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Adsorption of pentane isomers on metal-organic frameworks Cu-BTC and Fe-BTC

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ABSTRACT

Adsorption isotherms of *n*-pentane, isopentane and cyclopentane on Cu-BTC and Fe-BTC metal-organic frameworks, measured in a temperature range from 273 to 333 K, have been examined. For correlations, adsorption of nitrogen at 77 K and argon at 87 K has been studied as well. The analysis of adsorption isotherms was based on the calculation of differential distributions of the amount adsorbed with respect to the adsorption potential. It appears that the filling of Cu-BTC micropores with nitrogen occurs in two steps due to specific interaction of nitrogen molecules with open metal sites. In contrast to nitrogen, the filling of Cu-BTC micropores with argon takes place in one step. The micropores of Fe-BTC are filled with nitrogen and argon gradually in two featureless stages indicating the unordered porous structure. Adsorption isotherms of *n*-pentane, isopentane and cyclopentane display especially at 273 and 293 K a rectangular course with a long vertical part. This shape of C5 hydrocarbon isotherms on Cu-BTC is consistent with the shape of argon isotherms since the interactions with saturated hydrocarbons are nonspecific and thus the pores of Cu-BTC are filled in one step. The isotherms of C5 hydrocarbons on Fe-BTC show one saturation step being less sharp than in the case of Cu-BTC. Calculated isosteric adsorption heats suggest that the energy of lateral interactions between adsorbed molecules dominates the gas–solid energy heterogeneity. This domination is especially pronounced for cyclopentane adsorbed on Cu-BTC. In the case of Fe-BTC, almost constant isosteric adsorption heats show that the variations of the gas–solid interaction energy are compensated by the energy of lateral interactions.

1. Introduction

Metal-organic frameworks (MOFs) are novel materials constructed from multi-dentate organic ligands and metal atoms or small metal-containing clusters. Most of the MOF materials have 3D structures incorporating uniform pores and a network of channels possessing extremely large surface area and pore volume [1]. The number of potential MOFs is virtually unlimited as variations in ligands, secondary building blocks, or the linkers will produce novel MOFs with distinct properties. Large variety of available MOFs exhibiting high surface areas, flexible frameworks, or sometimes unsaturated metal species makes these porous materials highly attractive for investigations of their adsorption and catalytic properties [2].

Among various MOFs, Cu-BTC [$Cu_3(BTC)_2(H_2O)_3$, BTC = benzene-1,3,5-tricarboxylate], first reported by Chui et al. [3], is one of the most frequently studied MOFs for gas adsorption and storage. The pore network of Cu-BTC has a simple cubic symmetry [4] (Fig. 1). Two octahedrally coordinated Cu atoms are connected to eight oxygen atoms of tetra-carboxylate units to form a dimeric paddlewheel. Each BTC ligand holds three dimeric Cu paddlewheels to form a microporous open framework with face-centered cubic symmetry. The pore structure consists of two types of cages: (i) large main cavities (eight per unit cell), connected to each other by nearly square windows of ca. 0.9 nm edge and (ii) small octahedral-shaped pockets (eight per unit cell), accessible from the main cavities through small triangular windows whose inscribed circle is approximately 0.35 nm in diameter. The key structural characteristics are copper dimers being coordinated to the oxygen atoms of the BTC linkers in a paddlewheel arrangement. The remaining coordination sites (one per Cu atom) are occupied by water molecules. Prior to experimental measurements of adsorption, these water molecules are removed

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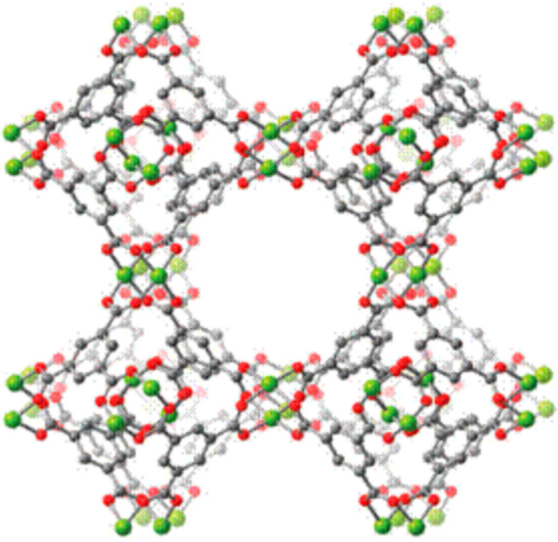

Fig. 1. Structure of CuBTC metal-organic framework. Cu, O, and C atoms are depicted in green, red, and gray colors, respectively.

by a degassing procedure. This dehydration leaves unsaturated Cu sites available for adsorption. Therefore, the partial positive charges on metal sites in Cu-BTC have the potential to enhance general adsorption properties.

The adsorption of small molecules such as H_2, Ne, Ar, N_2, O_2, CO_2, CH_4, and H_2O on Cu-BTC is frequently investigated. Vishnyakov et al. [4] made a first description of the preferential adsorption sites for the adsorption of Ar at low temperatures defining a sequence of adsorption as a gradual filling of the side pockets to a stepwise adsorption and condensation in the main channels. The simulation results agree quantitatively with the experimental isotherm of argon up to almost complete filling of the pore network. Adsorption properties of Cu-BTC for N_2, O_2, CO, CO_2, N_2O, CH_4, C_2H_4, C_2H_6, *n*-$C_{12}H_{26}$, and H_2O were reported by Wang et al. [5]. Experimental binary and ternary adsorption data of CO_2, CH_4, and CO on the Cu-BTC were reported by Hamon et al. [6]. Millward and Yaghi [1] showed exceptionally high capacity of several MOFs including Cu-BTC for storage of carbon dioxide. Liang et al. [7] measured adsorption isotherms of CO_2, CH_4, and N_2 in the broad ranges of pressure and temperatures and compared these isotherms with those on zeolite 13X. The obtained isotherms suggest a much higher working capacity for CO_2 adsorption on Cu-BTC relative to zeolite 13X. Argon adsorption was measured at temperatures between 66 and 143 K in the study by Krungleviciute et al. [8]. The experimental data were compared with theoretical results obtained by grand canonical Monte Carlo simulations. Isosteric adsorption heats of argon from the simulations were in good agreement with those obtained from the experiments. An identification of adsorption sites in Cu-BTC by experimentation and molecular simulation was performed by García-Pérez et al. [9]. Molecular simulation of $CO_2/CH_4/H_2$ mixture adsorption on Cu-BTC was performed by Yang and Zhong [10]. Combined DFT ab initio calculations with the periodic model were used in theoretical and experimental investigation of carbon dioxide or water on Cu-BTC was performed by Nachtigall and coworkers [11,12]. Finally, the most accurate theoretical adsorption isotherms for CH_4 on Cu-BTC were obtained by Chen et al. [13] based on ab initio GCMC simulations.

Investigation of adsorption of organic vapors was performed first with C3–C6 hydrocarbons. The butane adsorption capacity and heat of adsorption for Cu-BTC were determined by Klein et al. [14]. Study of propane/propylene separation and isobutene adsorption was carried out by Lamia et al. [15], Jorge et al. [16], and Rubeš et al. [17]. Adsorption and diffusion of *n*-butane, iso-butane, isopentane (i.e. 2-methylbutane), and 2,2-dimethylpropane in Cu-BTC was investigated by Chmelik et al. [18] using infrared microscopy combined with molecular simulations.

In contrast to Cu-BTC, the structure of Fe-benzene-1,3,5-tricarboxylate (Fe-BTC) is still unknown due to its poor crystallinity. In accordance with the data of producer (BASF), Fe-BTC is constituted by Fe^{3+} ions and BTC linkers and its composition can be expressed by the empirical formula $C_9H_3FeO_6$. The iron and carbon mass contents, which correspond to this formula, are 21 and 41%, respectively. However, in Ref. [19], the iron and carbon mass contents have been found to be 25 and 32%, respectively; another comment on the Fe-BTC composition was not given.

To the best our knowledge, adsorption properties of Fe-BTC were not investigated in details yet. Nevertheless, this MOF was successfully used in separation of small organic compounds in liquid phase [20].

Despite the fact that adsorption properties of Cu-BTC were studied using basically small probe molecules, there is still a lack of comparable investigations of the sorption processes involving larger (>C4) isomeric molecules. This issue is of considerable interest since various applications (in particular, most of the catalytic reactions for fine chemistry) are performed using quite bulky molecules. The motivation for the choice of Cu-BTC and Fe-BTC consists both in the differences of the regularity of their frameworks as well as in wide applicability of these MOFs for heterogeneous catalysis. Recently, Cu-BTC and Fe-BTC were used in coupling and cyclization reactions [21], Friedländer condensation [22–24], acylation reactions [25], *N*-methylation of aromatic amines [26], oxidation of alkanes [24], or in Claisen–Schmidt condensation [27,28], etc.

In addition to catalysis, extremely high surface areas and pore volumes of MOFs have led to the significant interest in their application in gas adsorption and gas storage. Therefore, the understanding of adsorption equilibrium of hydrocarbon vapors on Cu-BTC or Fe-BTC is of importance both from the views of fundamental investigation of adsorption equilibrium and application of MOFs in hydrocarbon separation.

In this paper, we report the results of the systematic investigation of the temperature dependence of adsorption of *n*-pentane, isopentane, and cyclopentane on Cu-BTC and Fe-BTC. For correlations with adsorption of simple gases, adsorption isotherms of nitrogen at 77 K and argon at 87 K were measured and interpreted for the first time. In addition to the fundamental knowledge of adsorption equilibrium of C5 hydrocarbon vapors, this study provides information on the influence of the nature of C5 hydrocarbon isomers and MOF framework structure on such parameters of adsorption equilibrium as potential, enthalpy, and entropy of adsorption.

2. Experimental

2.1. Materials

High-purity anhydrous *n*-pentane, isopentane, and cyclopentane from Aldrich were used for adsorption measurements. The metal-organic frameworks Cu-BTC and Fe-BTC were purchased from Aldrich under trademark Basolite C300 and Basolite F300, respectively.

2.2. Methods

X-ray powder diffraction data were recorded on a Bruker D8 X-ray powder diffractometer equipped with a graphite