Microporous and Mesoporous Materials 180 (2013) 8–13

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Time dependent water uptake in $Cu_3(btc)_2$ MOF: Identification of different water adsorption states by ^1H MAS NMR

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ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form 17 June 2013
Accepted 19 June 2013
Available online 28 June 2013

Keywords:
$Cu_3(btc)_2$ MOF
Cu^{2+} interaction
Water sites
Fast exchange
SSNMR

ABSTRACT

The hydration process in a deuterated $Cu_3(btc)_2$ (d-$Cu_3(btc)_2$) metal–organic framework (MOF) was followed by ^1H solid state NMR. Various hydrated states of d-$Cu_3(btc)_2$ are studied at definite time intervals after exposition of the MOF to atmospheric water. ^1H MAS NMR spectra indicate different positions of the water molecules inside the $Cu_3(btc)_2$ framework, and a distribution of chemical shifts. The change of the different water signals with time is followed by an intensity analysis. Fast exchange dynamics is observed when the amount of water is above two molecules per copper atom.

1. Introduction

$Cu_3(btc)_2$ [1] is one of the prominent metal-organic framework (MOF) materials because of its potential applications in gas adsorption, separation, catalysis, magnetism etc. [2–8]. It is well known that $Cu_3(btc)_2$ possesses so-called paddle wheel units with coupled Cu^{2+} ion pairs, that have an $S = 1$ excited electronic state at room temperature affecting the magnetic properties of the surrounding nuclei [9–12]. Thus, in the NMR spectra (e.g., of ^1H and ^{13}C) unusual shifts of the resonance line, as well as line broadenings are observed due to hyperfine interaction, resulting in complex resonance assignments [11–14]. Besides the hyperfine coupling, ^1H–^1H and ^1H–^{13}C dipolar couplings also contribute to the line broadening resulting in limited resolution and overlapping of the signals in the ^1H and ^{13}C NMR spectra. Selective deuteration has been proven to be an efficient technique to overcome some of these obstacles [15,16].

$Cu_3(btc)_2$ is very sensitive to water. The water adsorption isotherm in $Cu_3(btc)_2$ was previously studied, both experimentally and by molecular simulation [17–19]. Schlesinger et al. Henninger et al. and Jee et al. showed the instability of this MOF due to interaction with water using powder X-ray diffraction (PXRD), combined thermogravimetry and differential scanning calorimetry (TG/DSC), and electron paramagnetic resonance (EPR) spectroscopy [20–22]. In our previous contribution we reported on the interaction of defined amounts of water with the $Cu_3(btc)_2$ framework and its stability [12]. A varying chemical shift of the water protons has been observed due to adsorption of different amounts of water (0.5–5 water molecules per copper atom). Here we report on the water-MOF interaction due to a continuous hydration of $Cu_3(btc)_2$ from the surrounding atmosphere. ^1H MAS NMR is used to study the various states of hydrated $Cu_3(btc)_2$. Since the range of proton isotropic chemical shifts is small, in this work deuterated $Cu_3(btc)_2$ is used to achieve better resolution by removing NMR signal contribution from protons of the MOF itself, and to clearly distinguish adsorbed water.

2. Experimental

2.1. Synthesis

d-$Cu_3(btc)_2$ was prepared using the deuterated ligand following the procedure described elsewhere [5]. The perdeuterated 1, 3, 5 benzene-2, 4, 6-d_3-tricarboxylic acid (98.5%) was purchased from *CDN ISOTOPES*. The price for the labeled compound was 684 € per 0.5 g excluding VAT. For a filled rotor the respective cost is about 1/10 of this. Powder X-ray diffraction (XRD) data (Supplementary Fig. S1) reveal the formation of good quality samples in agreement with published data and the simulated pattern calculated from the crystal structure [1].

2.2. Sample preparation for NMR measurements

The sample was activated, i.e., dehydrated, in vacuum at 383 K for 24 h to remove residual water molecules coordinated to the

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http://dx.doi.org/10.1016/j.micromeso.2013.06.033

copper sites. The activated sample was then quickly packed in a 4 mm MAS rotor with an air-tight cap. Hydration of the sample was achieved by opening the rotor for defined periods of time at ambient conditions: NMR measurements were performed with the closed rotor for a maximum of five minutes. After each such measurement the rotor was reopened again, and left in contact with ambient air. The process was repeated for about 80 h. The spectra obtained were labeled with the total time of exposure (excluding the time taken for recording the spectra) to hydrate the sample before recording the corresponding NMR spectrum. An NMR measurement of the dehydrated sample was also performed for comparison.

2.3. NMR measurements and analysis of the data

^1H MAS NMR experiments of dehydrated and hydrated d-$Cu_3(btc)_2$ samples were carried out on a Bruker Avance 400 (9.4 T) spectrometer at 400.13 MHz. ^1H MAS spectra were recorded using the DEPTH sequence [23–24] to prevent spurious signals from probe background signals. The recycle delay was 50 ms, which is more than five times the longitudinal relaxation time (T_1) as measured with the inversion recovery technique (data not shown). The 90° pulse length was 2.6 μs. The experiments were carried out at room temperature (298 K) using a 4 mm MAS probe and spinning rates of typically 10 kHz. For the temperature dependent measurements in the range of 180–288 K, a 7 mm MAS probe was used. The simulation of the NMR spectra was carried out using the program dmfit [25]. For the intensity analysis, the small contribution from residual btc protons is always taken into account, assuming a constant signal at all times. The amount of water in the sample was determined by weighing the rotor before and after hydration at two time points. From the mass increase due to adsorbed water with respect to the mass of d-$Cu_3(btc)_2$, the number of water molecules per copper site was calculated.

3. Results and discussion

3.1. ^1H MAS spectra

In Fig. 1 the isotropic regions of the ^1H MAS spectra at room temperature of dehydrated and hydrated d-$Cu_3(btc)_2$ are plotted. For the time evolution of the line intensities we refer to the Supplementary Fig. S2. In the parent material only one resonance for the aromatic protons is visible as observed in previous studies [10–12]. The small signal results from the incomplete deuteration of btc (98.5%). This line will not be discussed further.

If the hydration of the sample is carried out only for a relatively short period of time (∼3 min) a sharp resonance line at ca. 14 ppm and a smaller shoulder at ca. 12 ppm appear in the proton NMR spectra, and they are labeled as H_2O-I and H_2O-II, respectively. A third water signal denoted by H_2O-III becomes visible after 20 h of hydration (initial shift of 7.2 ppm). After 56 h of hydration only the resonance line of H_2O-III is visible which is slightly asymmetric tailing to lower ppm values. This shows that an internal equilibrium is achieved which leads to this single line spectrum.

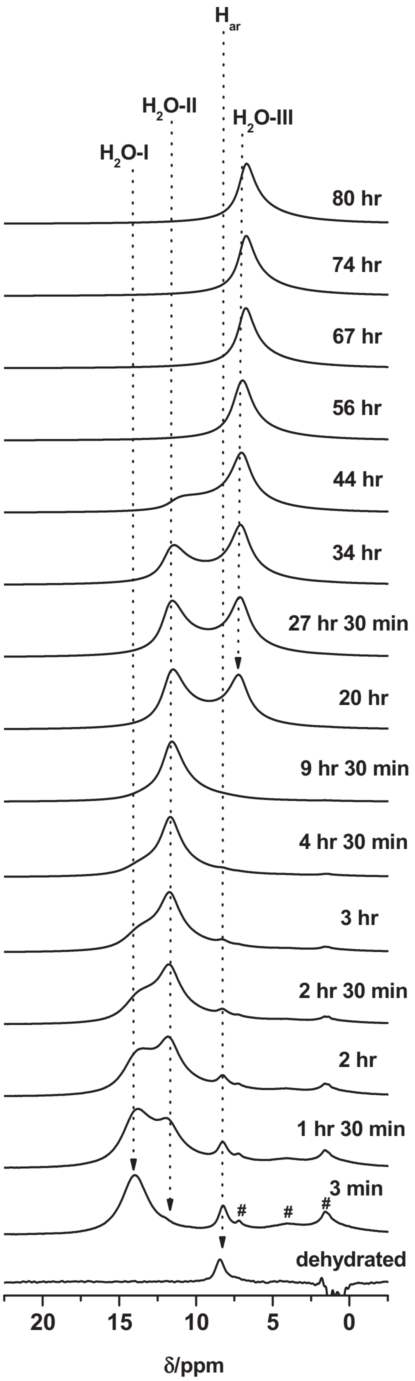

Fig. 1. Isotropic region of the ^1H MAS spectra of dehydrated and hydrated d-$Cu_3(btc)_2$ measured at different times. #denotes residual solvent (ethanol) signals. The intensity of the individual spectra is scaled.

Firstly, we try to understand the origin of the various water lines that appear in the course of hydration. It is well known from the crystal structure that water molecules have a great affinity for the metal center [1,7]. Therefore, we believe that the water molecules go to the unoccupied Cu^{2+} metal center, first (two water molecules can interact with one paddle wheel unit). Since in the ^1H MAS spectra the H_2O-I and H_2O-II resonances appear immediately after the hydration, one can assume that both resonances arise from water coordinated to the metal centers. Thus, the initial presence of the two distinct lines H_2O-I and H_2O-II is given by the coordination of one and two water molecules per paddle wheel unit, respectively, cf. Fig. 2 [26]. As the hydration of the sample proceeds, the amount of water molecules entering the vacant metal sites of each paddle wheel unit will increase steadily. Therefore it is not surprising that some of the paddle wheels have one unoccupied metal center and some are fully occupied with H_2O, which results in two separate ^1H NMR lines. Our results clearly indicate that the water molecules preferentially interact with the copper sites, so that both species H_2O-I and H_2O-II are visible in the spectra. The intensity of the line for H_2O-I is decreasing with hydration time at the cost of the H_2O-II line which also agrees with our