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Microporous and Mesoporous Materials

An aliphatic copper metal-organic framework as versatile shape selective adsorbent in liquid phase separations

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Jeroen Lannoeye [a], Ben Van de Voorde [a], Belgin Bozbiyik [b], Helge Reinsch [a], Joeri Denayer [b], Dirk De Vos [a,*]

[a] Centre for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium
[b] Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussel, Belgium

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ABSTRACT

Shape selective adsorption of organics on the metal-organic framework Cu(CDC) is demonstrated in both organic and aqueous media. Molecular sieving in the one-dimensional channels is responsible for the pronounced *para*-selectivity observed in the separation of C_8 alkylaromatics as well as in the adsorption of dihydroxybenzene isomers from water. This pronounced selectivity for linear compounds in both organic and aqueous media is further proven in the selective adsorption of the linear *n*-butanol over branched butanol isomers out of water. Moreover, the framework is extremely stable towards water and in a pH range between 2 and 12. This high stability, combined with a facile, multigram scalable room temperature synthesis in water, make Cu(CDC) a very promising adsorbent material for liquid phase separations.

1. Introduction

The separation and purification of chemicals is a critical and often highly energy demanding process in the chemical industry. Adsorption processes are considered to be energy-friendly alternatives for difficult distillations [1]. The adsorptive removal of side products in the production of fine chemicals and the treatment of waste waters contaminated with toxic compounds are processes in which porous adsorbents have already proven their performance [2]. Next to zeolites [3] or activated carbons [4], metal-organic frameworks (MOFs) have shown to be very promising adsorbent materials [5,6]. The defined and regular porosity can be readily tuned by the wide choice of metal centres and linker functionalizations. Adsorption behaviour on MOFs can be tuned by tailoring the open metal sites [7], pore sizes and shapes [8], functional groups [9] and taking advantage of structural flexibility [10]. Studies conducted on MOF adsorbents in liquid phase describe e.g. adsorptive denitrogenation [7,11,12] and desulfurization [7,12—15] of fuels, removal or separation of substituted aromatics [16—19] and the adsorption of alcohols [20] or contaminants [16,21,22] from water. The use of MOFs as adsorbent in industrial processes demands structural stability in organic solvents and especially in water [22], which is commonly present in at least small amounts in many feeds. Stability over a wide pH range is desired to prevent hydrolysis of the metal-organic framework [23], thereby driving the need to develop more robust and stable MOFs with selective adsorption behaviour.

In this work, liquid phase batch adsorption experiments are used to investigate the adsorption performance of a metal-organic framework material, Cu(CDC), in organic as well as in aqueous media. Cu(CDC) or copper *trans*-1,4-cyclohexanedicarboxylate (CDC) consists of dimeric copper four-blade paddle wheels [24], connected to each other by Cu—O—Cu bonds forming one-dimensional chains, providing the framework with a remarkable mechanical robustness [25]. The aliphatic CDC linkers, which typically assume the planar *e,e*-chair conformation, stack to link the Cu—O—Cu chains forming a three-dimensional framework with one-dimensional pore channels of 5.4 Å along the *a*-direction [24,26]. Such pore dimensions make Cu(CDC) an interesting candidate for separations in which molecular sieving and shape selectivity are decisive for selectivity, like differentiation between branched and linear aliphatic compounds or between *para*-, *meta*- and *ortho*-substituted aromatics. As the ease with which a MOF can be produced is a valuable asset in terms of economy of the eventual application [27], an alternative preparation method for Cu(CDC) was investigated. Finally, the stability of the sorbent material towards hydrolysis is tested in a wide pH range.

* Corresponding author.
  E-mail address: Dirk.DeVos@biw.kuleuven.be (D. De Vos).

2. Experimental section

2.1. Synthesis

Initially, the hydrothermal synthesis of Cu(CDC) was adapted from the literature [24]. In 150 g *N,N*-dimethylformamide (DMF), 2.95 g of the metal salt $Cu(NO_3)_2 \cdot 6H_2O$ and 2.15 g of the linker CDC were dissolved in a 1:1.25 ratio, followed by a 72 h solvothermal synthesis at 358 K. The material Cu(CDC)$_{DMF}$ was collected by filtration and washed with DMF to remove any residual linker molecules and afterwards solvent exchanged by repeated methanol soaking. The material was thermally activated at 423 K to remove all solvent from the pores.

Next, an alternative fast synthesis of Cu(CDC) was developed. In this 'instant' room temperature synthesis, Cu(CDC)$_{aq}$ was formed by adding the metal salt solution to a 1:2 mixture of CDC and NaOH in water. In a typical synthesis procedure, a solution of 2.41 g $Cu(NO_3)_2 \cdot 3H_2O$ in 35 mL H_2O was added to a solution containing 1.68 g CDC and 0.78 g NaOH in 85 mL H_2O. The reaction mixture was intensively shaken for 5 min and the resulting material was filtered off and washed with water and ethanol. The material was thermally activated at 423 K to remove all solvent from the pores. Adsorption measurements and stability experiments were performed with the Cu(CDC) material synthesised at room temperature.

2.2. Characterization

Powder XRD patterns were recorded on a STOE STADI-P Combi instrument in the Debye—Scherrer geometry (Cu-$K_{\alpha 1}$) using an IP position-sensitive detector ($2\theta = 0-60°$; $\Delta 2\theta = 0.03°$). A Philips XL30 FEG was used to acquire scanning electron microscopy (SEM) images of the MOF crystals. Thermogravimetric analysis (TGA) was performed on a TQA 500 of TA instruments. Samples were heated at a rate of 5 °C/min to 500 °C under oxygen containing atmosphere. Nitrogen physisorption isotherms were measured with a Micromeritics 3Flex surface characterization analyzer at 77 K. The BET surfaces were calculated using the points in the range p/p_0 0.005–0.05. Prior to the measurement, samples were outgassed at 423 K overnight under vacuum. For the localisation of the *para*-xylene molecules, XRD patterns were collected on a STOE STADI MP diffractometer in the Debeye—Scherrer geometry (Cu-$K_{\alpha 1}$) using a linear position-sensitive detector (6° 2θ window) and a capillary sample holder. A combination of force-field calculations and Rietveld-refinement was employed using Materials Studio [28] and TOPAS [29], see Supplementary data.

2.3. Water adsorption measurement

The water adsorption isotherm and heat of adsorption for Cu(CDC) were investigated by combined thermogravimetry (TG) and differential scanning calorimetry (DSC). A Setaram Sensys Evo device was coupled to a Wetsys humidity generator, in which the desired relative humidity (RH) is obtained by mixing a dry He flow with a water-saturated helium flow in a mixing chamber. The relative humidity of the mixed stream is controlled using a dew point metre. The humidified carrier gas flows through a heated transfer line into the TG/DSC measurement cell. The Cu(CDC) adsorbent was activated in situ by raising the temperature at a rate of 1 K/min from 303 K to 423 K and maintaining this temperature for 7 h. The carrier gas (He, purity $\geq$ 99,996%, $H_2O \leq$ 5 ppm) flow rate was set to 50 NmL/min. The sample and bath temperature in the Wetsys were set at 30 °C. The measurement was realized between 0% and 95% relative humidity under 1 atm He pressure.

2.4. Batch adsorption

Following a literature procedure [30], liquid phase batch adsorption experiments were performed in 1.8 mL vials containing 0.025 g of adsorbent or empty reference vials filled with a mesitylene or water solution. Mesitylene solutions contained one (single compound experiments) or more (competition experiments) xylene isomers, while the water solutions contained equimolar mixtures of hydroquinone/catechol, *n*-butanol/*tert*-butanol, *n*-butanol/*iso*-butanol or *n*-butanol/*sec*-butanol. The adsorbent material was pretreated at 423 K overnight under atmospheric conditions to remove all residual solvent molecules from the pores. Equilibrium concentrations and uptakes were calculated from gas chromatography (GC) output data. Adsorption isotherms were constructed by plotting the uptake, in weight %, versus the residual concentration in solution. For competitive adsorption experiments, selectivities $\alpha_{i,j}$ were calculated using Eq. (1):

$$\alpha_{i,j} = \frac{q_i}{q_j} \times \frac{c_j}{c_i} \tag{1}$$

with q_i and q_j the amounts ($mol\ g^{-1}$) of isomers i and j adsorbed per g of thermally activated Cu(CDC), and c_i and c_j the equilibrium concentrations ($mol\ L^{-1}$) of isomers i and j present in the liquid phase.

For all adsorbate molecules a critical diameter, i.e. the diameter of the narrowest cylinder in which the adsorbate molecule fits, was calculated (see Supplementary data).

2.5. Stability and regeneration

Stability is checked by using powder X-ray diffraction (PXRD) and N_2 sorption measurements of Cu(CDC) after treatment in boiling water or in solutions with varying pH. Water stability is investigated by stirring the MOF material for 7 d in boiling water, while pH stability is examined by stirring the material in solutions with a pH ranging between 0 and 14 using HCl and NaOH for acidic and basic solutions, respectively. The regeneration of the adsorbent material was adapted from a literature procedure for HKUST-1 [31], and comprised stirring the isolated MOF for 5 min in methanol, followed by centrifugation and thermal activation at 423 K. The adsorption capacity of the regenerated Cu(CDC) was investigated for 5 runs using liquid phase batch adsorption experiments (see Section 2.4). The stability after regeneration was also checked by PXRD and nitrogen sorption measurements.

3. Results and discussions

3.1. Instant room temperature synthesis

A room temperature synthesis of Cu(CDC) in water was developed as a fast and easy alternative for the solvothermal synthesis methods of the material. At room temperature, the crystallisation can be induced by the addition of the base NaOH in a 1:2 molar ratio with the linker. Upon addition of the copper salt very fast nucleation and growth of Cu(CDC)$_{aq}$ are observed. Multigram quantities can readily be prepared within minutes, while in the solvothermal synthesis of Cu(CDC)$_{DMF}$ heating at 353 K for 72 h is required to obtain the material in good yields. PXRD measurements show virtually identical patterns compared to solvothermally synthesized materials, indicating that they have the same structure (Fig. 1). The activation temperature of the material was found to be 373 K using TGA on the methanol washed material (Fig. S1).

Further characterisation using N_2-physisorption showed differences in BET surface areas and micropore volumes. When