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Adsorptive separation of C2/C3/C4-hydrocarbons on a flexible Cu-MOF: The influence of temperature, chain length and bonding character

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A B S T R A C T

In this work, manometrically and gravimetrically measured adsorption isotherms on the flexible copper MOF material $Cu_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2(Me_2trzpba)_4$ (**1**) are presented and discussed. This includes nitrogen (N_2) adsorption at 77.3 K, carbon dioxide (CO_2) adsorption at 298.15 K (Supplementary Material) and the adsorption of the five hydrocarbons ethane, ethene, propane, n-butane and 1-butene at 273.15 K, 298.15 K and 323.15 K. Up to the saturation pressure, all isotherms show distinct inflection characteristics, that are relatable to structural transitions of the flexible solid. The number of inflections and the relative pressure at which the inflections manifest depend on the characteristics of the relevant adsorptive and on temperature. For the hydrocarbon adsorption isotherms, we studied the influence of i) measurement temperature, ii) bonding character, and iii) the chain length of the alkanes and alkenes. In addition, the origin of decreasing equilibrium pressure with increasing adsorbed volume in the nitrogen adsorption isotherms on the flexible MOF material **1** is discussed. Calculations using the Ideal Adsorbed Solution Theory (IAST), based on the unary isotherm fits, along with transient breakthrough simulations, are used to demonstrate that Cu-MOF **1** has the potential to separate 5-component ethane/ethene/propane/n-butane/1-butene mixtures to yield three different fractions with increasing carbon numbers.

1. Introduction

Metal-organic frameworks (MOFs) as microporous materials with high adsorption capacity represent a challenge for the search of applications in many processes such as gas storage, separation or purification [1,2]. Frameworks of the third generation, according to the classification of Kitagawa et al., possess a more or less high degree of flexibility [3] that can depend on the solid structure itself, the fluid pressure and/or the loading with guest molecules – a special feature that may be exploited to find useful applications.

Fluid-dependent adsorption connected with definite solid–solid phase transitions, for instance, may be used for noble gas or hydrocarbon separation [4,5]. Since ethane and ethene possess very similar boiling points and molecular dimensions, mixtures of ethane/ethene are difficult to separate by distillation or molecular sieving. Therefore, energy-intensive processes such as cryogenic distillation are widely used for industrial ethane/ethene separation [6–8] which is important for feedstock purification in polyethene manufacture. In order to find a suitable adsorbent for ethane/ethene separation, Mofarahi et al. examined the usability of 5A zeolite. According to their simulations, 5A zeolite can be applied for separation of ethane/ethene by means of pressure swing adsorption (PSA) [9]. Different MOF materials have been investigated via olefin and paraffin adsorption, too. Martins et al. found that Cu-BTC has a distinct higher adsorption capacity for hydrocarbons than NaX and zeolite 13X [10]. In that work, the Cu-BTC shows a slightly higher adsorption affinity for ethene than for

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ethane. It is assumed that, additionally to the smaller kinetic diameter, the higher quadrupole moment of ethene may be a reason for this finding. However, a possible π-bonding-interaction of ethene with the open metal sites of the framework is discussed as the main reason. Neutron powder diffraction experiments on the Fe-MOF Fe_2(dobdc) support this thesis [11]. A further plausible influencing factor is the binding of the hydrocarbons with framework oxygens due to the convenient conformation of ethene molecules compared with ethane molecules, which was simulated by Nicholson [12]. By means of transient breakthrough experiments, Gücüyener et al. [13] have demonstrated the separation of ethene/ethane mixtures using zeolitic imidazolate framework material (ZIF 7). In this case, ethane is preferentially adsorbed from the mixture; the selectivity has been attributed to gate opening mechanism and subtle differences in molecular configurations.

The Cu-MOF $Cu_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2(Me_2trzpba)_4$ (**1**, $Me_2trzpba^- =$ 4-(3,5-dimethyl-4H-1,2,4-triazol-4-yl)benzoate) investigated in this work, has been examined already in earlier studies [14–16]. Lincke et al. [14] described the synthesis of the material and found two distinct steps in the adsorption isotherms of N_2, Ar and CO_2 which are explained by gate-opening processes. Reichenbach et al. [15] proved the influence of handling and storage of the material on textural properties and showed that external stimuli, like temperature- and pressure gradients, can change the sorption characteristics and the degree of flexibility. Lange et al. [16] studied the adsorption behavior of n-butane, 1-butene, isobutane and isobutene on the Cu-MOF **1**.

The present communication has two major objectives. The first objective is to investigate systematically how measurement temperature, chain-length and bonding character influence the adsorption of alkanes and alkenes on the flexible Cu-MOF. The second objective is to demonstrate its potential for separation of hydrocarbon mixtures containing C2, C3, and C4 hydrocarbons; such separations are of importance in the petrochemical industries [17,18]. Published research on MOFs for the separation of mixtures of C4 hydrocarbons is extremely limited. For example, Hartmann et al. [19] have presented breakthrough experimental data to demonstrate the separation of isobutane/isobutene mixtures using CuBTC.

2. Experimental

2.1. Adsorbent

The Cu-MOF **1** was prepared using the synthesis route given by Lincke et al. [14]. The protonated ligand H(Me_2trzpba) was refluxed with copper acetate hydrate for two days in ethanol, followed by a Soxhlet extraction of the obtained material with methanol.

According to the single crystal structure analysis [14], the nodes of the framework are composed of four copper ions, each showing N_2O_3 pyramidal coordination sphere. A central O^{2-} ion represents the common vertex of the four pyramids and is therefore the central assemblage point surrounded by the four copper ions. Additionally, pairs of copper ions are bridged with each other either via bidentately binding triazole units or via hydroxyl groups. A body centered cubic topology is built up by connection of $Cu_4(\mu_4\text{-}O)(\mu_2\text{-}OH)_2$ nodes via organic linkers which leads to a three-dimensional pore system consisting of two different types of windows. Their dimensions are 450 × 550 pm in crystallographic *a* and *b* directions and 350 × 850 pm in *c* direction presented in Fig. 1 [14].

The MOF material was stored in methanol. Before activation, excessive solvent was decanted, and the material was first dried at 373.15 K for about 30 min, the pre-dried solid then was stored in methanol vapor in a desiccator.

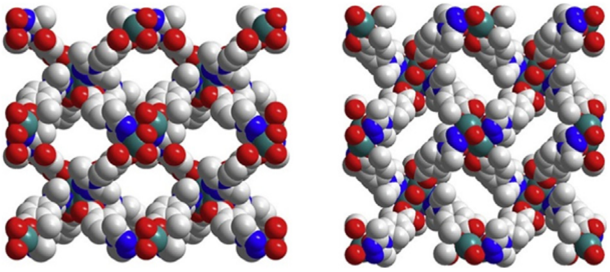

Fig. 1. Projections of the crystal structure of **1** which forms a three-dimensional pore system; view in crystallographic a and b directions 450 × 550 pm (left), c direction 350 × 850 pm (right) [14].

2.2. Manometric and gravimetric adsorption measurements

N_2 adsorption isotherms were measured at 77.3 K with a manometric ASAP 2010 device (Micromeritics Instrument Corporation) [20]. About 200 mg of the pre-dried substance were activated and weighed before the measurement. In order to avoid contact with atmospheric gases, a seal frit was used to cap the sample tube. For minimizing the sample tube volume during the manometric measurement, a filler rod was used. Defined volume increments were dosed automatically until the targeted relative pressures were reached.

Hydrocarbon adsorption isotherms at 273.15 K, 298.15 K and 323.15 K and the CO_2 adsorption isotherm at 298.15 K were measured with a magnetic suspension balance (Fa. Rubotherm) [21]. The pre-dried material was filled in a sample holder and brought into the vacuum system of the balance. Different pressure transducers were used depending on the expected pressure ranges of the measurement fluids. The saturation pressures of the used hydrocarbons at different temperatures are listed in Table 1.

After activation, the fluids were dosed stepwise to the measurement system. The adsorption equilibrium was monitored manually. Before changing the measurement fluid, the balance system was purged with the new fluid several times in order to remove remaining molecules from the previous adsorption experiment. The resulting sorption isotherms were corrected via helium buoyancy correction as discussed in Ref. [23].

3. Results and discussion

3.1. Nitrogen adsorption isotherm

We measured manometrically the N_2 adsorption isotherms on the Cu-MOF several times. We were able to reproduce the isotherms already published in Refs. [14] and [15] for the same material which show two strong increases (steps) of the adsorbed volume above a relative pressure of 10^{-3}. The second strong increase is associated with a large hysteresis loop. It is well-known

Table 1
Saturation pressures of the used adsorptives at all measured temperatures; calculated using a correlation provided by the Design Institute for Physical Properties (DIPPR) [22].

Adsorptive	Saturation pressure [bar]		
	273.15 K	298.15 K	323.15 K
ethane	23.9	41.9	68.6
ethene	41.1	69.8	111.7
propane	4.8	9.5	17.2
n-butane	1.0	2.4	5.0
1-butene	1.3	3.0	5.9