Using Molecular Dynamics simulations for elucidation of molecular traffic in ordered crystalline microporous materials

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ABSTRACT

Robust models to describe mixture diffusion in ordered crystalline microporous materials such as zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) are essential for the development of separation and reaction technologies. The development of appropriate models requires insights into a wide variety of factors that influence the mobilities of guest molecules in the microporous hosts. Such factors include: molecular size, shape, and configuration, degree of confinement, pore topology and connectivity, strength of adsorption on pore walls, molar loadings of guest constituents, and correlations in the molecular jumps between partner molecules. Experimental data, on their own, do not provide sufficient information to set up the requisite models to describe mixture diffusion. The primary objective of this article is to demonstrate the potency of Molecular Dynamics (MD) simulations to offer insights that assist in the interpretation of experimental observations and development of descriptive models. Computational snapshots and video animations are used to provide a visual appreciation of phenomena such as traffic junction, slowing-down, and hindering effects in diffusion.

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1. Introduction

Ordered crystalline microporous materials such as zeolites (crystalline alumino-silicates), metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and zeolitic imidazolate frameworks (ZIFs) offer the potential for use as adsorbents or catalysts in several separation and reaction technologies, that are of interest in the process industries [1–10]. Such materials can also be employed as thin layers, with thickness of the order of the order of a few tens of micrometers, in membrane devices [11,12].

For reaction and separation process design and development, it is necessary to have reliable models to describe diffusion of mixtures of guest molecules inside the microporous materials. The proper description of diffusion is important for the following reasons.

- In many membrane separations, the permeation selectivity is significantly influenced by the relative mobilities of the adsorbed species within the pores. Indeed, in H_2-selective membrane processes, the separation relies on the fact that H_2 is more mobile than partner species such as CO_2, or CH_4 [13–15].
- The separation performance of microporous adsorbents in fixed bed devices may be influenced by intra-crystalline diffusion limitations; such diffusion influences result in transient breakthroughs that possess distended characteristics and diminished separation capabilities [3,16,17].
- In some cases of pressure swing adsorption, the separation principle is based on diffusion selectivities; this is the case for example for separation of N_2/O_2 mixtures with LTA-4A zeolite [3,17].
- In catalytic processes, intra-crystalline diffusional effects affect both reaction rates and selectivities. Often, diffusional effects are undesirable because catalyst effectiveness is reduced [5,18,19].

A number of different channel topologies and connectivities are encountered in zeolites, MOFs, COFs, and ZIFs. For the purposes of describing the diffusion characteristics, these can be divided into five broad classes.
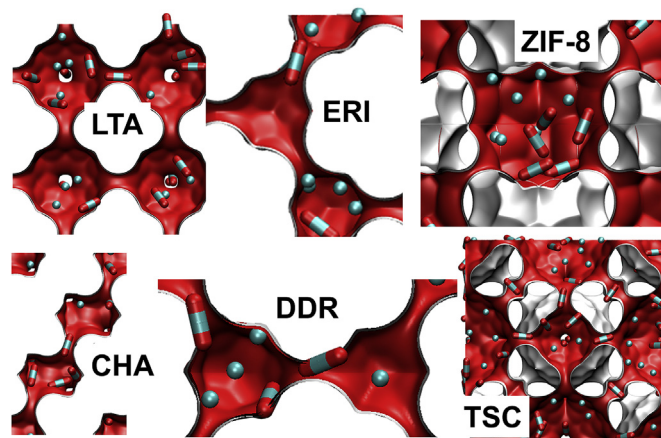
- One-dimensional (1D) channels: e.g. AFI, LTL, TON, CoFormate [20], MIL-47 [21], MIL-53(Cr) [22,23], Co(BDP) [24]; see Fig. 1.
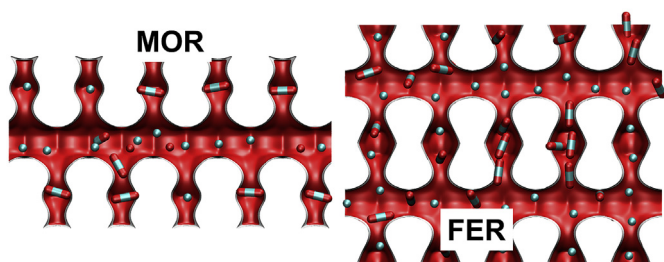- 1D channels with side pockets: e.g. MOR, FER; see Fig. 2.

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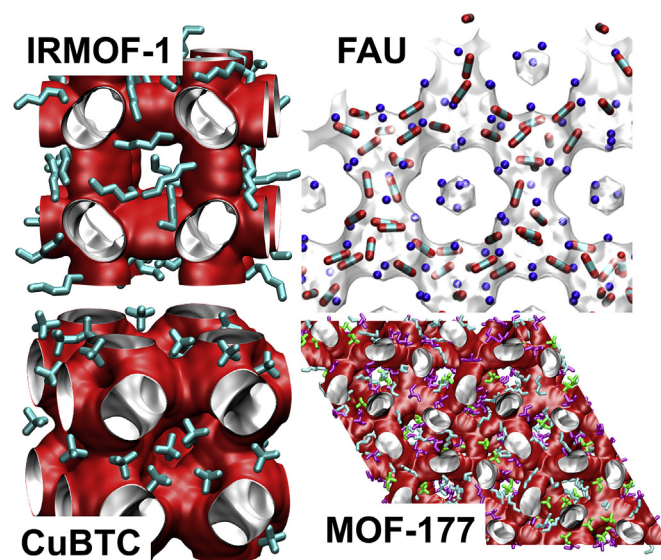*E-mail address:* r.krishna@contact.uva.nl (R. Krishna).
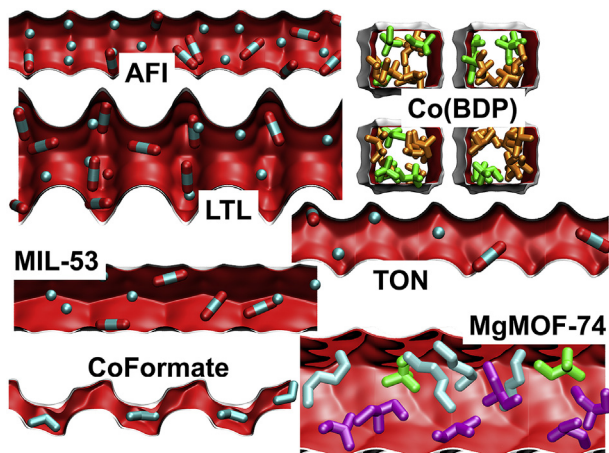
Fig. 1. Examples of one-dimensional (1D) channel structures: AFI, LTL, TON, MgMOF-74, MIL-53(Cr), and Co(BDP). We use iso-potential energy surfaces as representation of porous structures; we refer the reader to Keffer et al. [109] for an explanation of how these surfaces are to be interpreted.

Fig. 2. Examples of 1D channel structures with side pockets: MOR and FER.

- Intersecting channels: e.g. MFI, BEA, ISV, Zn(bdc)dabco [25], Co(bdc)dabco [26]; see Fig. 3.
- Cages separated by narrow windows: e.g. AFX, LTA, CHA, DDR, TSC, ERI, ITQ-29, ZIF-8; see Fig. 4.
- Cavities with large windows: e.g. NaX, NaY, IRMOF-1 [27], CuBTC [28], MOF-177; see Fig. 5.

Fig. 3. Examples of structures consisting of intersecting channels: MFI, ISV, BEA, and Co(bdc)dabco, and Zn(bdc)dabco.

Fig. 4. Structures consisting of cages separated by narrow windows: LTA, CHA, DDR, ERI, TSC, and ZIF-8.

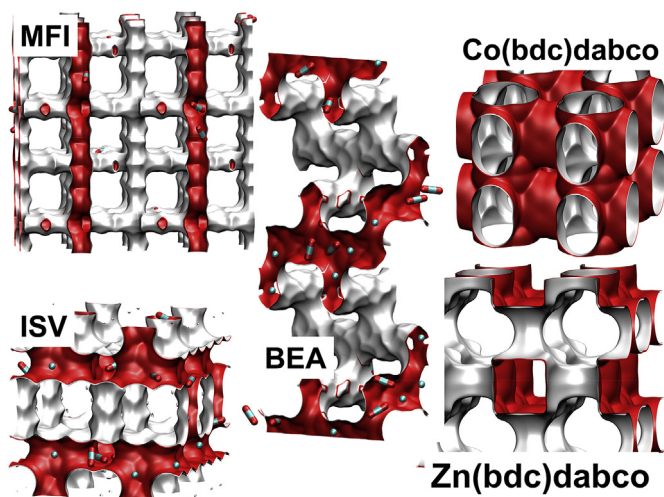**Fig. 5.** "Open" structures that consist of cages separated by large windows: IRMOF-1, MOF-177, CuBTC, and FAU.

For zeolites, the crystallographic data are available on the zeolite atlas website of the International Zeolite Association (IZA) [29]. Further details on the structure, landscape, pore dimensions of a very wide variety of micro-porous materials are available in the published literature [16,30–36]. Generally speaking, the frameworks are not rigid. The zeolite framework flexibility is illustrated by animations of LTA-4A (see Video 1, uploaded as Supplementary Material), and LTA-5A (see Video 2). The consequences of framework flexibility for transport across 8-ring windows of LTA, CHA, DDR, and ERI have been investigated using molecular dynamics (MD) simulations [37–42]. Many MOFs possess soft "dynamic" frameworks whose cell dimensions change in a reversible manner to external stimuli [23,43–45]. Lattice flexibility of IRMOF-1 (see Video 3), that has large size cavities, has been found to increase the diffusivity by about 20%–50% [46]. It may be expected that lattice flexibility will have a greater influence when the molecule is more tightly constrained within a MOF framework. For ethane diffusion at high loadings in the 0.45 nm 1D channels of Zn(tbip), MD simulations have also shown that accounting for framework flexibility leads to diffusivity values that are about one order of magnitude