Zeolitic imidazolate frameworks for separation of binary mixtures of CO_2, CH_4, N_2 and H_2: A computer simulation investigation

Anna Battisti [a,b], Simone Taioli [a,b], Giovanni Garberoglio [a,*]

[a] Interdisciplinary Laboratory for Computational Science (LISC), FBK-CMM and University of Trento, via Sommarive 18, I-38123 Povo (TN), Italy
[b] Department of Physics, University of Trento, via Sommarive 14, I-38123 Povo (TN), Italy

ARTICLE INFO

ABSTRACT

We studied adsorption and dynamics of CO_2, CH_4, N_2, H_2 and binary mixtures thereof in the zeolitic imidazolate frameworks ZIF-2 to ZIF-10, using computer simulations.

The results of grand canonical Monte Carlo calculations showed that the amount of gas adsorbed in these materials is smaller than what can be stored in other organic frameworks, due to the small-pore structure of these crystals.

The results of molecular dynamics simulations showed that three of these materials (ZIF-5, ZIF-7 and ZIF-9) fulfill the condition for molecular sieving separation of H_2, whose diffusion is orders of magnitude faster than that of other species.

Analysis of the adsorption and permeance selectivity for the other materials, in which all the species considered have comparable self-diffusion coefficients, points out ZIF-4 as the best performing material for a large variety of gas separations.

Our results indicate the importance of complementing Monte Carlo data with molecular dynamics simulations in assessing the performance of small-pore organic frameworks for gas adsorption and separation. In particular, the explicit modeling of framework flexibility is crucial to obtain reliable gas-diffusion properties of small-pore frameworks.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Metal-organic frameworks (MOF) are a new class of crystalline compounds, whose microscopic structure is characterized by metal-oxide centers (acting as joints) connected by organic linkers (acting as struts). Since their synthesis by Li and collaborators [1], MOFs received a considerable attention for their promising applications to gas adsorption, storage, and separation.

In fact, the properties of MOFs can be tuned by varying the composition of the metal center as well as the type of organic linker, as shown in Ref. [2]. Many MOFs have been tested for their capacity of storing methane and hydrogen showing a very good performance [3,4].

Further improvements in the gas storage capacity were obtained by the discovery of covalent organic frameworks (COF) [5,6]: in these materials boron was used to replace the metal cluster, obtaining light rigid structures still with tailorable porosity. Among the materials of this series, COF-108 is the crystalline material with the lowest density known to date. Hydrogen and methane storage capacity of COFs, both from a volumetric or a gravimetric

point of view, is actually among the highest known for nanoporous materials [7].

Very recently a new class of nanoporous materials has been synthesized and characterized [8,9]. Zeolitic imidazolate frameworks (ZIF) have a pore size topology resembling that of zeolites, and offer a larger variability, obtained by replacing the linker with various kind of organic moieties. ZIFs demonstrated a considerable affinity to carbon dioxide, and have being considered as viable substrates for CO_2 removal from gas flows [10].

Organic frameworks are currently the subject of many experimental and theoretical investigations to assess their ability to store gases and separate components from a given mixture. We refer to the recent and comprehensive reviews in Refs. [11,12] where the current state-of-the-art in these two applications is summarized.

Since an enormous number of MOF, COF and ZIF structures can be designed, the availability of reliable molecular models able to describe the interaction of gases with these organic frameworks are of paramount importance, for two main reasons.

On the one hand, a detailed atomistic description of gas interaction with these materials could suggest the optimal characteristics for any specific application, be it gas storage or gas separation. On the other hand, well validated models can be of use both in the screening of synthesized materials to select the most promising

* Corresponding author. Tel.: +39 0461 314667; fax: +39 0461 314501.
E-mail address: garberoglio@fbk.eu (G. Garberoglio).

for a particular task, and to focus experimental effort into a valid direction for material testing.

Usually, the development of such numerical models starts from general force fields, which are tested and adapted to the particular materials under consideration by comparing their results with actual experimental data. Subsequently, these refined force fields can be safely used to obtain insight into material properties relevant to select those worthy of further investigation.

In this paper we apply this theoretical framework to calculate gas adsorption and dynamics in ZIF-2 to ZIF-10, which are described in Ref. [8]. We focus on the capacity of these compounds to perform gas adsorption and separation, analyzing, in particular, the CO_2/H_2, CO_2/CH_4, CO_2/N_2 and CH_4/H_2 mixtures. We use a potential model that correctly reproduces the adsorption isotherms of CH_4, CO_2 and N_2 in ZIF-8, even if the experimental data are not completely consistent in this latter case.

There are two main processes that are exploited to perform gas separations using microporous materials: the first depends on the ability of a given compound to selectively adsorb one species with respect to another. The second mechanism is related to the difference in the diffusion coefficients of the mixture components within the material. Given the microscopic structure of ZIFs, which present nanoscopic cages connected by relatively small openings, both of the mechanisms outlined above can be expected to be present, and therefore we analyze both of these processes.

In the first case, we use grand canonical Monte Carlo (GCMC) simulations to calculate adsorption isotherms, adsorption selectivities and generate molecular configurations. These configurations are in turn used as starting points for molecular dynamics (MD) simulation, from which the diffusion coefficients of the gases in ZIFs are calculated. Given the smallness of the openings connecting the adsorption cages, we adopt a fully flexible model to describe the dynamics of the adsorbent.

Our results will be used to single out the most promising ZIFs for the gas separations discussed above.

2. Computer modeling

2.1. The materials studied

In this paper we will investigate CO_2, CH_4, N_2 and H_2 adsorption in materials of the ZIF family, namely the series from ZIF-2 to ZIF-10. These materials are formed by metal centers (cobalt, zinc or indium), connected by imidazole-based linkers. Their structure is generally formed by cages of size from 2 to 12 Å (evaluated as the diameter of the largest sphere that will fit into the framework, see Ref. [8]), connected by openings with geometrical size between 3 and 4 Å. These openings have dimensions comparable with the kinetic diameters of the species that we are going to study: CO_2 (3.3 Å), CH_4 (3.8 Å), N_2 (3.6 Å) and H_2 (2.9 Å). One can therefore expect to reach a regime of molecular sieving for the materials with the smallest pores, which are ZIF-5, ZIF-7 and ZIF-9.

We report in Table 1 some relevant characteristics of the unit cell for the materials studied, and we refer the reader to the original paper for further details on their atomistic structure [8].

2.1.1. Fluid–fluid potentials

A reliable computer model for gas adsorption in microporous materials is based on a realistic description of both gas–gas and gas–adsorbent interaction. In the first case it is customary to describe the interaction using Lennard–Jones centers suitably placed on the various atoms. When the intermolecular interactions are characterized by considerable electrostatic interactions, point charges are generally used in order to reproduce the correct moments of the charge distribution. For the gases studied in the pres-

Table 1
Main characteristics of the unit cell of the materials studied in this work. ZIF-4 and ZIF-5 do not correspond to any known zeolite. The free volume is defined in Eq. (2).

Material	Zeolite	Volume (Å^3)	Free volume (Å^3) (%)	Density (g cm^{-3})
ZIF-2	BCT	5707	2809 (49.2)	0.929
ZIF-3	DFT	6024	3482 (57.8)	0.880
ZIF-4	–	4342	1581 (36.4)	1.22
ZIF-5	–	10590	1962 (18.5)	1.57
ZIF-6	GIS	6940	4353 (62.7)	0.764
ZIF-7	SOD	7214	2075 (28.8)	1.24
ZIF-8	SOD	4905	2124 (43.3)	0.924
ZIF-9	SOD	7179	1057 (14.7)	1.22
ZIF-10	MER	14211	9239 (65.0)	0.746

ent work, this happens only for CO_2, where the first non-zero moment is the quadrupole. In this case, three point charges are placed on the atomic sites to reproduce its value.

In this work we will describe H_2 and CH_4 as single Lennard–Jones centers, using the parameters validated by Buch [13] and Goodbody [14], respectively. The N_2 molecule will be described with a two-site Lennard–Jones model, using the potential parameters described in Ref. [15]. Carbon dioxide will be modeled as a rigid linear molecule using the EPM2 potential [16]. All of these potentials have been shown to reproduce very accurately the pure-fluid phase diagrams of the corresponding gases.

2.1.2. Fluid–adsorbent interaction

Various force fields are available in the literature to model the dispersive part of the gas-adsorbent interactions. Among these, the DREIDING [17], UFF [18] and OPLS [19] potentials have been successfully used to model adsorption in a wide range of organic frameworks, such as MOFs [20,21], COFs [22,23] and ZIFs [24–29].

Although these force fields usually give a reasonable description of the gas–adsorbent interaction, they are usually augmented with framework charges in order to adapt them to a particular adsorbate. This procedure is particularly important when CO_2 is considered, due to the strong quadrupolar moment of this molecule, especially when the microscopic structure of the adsorbent is characterized by the presence of moieties with a non-negligible charge distribution (e.g. those made by highly electronegative atoms, such as oxygen or chlorine). The way of choosing these charges has been longly debated.

In fact, Liu and collaborators investigated CO_2 adsorption in ZIF-68 and ZIF-69 using framework charges calculated *ab initio* together with a non-standard CO_2–CO_2 potential [25], obtaining a good agreement with the experimental data reported in Ref. [30]. This approach has been criticized by Rankin and collaborators [26], who demonstrated that the CO_2–CO_2 potential developed by Liu et al. is not able to properly describe the phase diagram of pure carbon dioxide. On the other hand, they find that the DREIDING potential with no additional framework charges is able to reproduce fairly well the available experimental data.

In the case of the ZIFs studied in this work, we will use the potential developed in Ref. [31], where it was found that a simple rescaling of the UFF potential parameters ($\varepsilon = 0.69 \ \varepsilon_{UFF}$ and $\sigma = 0.95 \ \sigma_{UFF}$) is able to reproduce satisfactorily the experimental adsorption isotherms of CH_4 and CO_2 in ZIF-8. No additional framework charges where required, due to the absence of strongly electronegative atoms in the structure of ZIF-8.

In a series of preliminary calculations, we verified that this force field is able to reproduce in a satisfactory way both the experimental isotherms reported in Ref. [31], but also a series of independent adsorption measurement reported by other authors. In particular, we have been able to reproduce the H_2 isotherms reported by Zhou et al. [32] (see Fig. 4 below), the amount of gases adsorbed in ZIF-8 at $p = 30$ bar reported by Nune et al. [33] (CO_2: 7.9 mmol g^{-1}, N_2