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Unexpected Molecular Sieving Properties of Zeolitic Imidazolate Framework-8

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Ⓢ Supporting Information

ABSTRACT: We studied molecular sieving properties of zeolitic imidazolate framework-8 (ZIF-8) by estimating the thermodynamically corrected diffusivities of probe molecules at 35 °C. From helium (2.6 Å) to iso-C_4H_{10} (5.0 Å), the corrected diffusivity drops 14 orders of magnitude. Our results further suggest that the effective aperture size of ZIF-8 for molecular sieving is in the range of 4.0 to 4.2 Å, which is significantly larger than the XRD-derived value (3.4 Å) and between the well-known aperture size of zeolite 4A (3.8 Å) and 5A (4.3 Å). Interestingly, because of aperture flexibility, the studied C_4 hydrocarbon molecules that are larger than this effective aperture size still adsorb in the micropores of ZIF-8 with kinetic selectivities for iso-C_4H_8/iso-C_4H_{10} of 180 and n-C_4H_{10}/iso-C_4H_{10} of 2.5×10^6. These unexpected molecular sieving properties open up new opportunities for ZIF materials for separations that cannot be economically achieved by traditional microporous adsorbents such as synthetic zeolites.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis
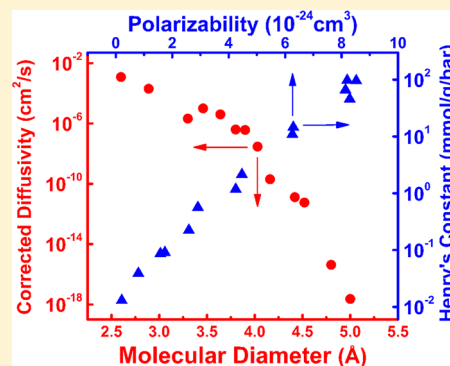
S ince Union Carbide marketed the ISOSIV process in the late 1950s, microporous crystalline zeolitic molecular sieves comprising SiO_4 tetrahedrons have reshaped the refinery and petrochemical industries as selective adsorbents and catalysts thanks to their favorable adsorption and molecular sieving properties. More recently, zeolitic imidazolate frameworks (ZIFs), a subcategory of metal−organic frameworks (MOFs) with zeolite or zeolite-like topologies,[1,2] have emerged as a new class of microporous materials that are promising for gas/vapor separations and heterogeneous catalysis.[3−27] Unlike the small pore aluminosilicate zeolite A with well-defined aperture size at which sharp molecular sieving takes place, the molecular sieving mechanism and properties of ZIFs remain unclear.[3−16] ZIF-8 (Zn(MeIM)$_2$, MeIM = 2-methylimidazole) with sodalite (SOD) topology has been among the most extensively studied ZIF materials. The β-cage aperture of ZIF-8 has been determined to be 3.4 Å by single-crystal XRD.[1] However, unlike zeolite A with relatively rigid frameworks and apertures, there is increasing evidence that the aperture of ZIF-8 is rather flexible at room temperature, and there exists no sharp molecular sieving "cut-off" at 3.4 Å,[4−7] presumably due to rotation of the MeIM ligand upon pressure or introduction of guest molecules.[26] Therefore, to demonstrate conclusively the flexibility of the ZIF-8 framework and determine the effective aperture size of its β-cage, we have conducted a systematic study of gas/vapor diffusion and adsorption properties. The experimental determination of the effective aperture size of ZIF-8 will facilitate not only the understanding of the molecular sieving behavior and framework flexibility of ZIFs, but also the

development of selective membrane materials and adsorbents for more efficient separations.

Here we demonstrate the unexpected molecular sieving properties of ZIF-8 by estimating the thermodynamically corrected diffusivities of He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_2H_5OH, C_3H_8, 1-C_4H_8, n-C_4H_{10}, iso-C_4H_8, and iso-C_4H_{10} in ZIF-8 at 35 °C. The transport diffusivities of C_3−C_4 hydrocarbons and C_2H_5OH were obtained by fitting the kinetic uptake curves in synthesized ZIF-8 nano- and microcrystals (Figure 1) with transient diffusion models. The transport diffusivities of He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 in ZIF-8 were obtained using a hybrid permeation model with permeation data of ZIF-8/6FDA-DAM mixed matrix membranes and adsorption isotherms.

The ability to manipulate crystal size enabled the possibility of using classical kinetic uptake methods to study intracrystalline diffusion phenomena in ZIF-8. As demonstrated in the following sections, transport diffusivities of C_3 and C_4 hydrocarbons differ by 10 orders of magnitude in ZIF-8, and hence it was impractical to reliably and conveniently measure diffusivities of all studied adsorbates in a ZIF-8 sample with a particular crystal size.

ZIF-8 samples with average crystal radii of 26 nm, 7.9 μm, and 162 μm were synthesized for kinetic uptake rate measurements, in which uptake of iso-C_4H_8/iso-C_4H_{10}, 1-C_4H_8/n-
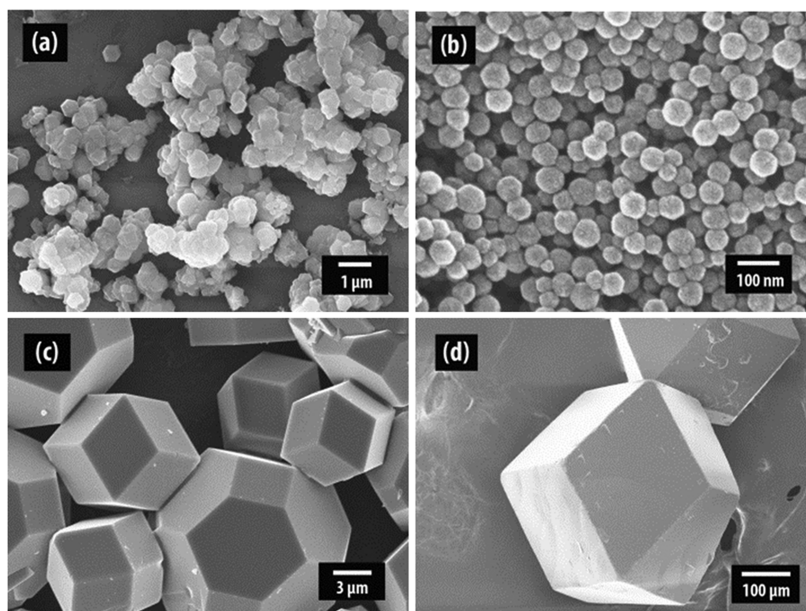
Figure 1. SEM images of ZIF-8 crystals used for mixed matrix membrane fabrication (a) ~200 nm (radius) BASF ZIF-8 sample and kinetic uptake rate measurements (b) 26 nm (radius) synthesized ZIF-8 crystals, (c) 7.9 μm (radius) synthesized ZIF-8 crystals, and (d) 162 μm (radius) synthesized ZIF-8 crystals. See the Supporting Information for crystal size distributions.

C_4H_{10}, and $C_3H_6/C_3H_8/C_2H_5OH$, respectively, was sufficiently slow to permit reliable estimates of intracrystalline diffusivity at 35 °C. Scanning electron microscope (SEM) micrographs of the synthesized nano- and microcrystals are illustrated in Figure 1 and reveal (truncated) rhombic dodecahedron-shaped microcrystals. The nanocrystals have a spherical shape. Detailed synthesis procedures, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), crystal size analysis, as well as N_2 physisorption results can be found in the Supporting Information.

The kinetic uptake curves (Figure 2) of C_3 and C_4 hydrocarbons exhibited classic internally limited Fickian responses for transient diffusion in spherical particles. Transport diffusivities were calculated by fitting the kinetic response in the short time region with eq S13, and the loading-dependent nature of transport diffusivity was accounted for (see the Supporting Information). To complement the diffusion analysis, we show adsorption isotherms of the studied gases and vapors in ZIF-8 in Figure S5 of the Supporting Information. The logarithm of Henry's constants generally increases linearly with polarizability of adsorbate molecules (Figure 3), revealing that the interaction potentials of adsorbate molecules and the nonpolar ZIF-8 surface were dominated by nonelectrostatic energies.[28] The C_4 hydrocarbons adsorb very strongly in ZIF-8.

However, the uptake of He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, and C_2H_6 in the ZIF-8 sample with the largest crystal size (162 μm) at 35 °C was still too fast to permit reliable diffusivity estimates. Instead of pursuing the synthesis of ZIF-8 samples with even larger crystal sizes (which are of less practical importance), we used mixed matrix membrane permeation as an alternative to obtain the transport diffusivities of these faster diffusing gases in ZIF-8.

Mixed matrix membranes, which are formed by dispersing highly selective molecular sieve particles within a polymer matrix, offer promising approaches for gas separations that combine the ease of processing polymeric membranes with the superior separation performance of molecular sieving materi-
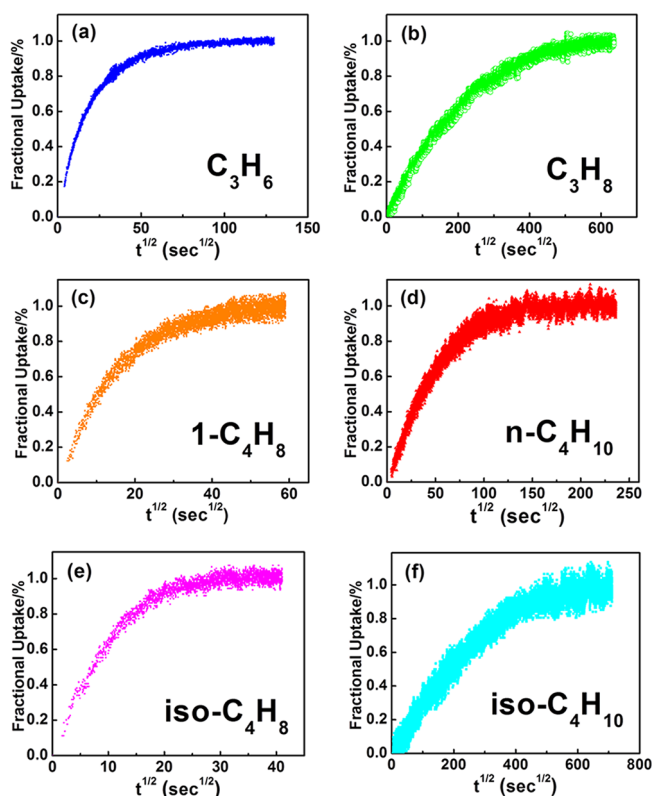

Figure 2. Kinetic uptake curves in ZIF-8 at 35 °C (a) Kinetic uptake curve of C_3H_6 in the 162 μm sample. (b) Kinetic uptake curve of C_3H_8 in the 162 μm sample. (c) Kinetic uptake curve of 1-C_4H_8 in the 7.9 μm sample. (d) Kinetic uptake curve of n-C_4H_{10} in the 7.9 μm sample. (e) Kinetic uptake curve of iso-C_4H_8 in the 26 nm sample. (f) Kinetic uptake curve of iso-C_4H_{10} in the 26 nm sample.

als.[29] In our previous work,[3] we showed that C_3H_6/C_3H_8 permselectivity was significantly enhanced with the addition of ZIF-8 particles into the tailored polyimide 6FDA-DAM[30]

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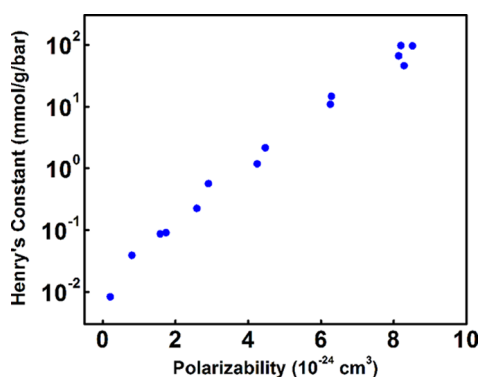dx.doi.org/10.1021/jz300855a | J. Phys. Chem. Lett. 2012, 3, 2130–2134

Figure 3. Henry's constants in ZIF-8 (35 °C) versus adsorbate polarizability.

polymer dense film. Here we report the He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, and C_2H_6 permeation data of ZIF-8/6FDA-DAM mixed matrix membranes. Permeabilities in ZIF-8 were calculated using Maxwell's model (eq S17 of the Supporting Information) for electrical conductivity of particulate composites,[31] which is appropriate due to the close analogy between thermal/electrical conduction and gas permeation[32] and is valid for low filler loadings and for spherical particles. Using the solution-diffusion model for permeation in conjunction with the adsorption isotherms, the corrected diffusivities were obtained (see the Supporting Information).

The corrected diffusivities of probe molecules in ZIF-8 are plotted in Figure 4 and tabulated in Table S3 and S6 of the
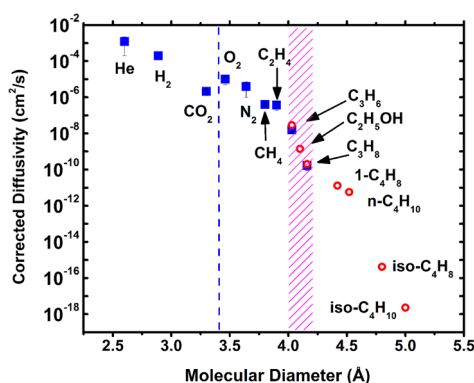

Figure 4. Corrected diffusivities in ZIF-8 at 35 °C versus molecular diameter of probe molecules. (Solid blue squares: diffusivities estimated from mixed matrix membrane permeation. Hollow red circles: diffusivities calculated from kinetic uptake rate measurements. Blue line: XRD derived aperture size of ZIF-8.[1] Magenta region: effective aperture size range of ZIF-8.).

Supporting Information. The C_3H_6 and C_3H_8 diffusivities obtained from *kinetic* uptake rate measurements (2.9×10^{-8} and 2.0×10^{-10} cm^2/s) match well with the values estimated from *steady state* measurements ($1.6 \pm 0.3 \times 10^{-8}$ and $1.7 \pm 0.8 \times 10^{-10}$ cm^2/s, using mixed matrix membrane permeabilities and adsorption isotherms). There have been several recent papers reporting transport and self-diffusivities of CO_2, CH_4, C_2H_4, and C_2H_6 in ZIF-8 determined using the IR-microscopy and PFG-NMR techniques.[10,11,33] Their results are in general agreement with those presented in Figure 4 (see the Supporting Information).

As demonstrated in Figure 4, the molecular sieving properties of ZIF-8 are unexpected compared with the well-

studied small pore aluminosilicate zeolite A. The α-cage aperture size of zeolite 5A determined by crystallographic analysis (4.2 Å) matches satisfactorily with its effective aperture size (4.3 to 4.4 Å) estimated by complete exclusion of CF_2Cl_2 (4.4 Å) and larger probe molecules.[34] For ZIF-8, however, a similar sharp "cut-off" phenomenon does not exist, so we have defined the effective aperture size to be in the range where the slope of "corrected diffusivity vs molecular diameter" curve (Figure 4) starts to drop (4.0 to 4.2 Å). This size range is considerably larger than the XRD derived value (3.4 Å).[1] In addition, whereas the α-cage aperture of zeolite A dilates with temperature, it is rather rigid at room temperature, as evidenced by complete exclusion of C_3H_8 and *iso*-C_4H_{10} by 4A and 5A, respectively.[28,34,35] The β-cage aperture of ZIF-8 appears to be somewhat flexible at the studied temperature (35 °C). All studied C_4 hydrocarbon molecules that are considerably larger than the effective aperture size range diffuse into the micropores of ZIF-8 with remarkably high adsorption capacities, albeit slowly.

For molecules with diameters no larger than the effective aperture size (i.e., He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, and C_2H_6), micropore diffusion is not significantly constrained by steric hindrance, and the microporous ZIF-8 is not particularly size/shape-selective, as linear CO_2 (3.3 Å) diffuses only approximately five times as fast as the larger, spherical CH_4 (3.8 Å), although the "rigid" pore aperture assumption would predict a dramatic diffusion selectivity between these two molecules. Nonetheless, as the molecular diameters are within or become larger than the effective aperture size range of the freely mobile ZIF-8 (i.e., C_3H_6, C_2H_5OH, C_3H_8, 1-C_4H_8, n-C_4H_{10}, *iso*-C_4H_8, and *iso*-C_4H_{10}), the diffusivity drops remarkably by 10 orders of magnitude over molecular diameter difference of merely 1.0 Å (from C_3H_6 to *iso*-C_4H_{10}), and thus molecular sieving is truly realized.

We hypothesize that the aperture of ZIF-8 does not show unlimited flexibility at a fixed temperature, so there should exist a limiting aperture size above that sufficiently large molecules are totally excluded. The identification of such a limiting aperture size was not pursued in this work, which requires knowledge of adsorption properties of even larger probe molecules than *iso*-C_4H_{10} (e.g., dibranched paraffins and aromatics). Even if they diffuse into micropores of ZIF-8, conveniently measuring adsorption of these larger molecules is expected to be challenging at ambient temperatures even in the smallest ZIF-8 nanocrystals known to date[36] (~9 nm in radius) due to extremely slow diffusion rates, as predicted by Figure 4. A recent paper[5] reported significant uptake of *para*-xylene by ZIF-8 at an elevated temperature (100 °C). Although the large *para*-xylene molecules might be unable to diffuse into micropores of ZIF-8 at 35 °C, the combination of aperture flexibility and dilation at the high temperature may explain the uptake noted by Peralta et al. Even the aperture of more rigid zeolite A dilates at elevated temperatures to admit molecules that are unable to adsorb at lower temperatures.[28,34]

These unexpected and interesting molecular sieving properties shown in this study enable the application of ZIF-8 in gas/vapor separations that cannot be economically achieved by zeolites. The potential of using ZIF-8 as selective adsorbents and membranes for separation of C_3 and C_4 hydrocarbon mixtures was evaluated based on the above membrane permeation and adsorption results. (See the Supporting Information.) As adsorbents based on kinetic selectivity, ZIF-8 will be attractive for separation of n-C_4H_{10}/*iso*-C_4H_{10} isomers,

in which the slower and less adsorbed *iso*-C_4H_{10} can be efficiently enriched in the raffinate due to large differences in diffusion rates. However, unlike cationic zeolites and a recently developed large pore MOF Fe_2(dobdc),[37] paraffins adsorb slightly stronger than corresponding olefins in ZIF-8 and the equilibrium selectivity of paraffin/olefin pairs in ZIF-8 is quite limited ($\alpha < 2$).

Our analysis shows that efficient separation of hydrocarbon mixtures could be realized by membranes fabricated using ZIF-8. As shown by Figure 5 and Table S10 of the Supporting
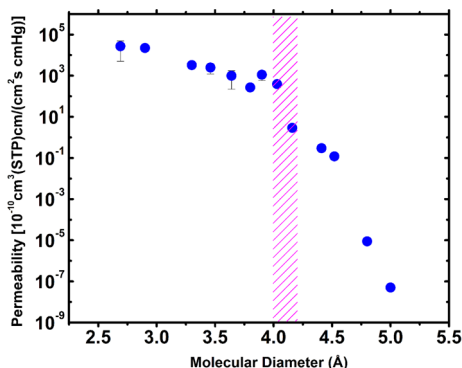

Figure 5. Estimated pure component permeabilities in a pure ZIF-8 membrane operated at 35 °C and 2 bar upstream pressure. (Dashed magenta region: effective aperture size range of ZIF-8.)

Information, the ideal permselectivities of C_3H_6/C_3H_8 (130), *iso*-C_4H_8/*iso*-C_4H_{10} (180), and *n*-C_4H_{10}/*iso*-C_4H_{10} (2.4×10^6) suggest that it is promising to create highly pure product streams using a pure ZIF-8 membrane. With C_3H_6 diffusivity that is two to four orders of magnitude higher,[38,39] ZIF-8 is obviously the preferred membrane material for separation of C_3H_6/C_3H_8 mixtures over small pore (~3.8 Å) eight-ring zeolites (4A, AlPO-14, SAPO-34, SiCHA, and DD3R) in terms of overall process economics. Already, ZIF-8 has been shown to be quite promising to enrich C_3H_6 from mixtures of C_3H_6/C_3H_8, in the form of both dispersed particles in mixed matrix membranes as well as pure membranes.[3,8]

To conclude, our study suggests that the effective aperture size of ZIF-8 for molecular sieving is in the range of 4.0 to 4.2 Å, which is significantly larger than the XRD-derived value (3.4 Å) and between the well-known aperture size of aluminosilicate zeolite 4A (3.8 Å) and 5A (4.3 Å). Interestingly, due to aperture flexibility, the studied C_4 hydrocarbon molecules considerably larger than the effective aperture size range are still able to diffuse into the micropores of ZIF-8, albeit slowly. Because slower diffusing adsorbates often show higher adsorption coefficients, the decrease in permeability with increasing molecular diameter is less dramatic than that for corrected diffusivity. From He (2.6 Å) to *iso*-C_4H_{10} (5.0 Å), the corrected diffusivity drops by 14 orders of magnitude, whereas the permeability decreases by 11 orders of magnitude. In addition to their structural and chemical diversities, the unexpected and interesting molecular sieving properties revealed in this study indicate that ZIF materials are potentially attractive alternatives to traditional synthetic zeolites as permselective membranes as well as kinetically selective adsorbents for separations of gas/vapor mixtures.

ASSOCIATED CONTENT

S **Supporting Information**

Details of synthesis and characterization of ZIF-8 crystals (adsorption isotherms, SEM, PXRD, TGA, crystal size analysis, N_2 physisorption), kinetic uptake rate measurements, membrane permeation results, and calculation of diffusivities. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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