

Results and Discussion

Our calculations show that the physisorption of H_2 in MOFs is mainly due to the weak London interaction between linkers and connectors with hydrogen. The small charge separation in the MOF can not induce significant dipole and quadrupole moments in H_2 and thus, electrostatic interactions play a minor role.

We pointed out that the correct treatment of correlation effects and application of BSSE (Basis Sets Superposition Error) corrections are essential for the correct estimation of H_2-MOF interaction potentials. For our connector and linker models we find similar interaction energies with molecular hydrogen. The strength of interaction is in qualitative agreement between experiment[2] and our findings: the strongest interaction is found for site α, with the sequence $\alpha > \beta > \delta >> \varepsilon$. The most favorable orientation of hydrogen is the perpendicular orientation to the benzene ring or to the central Zn-O bond for the linker and the connector, respectively. However, H_2 rotates nearly freely and therefore appears as a physisorbed sphere rather than a linear molecule, and mean interaction energy cannot be compared only with the most stable orientation of hydrogen molecule but has to be averaged over all orientations.

In solid MOFs the always attractive long-range interaction potentials of the nanopores will overlap and superpose to considerable values, hence a stronger interaction with H_2 is expected. The nanoporosity of MOFs can be tuned in order to maximize the interaction with H_2.

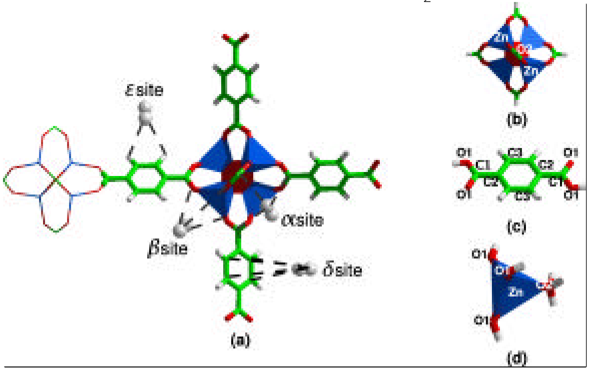

Figure 1 The considered adsorption sites within the IRMOF-1 unit call (a) and the used model systems: (b) the connector, $Zn_4O(HCO_2)_6$, (c) the linker, $C_6H_4(COOH)_2$ and (d) the alternative connector model, ZnO_4H_6. The atom numbering is shown, as well.

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