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Adsorption and diffusion of alkanes in CuBTC crystals investigated using infra-red microscopy and molecular simulations

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A B S T R A C T

The adsorption and intra-crystalline diffusion of *n*-butane (nC4), iso-butane (iC4), 2-methylbutane (2MB), and 2,2-dimethylpropane (neoP) in CuBTC ($Cu_3(BTC)_2$ where BTC = benzene-1,3,5-tricarboxylate) has been investigated using infrared microscopy (IRM), combined with molecular simulations. Both experiments and simulations show strong inflection characteristics in the adsorption isotherms. The primary cause of the inflection is due to the strong preference for adsorption within, and in the regions close to the mouths of tetrahedral pockets. The isotherm inflection has a significant influence on the dependence of the Maxwell–Stefan diffusivity, $Đ_i$, on the fractional occupancy, $Đ_i$. Both IRM experiments and simulations show that the $Đ_i$–θ_i behavior appears to be influenced by the loading dependence of the inverse thermodynamic factor $1/\Gamma_i = \mathrm{d}\ln\theta_i/\mathrm{d}\ln p_i$. For nC4 and iC4, the $Đ_i$ increase sharply by about one order of magnitude as the occupancy θ_i increases from 0 to about 0.2. This increase is caused by the fact that the diffusion characteristics undergo a transition from being dominated by hops across narrow 4.6 Å windows at low loadings to hops across large 9 Å windows for loadings higher than 8 molecules per unit cell. For loadings higher than 8 molecules per unit cell the $Đ_i$–θ_i dependence of nC4 and iC4 is dictated by $1/\Gamma_i$, characteristic of more open channel structures such as FAU zeolite. For 2MB and neoP, the IRM experiments show evidence of phase transition and except for the region in which this occurs the $Đ_i$ follows the occupancy dependence of $1/\Gamma_i$ for the entire range of loadings.

1. Introduction

In recent years there has been a remarkable upsurge in research activity on metal-organic frameworks (MOFs), in view of several potential applications in storage, separations, and catalysis [1–4]. A wide variety of MOFs have been synthesized, and investigated. The potential of MOFs for separations of variety of mixtures such as CO_2/N_2, CO_2/CH_4, CO_2/CO, CO_2/C_2H_4, C_2H_6/C_2H_4, and hydrocarbons have been investigated both experimentally [5–13] and by use of molecular simulations [14–20].

In the development of separation technologies using MOFs, data are required on both adsorption and diffusion of guest molecules. Both experimental and molecular simulation studies have shown the adsorption characteristics of a variety of guest-MOF host combinations to be rather complex and often exhibiting inflection characteristics in the isotherm, caused due to the existence of different adsorption sites of significantly varying strengths [21–27]. For zeolites, inflection in the isotherm is known to have a significant influence on the dependence of the Maxwell–Stefan (M–S) diffusivity, $Đ_i$ on the fractional occupancy, θ_i [28–30]. The only published experimental studies on diffusion in MOFs, that we are aware of are due to Stallmach et al. [31] who investigated the temperature dependence of self-diffusivities of alkanes in IRMOF-1 using PFG NMR, and Kortunov et al. [32] who used interference microscopy to study diffusion of methanol in manganese formate. Molecular dynamics (MD) simulation results have been published on the $Đ_i$–θ_i relation for small molecules such as Ar, CH_4, CO_2, N_2, Ar, Ne and H_2 [26,33,34]. In none of these MD simulations, inflection in $Đ_i$–θ_i dependence has been reported.

The current work focuses on one important MOF, i.e. CuBTC ($Cu_3(BTC)_2$ with BTC = benzene-1,3,5-tricarboxylate), whose synthesis was first reported by Chui et al. [35]. Our major objective is to gain insights into the adsorption and diffusion of a variety of linear and branched alkanes in CuBTC, with a view to examining the potential of this material in alkane separations. We aim to demonstrate the strong influence of isotherm inflection on the θ_i-dependence of the M–S diffusivity $Đ_i$. Our study uses a combination of molecular

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Nomenclature

D_i	Fick, or transport, diffusivity, $m^2\ s^{-1}$
Đ_{ii}	self-exchange coefficient, $m^2\ s^{-1}$
Đ_i	Maxwell–Stefan diffusivity of species *i*, $m^2\ s^{-1}$
$\text{Đ}_i(0)$	zero-loading M–S diffusivity of species *i*, $m^2\ s^{-1}$
f_i	fugacity of species *i*, Pa
ΔH_{st}	isosteric heat of adsorption, $J\ mol^{-1}$
n_i	number of molecules of species *i* in simulation box, dimensionless
p_i	pressure, Pa
q_i	loading of species *i*, molecules per unit cell
$q_{i,sat}$	saturation loading of species *i*, molecules per unit cell
r	position vector, m
R	gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
t	time, s
T	absolute temperature, K
x	spatial distance, m

Greek letters

Γ_i	thermodynamic correction factor, dimensionless
θ_i	fractional occupancy, $\theta_i = q_i/q_{i,sat}$, dimensionless
ν_i	power in Sips isotherm, dimensionless
μ_i	molar chemical potential, $J\ mol^{-1}$
ρ	framework density, $kg\ m^{-3}$

Subscripts

sat	referring to saturation conditions
i	referring to component *i*

simulations (Configurational-Bias Monte Carlo (CBMC) for adsorption, and MD for diffusion), and Infra-red Microscopy (IRM) [36,37]. Details of the crystal synthesis, IRM experimental set-up, experimental technique, molecular simulation methodology,

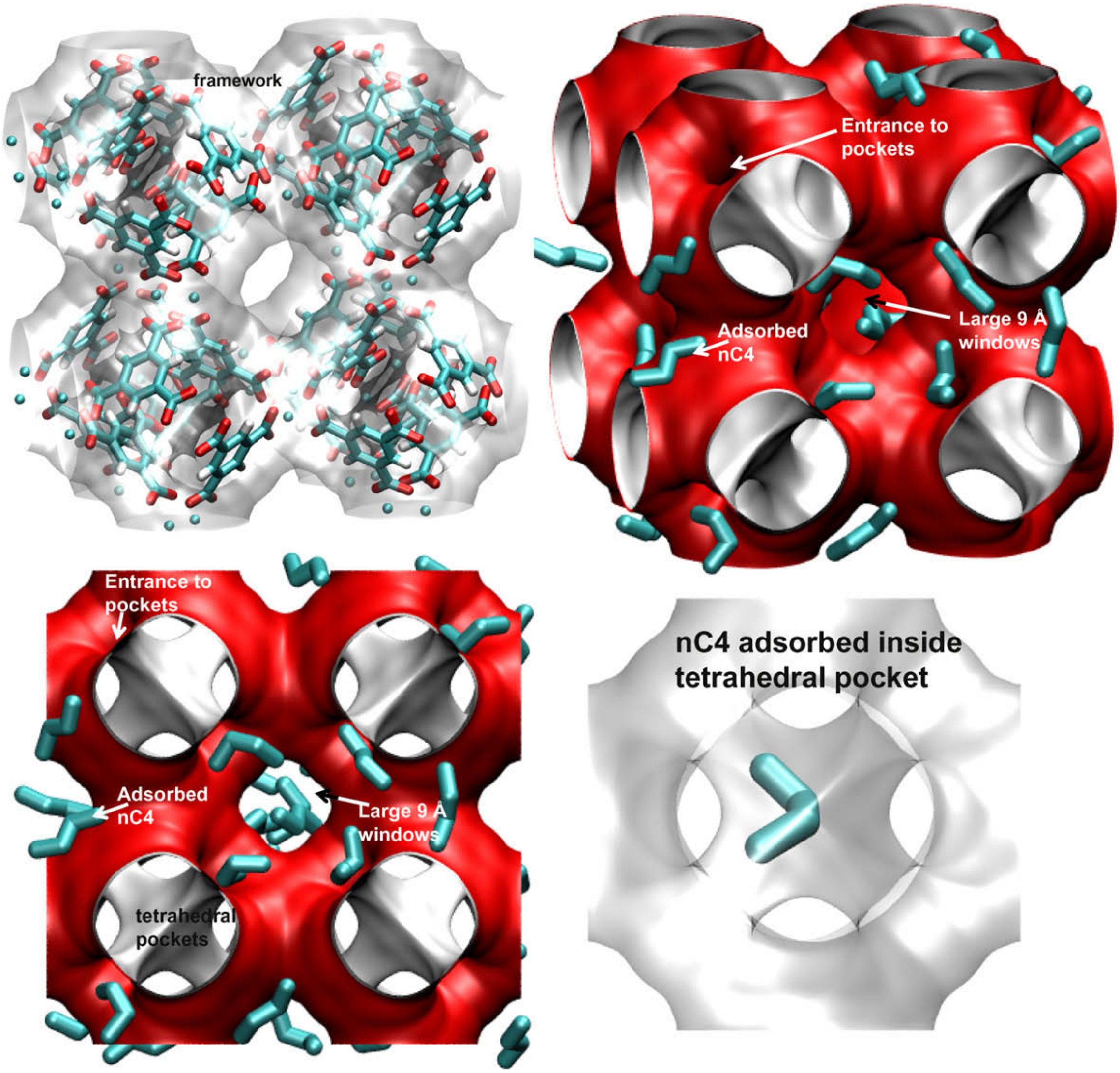

Fig. 1. The framework structure and different views of the pore landscape of CuBTC. The red areas are accessible to guest molecules in the large cage, such as nC4 pictured here. Also shown is one nC4 molecule adsorbed within a tetrahedral pocket.