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Hydrogen storage in zeolite imidazolate frameworks. A multiscale theoretical investigation

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ABSTRACT

A multiscale approach is used to investigate the hydrogen adsorption in nanoporous Zeolite Imidazolate Frameworks (ZIFs) on varying geometries and organic linkers. Ab initio calculations are performed at the MP2 level to obtain correct interaction energies between hydrogen molecules and the ZIF structures. Subsequently, classical grand canonical Monte-Carlo (GCMC) simulations are carried out to obtain the hydrogen uptake of ZIFs at different thermodynamic conditions of pressure and temperature.

1. Introduction

In the perspective of a rapid exhaustion of hydrocarbon resources, hydrogen has been indicated as sustainable 'clean' fuel, optimally suited for transportation applications. Besides sourcing, storage remains one of the principal limiting factor for an economy based on hydrogen. Porous materials are capable of storing practical amounts of hydrogen [1–9]. However, no material yet fully meets the recommendations of the U.S. Department of Energy for reversible hydrogen storage under near ambient conditions. Recently, zeolitic imidazolate frameworks (ZIFs) have appeared as a novel class of materials [10]. Their crystal structure is based on aluminosilicate zeolite nets, whereby the tetrahedral Si(Al) sites are replaced by transition metals M (M = Zn(II), Co(II), In(III)) tetrahedrally coordinated by imidazolate ligands (Fig. 1). Like metal-organic framework (MOF) materials, ZIFs exhibit high porosity and chemical functionality with the advantages of exceptional chemical stability and large structural diversity [11]. The

combination of these features makes ZIFs promising candidates for hydrogen storage applications.

ZIF-8 (SOD topology) and ZIF-11 (RHO topology) contain only one cage type, and result from organic linkers 2-methylimidazolate (mIM) and benzimidazolate (bIM) [10] (for the description of topology symbols, see Database of Zeolite Structures, http://www.iza-structure.org/databases/). The more involved LTA topology of ZIF-20, which has two cage types, can be obtained by linker functionalization [12]. Yaghi *et al.* synthesized ZIF-95, with an unprecedented topology (denoted by poz) [13]. ZIF-95 features a tetragonal, neutral framework made of 128 Zn nodes tetrahedrally coordinated by chlorobenzimidazolate (cbIM). It has two types of cages (A and B) with remarkably large pore sizes of 25.1 × 14.3 Å and 30.1 × 20.0 Å, respectively.

Unlike MOFs, only few experimental studies concerning hydrogen storage in ZIFs have been reported so far [10,12,14,15]. Yildirim *et al.* measured the adsorption isotherm of ZIF-8 over a wide range of pressures and temperatures.
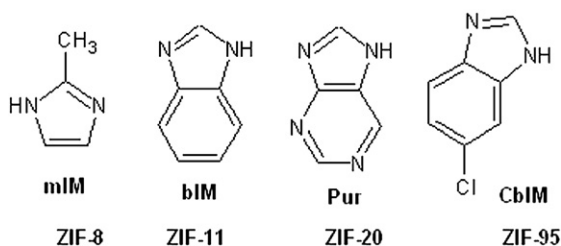

Fig. 1 – Imidazole-type linkers in ZIFs.

At low temperatures the maximum of H_2 adsorption capacity amounts to 4.4 wt% [15].

In coordination with experiments, some theoretical studies of H_2 adsorption on ZIFs have been reported. Wang *et al.* [16] used the refined OPLS-AA (Optimized Potentials for Liquid Simulations-All Atoms) force field model in grand canonical Monte Carlo (GCMC) simulations to investigate the adsorption sites using computer tomography (mCT) techniques. A combination of the Dreiding [17] and the all-atom OPLS (OPLS-AA) [18] force fields was adopted to describe the atomic interactions in the ZIF-8 framework. Fröba *et al.* [19]

approached the adsorption of hydrogen in ZIF-8 with the Universal Force Field (UFF).

Recently, Han et al. [20] reported H_2 uptakes of 10 different ZIFs, based on GCMC simulations. The GCMC results show a good agreement with an experimental data set of ZIF-8. Therein, the force fields used to describe the interactions between H_2 and ZIF were based on ab initio calculations. However, the interaction terms between H_2 and Nitrogen in different imidazolate rings were developed from the interaction between H_2 and $C_3N_3H_3$, which is different from imidazolate rings.

The large numbers of GCMC moves requires a prompt calculation of intermolecular forces, made possible by versatile force field parameters. Although general potentials can describe the adsorption effects rather well, sometimes they may lead to unpredictable results for certain materials. On the other hand, tuning force field parameters for a particular compound may impair property prediction upon transferring these parameters to different systems.

To provide a fundamental understanding of adsorption mechanisms in ZIFs and to achieve a more accurate prediction of H_2 storage capacity we have constructed a force field from first-principles. This force field is employed to study H_2
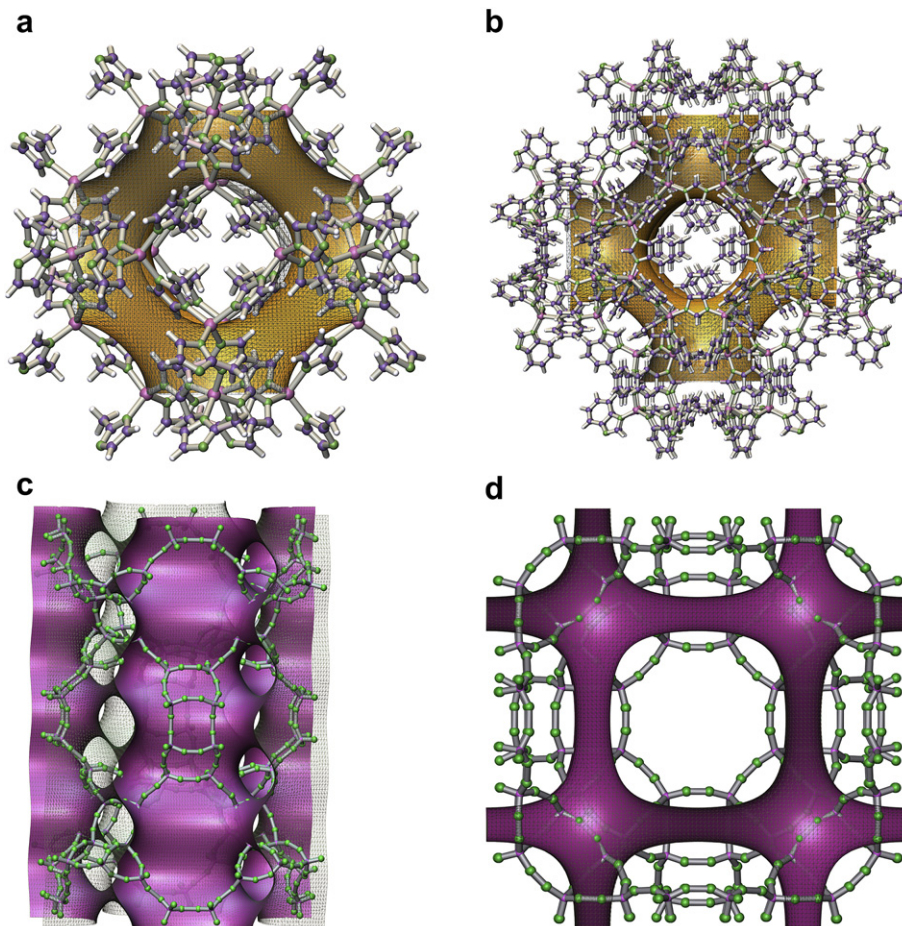

Fig. 2 – Crystal structures of the ZIFs considered in the study: a) ZIF-8, b) ZIF-11 (same topology for ZIF-20) and c) ZIF-95 side and d) top view. The topology of the framework is made explicitly by a minimal surface. Zinc, Carbon, Nitrogen and Hydrogen atoms are shown in pink, blue, green, and white, respectively. For ZIF-95 (c,d) only the Zn-N framework is shown, for clarity. Figure a) and b) are adapted from Ref. [27]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)