



Screening of mixed-linker CAU-10 MOF materials for humidity sensing by impedance spectroscopy



Alexander Weiss^{a,1}, Nele Reimer^b, Norbert Stock^b, Michael Tiemann^{a,1},
Thorsten Wagner^{a,*}

^a Department of Chemistry, University of Paderborn, Warburger Str. 100, D-33098 Paderborn, Germany

^b Institute of Inorganic Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 2, D-24118 Kiel, Germany

ARTICLE INFO

Article history:

Received 24 February 2015

Received in revised form

13 August 2015

Accepted 14 August 2015

Available online 24 August 2015

Keywords:

MOF

Surface functionalization

Humidity sensing

Impedance

Water sorption

ABSTRACT

The sorption properties of mixed-linker CAU-10 type metal organic frameworks (MOFs), $[\text{Al}(\text{OH})(1,3\text{-BDC-X})_n(1,3\text{-BDC-SO}_3\text{H})_m]$ with 1,3-BDC = 1,3-benzenedicarboxylate, X = H, NO₂ or OH, $0.76 \leq n \leq 0.89$ and $0.11 \leq m \leq 0.24$, can be varied by surface modification through variation of the respective linker molecules. It is thus possible to design surface-modified CAU-10 type MOFs with variable affinity and accessibility of the pores for water vapour. When used as a dielectric in a capacitor, the MOF material will change its permittivity depending on the amount of physisorbed water; this is the working principle of capacitive humidity sensors.

Three different mixed-linker compounds with CAU-10 structure are compared regarding their water sorption and impedance characteristics. A setup was developed allowing the characterization of the MOF samples under exposure to different relative humidity values in air by impedance spectroscopy. Interpretation of the results by means of standard models shows that the MOFs are qualified for functional layers of capacitive humidity sensors. Since the prepared MOFs are more temperature-stable than many commonly used polymers they offer the potential to build a new generation of high-temperature (up to 350 °C) humidity sensors.

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1. Introduction

Metal-organic frameworks (MOFs) are crystalline structures built up by metal clusters interconnected by organic linkers. The possibility to combine various clusters and linkers leads to a multiplicity of compositions with tuneable chemical and physical properties. Because of their high (micro)porosity and large surface area they are interesting for such applications as gas storage, separation, catalysis, drug delivery [1] or water procurement in dry regions [2]. Modified MOFs with semiconducting or ohmic properties are promising for conformal electronic devices and reconfigurable electronics [3]. Their highly ordered structure in combination with tuneable surface and porosity properties also provides a high potential for sensor applications. The spectrum of potential transducers reach from optical (e.g. luminescence [4,5])

over mechanical (e.g. coating of quartz-crystal microbalances [1] or microcantilevers [6]), to electronic mechanisms [7].

However, it was shown that the sensitivity of several MOFs is rather low when exposed to some common gases (Basolite® A100 (Al-BDC), [Al(OH)(1,4-BDC)] 1,4-BDC = 1,4-benzenedicarboxylate), Basolite® F300 (Fe-BTC), Basolite® C300 (Cu-BTC, [Cu₃(H₂O)₃(BTC)₂], BTC = 1,3,5-benzenetricarboxylate), 10% O₂, 10% CO₂, 1000 ppm C₃H₈, 1000 ppm NO, 1000 ppm H₂ [7]; Basolite® C300 (Cu-BTC), [Cu₃(H₂O)₃(BTC)₂], CO₂, O₂, CH₄ H₂ up to 2000 ppm [8]). Ethanol and methanol lead to a measurable reaction, whereas water causes the highest sensor response. Consequently MOFs are promising candidates for humidity sensing applications. Among all humidity sensing mechanisms resistive- and, particularly, capacitive-type sensors are the most frequent ones. With their variable affinity and pore accessibility for water vapour, MOFs can be utilized as sensitive layers. It is therefore worthwhile to investigate their conducting and dielectric properties in the presence of water vapour.

With CAU-10, [Al(OH)(1,3-BDC-H)], we chose a recent type of functionalized MOF, which was first described by Reinsch et al. [9]

* Corresponding author. Tel.: +49 5251 602486.

E-mail address: thorsten.wagner@upb.de (T. Wagner).

¹ Fax: +49 5251 603423.

The structure of CAU-10 is built up by cis-corner-sharing AlO_6 octahedra to form a helix (Fig. 1). One helix is connected via the carboxylate groups of the isophthalate ions to four adjacent helices with alternating rotational orientation. Hence, a three-dimensional framework is formed with square-shaped one-dimensional channels with a maximum diameter of 7 Å. The single-linker compound CAU-10-H shows a permanent porosity of $a_{\text{s,BET}} = 635 \text{ m}^2 \text{ g}^{-1}$ and a micropore volume of $V_{\text{mic}} = 0.25 \text{ cm}^3 \text{ g}^{-1}$ and is accessible for H_2 and CO_2 gas as well as H_2O vapour. [9] The characteristic S-shape of the water vapour isotherm as well as exceptional hydrothermal stability, which was shown by Fröhlich et al. by multi-cycle water vapour measurements open the possibility for an application in the field of heat transformation processes of this material [10]. In addition, it was possible to grow this compound directly on γ -alumina and metallic alumina without any loss of performance in repeated water vapour adsorption measurements, which is advantageous for industrial use [11].

The isophthalate linker in CAU-10 can be functionalized in 5-position of the aromatic ring with CH_3 , OCH_3 , NO_2 , NH_2 , OH or Br groups [9,12]. The additional functional group has a strong influence on the sorption properties of the respective material. Based on that fact, a fine-tuning of this property was performed using a mixed-linker approach [12,13]. Recently Reimer et al. synthesized the mixed-linker compounds CAU-10-H/ SO_3H , CAU-10- NO_2 / SO_3H and CAU-10- OH / SO_3H containing different ratios of the two linker molecules, respectively. With increasing amounts of $-\text{SO}_3\text{H}$ groups the hydrophobic/hydrophilic character of these compounds could be varied [13]. The strong affinity towards water vapour in combination with a high thermal stability up to 350–400 °C, which is considerably higher than typical operating temperatures of commonly used polymer-based humidity sensor devices, turns these compounds into promising candidates even for high-temperature humidity sensing.

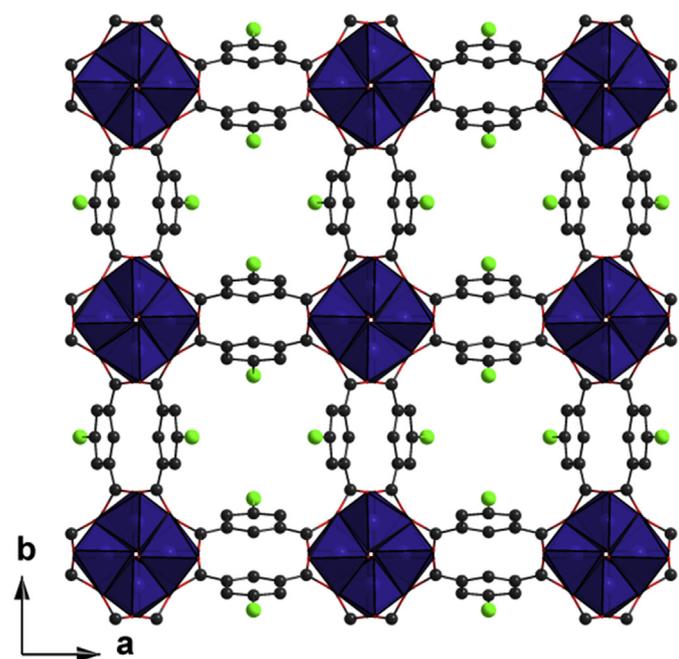


Fig. 1. Structure of the CAU-10 MOF with AlO_6 octahedra helices (blue), isophthalate linkers (black), and position of the functional groups (green)[CIF file from Ref. [12]]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. MOF synthesis and characterization

Three samples are compared (CAU-10-H, CAU-10- NO_2 , and CAU-10- OH), in which parts of the functional groups are replaced by sulfonic acid groups. The synthesis of CAU-10- $\text{H}_{0.76}/(\text{SO}_3\text{H})_{0.24}$ was performed in a custom-made steel autoclave with a Teflon inset with a volume of 30 mL. The reaction was performed in an oven at 135 °C for 12 h with 1 h heating and cooling ramp, respectively. The resulting precipitate was filtered off, washed with water, and dried in air. Further synthesis details have been reported elsewhere (N. Reimer et al. [13]).

Synthesis of CAU-10- $(\text{NO}_2)_{0.79}/(\text{SO}_3\text{H})_{0.21}$ and CAU-10- $(\text{OH})_{0.89}/(\text{SO}_3\text{H})_{0.11}$ was performed in a 100 mL glass reactor equipped with a screw cap in an oven at 120 °C for 12 h with 2 h heating and cooling ramp, respectively. The resulting precipitate was filtered off, washed with water and dried in air. The molar ratios of incorporated linker molecules were determined from ^1H NMR measurements of the respective dissolved CAU-10 material using the peak integrals.

Water sorption isotherms were recorded using a BEL JAPAN INC. Belsorp_{max} instrument. Prior to each measurement the samples were activated at 200 °C over night under vacuum (10^{-2} kPa).

2.2. Sample preparation

To measure the capacitance of the MOFs, a plate capacitor geometry was chosen. Powder samples were pressed to pellets with a diameter of 13 mm and 0.5 mm thickness and coated with layers of gold by thermal vapour deposition on both sides. A gold layer thickness of 80 nm provides conductivity on the rough pellet surface with sufficient gaps to allow gases to diffuse into the pellet. Conductivity of the electrodes was confirmed by measuring the surface resistance. The electrodes were connected utilizing a cylindrical custom-built sample holder, which allows gases to flow through the pellet in an advanced set-up developed from earlier work [14]. Details regarding sample preparation can be also found in a more comprehensive study on the impedance characteristics of the surface modified MOFs [15].

2.3. Measurement setup

Defined atmospheres were provided by a gas mixing system consisting of two mass flow controllers. One stream delivered dry synthetic air, whereas the second one was humidified by flowing through a washing bottle with pure water. A mixing ratio of 0:1 (0% dry air, 100% humidified air) corresponds to an absolute humidity of ca. 26 g/m^3 at room temperature (27 °C). The mixture was transferred to a tube containing the sample holder. Impedance spectra were taken on a Solartron SI1260 frequency response analyser (FRA). A simple setup (Fig. 2) was used for the screening in the range from 10 Hz to 1 MHz; the sample was connected in a four-point arrangement to minimize effects from the connection lines. Measurements were conducted using a Sin-Signal with an amplitude of 500 mV. More detailed measurements and interpretations can be found in Ref. [15].

3. Results and discussion

3.1. Water vapour sorption measurements

Water vapour sorption measurements Fig. 3 were performed at 298 K. Comparison of the single-linker with the mixed-linker compounds CAU-10- $(\text{OH})_{0.89}/(\text{SO}_3\text{H})_{0.11}$ sample shows the

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