

Structure and spectroscopy of hydrogen adsorbed in a nickel metal–organic framework



Craig M. Brown^{a,b,*}, Anibal Javier Ramirez-Cuesta^c, Jae-Hyuk Her^{a,d,1}, Paul S. Wheatley^e, Russell E. Morris^e

^a National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD 20899, USA

^b Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

^c Chemical and Engineering Materials Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6460, USA

^d Department of Material Science and Engineering, University of Maryland, College Park, MD 20742, USA

^e EaStCHEM School of Chemistry, University of St Andrews, St Andrews KY16 9ST, United Kingdom

ARTICLE INFO

Article history:

Available online 28 August 2013

Keywords:

Neutron scattering

Hydrogen storage

Metal–organic framework

Porous crystal

ABSTRACT

The structure of Ni₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate) as a function of deuterium adsorption has been determined through the application of *in situ* neutron powder diffraction. Detailed information concerning the local adsorption potential for hydrogen at each site has also been probed using inelastic neutron scattering techniques. These results are compared to those previously published on isostructural analogs and the Ni²⁺ variant shows the shortest deuterium–metal distance in the M₂(dobdc) series (M = Mg, Zn, Co, Fe) that have been studied so far.

Published by Elsevier B.V.

1. Introduction

Hydrogen storage has been viewed as a potentially viable mechanism for moving to a non-fossil-fuel based energy infrastructure [1]. One of the main stumbling blocks is being able to store enough hydrogen at ambient temperatures on a gravimetric and volumetric basis. While no single material has been proven to be viable at this point, the concept of using physical adsorption in metal–organic frameworks (MOF) with enhanced interactions with unsaturated metal centers has been proposed [2–6]. Thermodynamic considerations indicate that the enthalpy for adsorption should be around 20 kJ/mol to have reversible storage around ambient temperature [7].

M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn) forms an extensive family of isostructural MOFs. The connectivity and pore structure of M₂(dobdc) is based on a 1-dimensional honeycomb-like channels, with pores of ~12 Å diameter and helical chains of edge sharing metal oxygen octahedra running down the intersections of the pore walls formed from 2,5-dioxido benzenedicarboxylate (dobdc²⁻) ligands. One of the pseudo-octahedra coordination sites at the transition metal is initially solvated at synthesis with this one molecule easily removed to provide a square-based pyramidal coordination with one site now accessible through the pore [8–15]. These highly reactive, electron deficient sites allow for strong

polarization of adsorbed H₂ molecules resulting in zero coverage isosteric heats ranging from –8.8 to –13.5 kJ/mol [16,13,17–19]. These values are some of the highest reported [20–25], and are significantly larger than isosteric heats observed for frameworks lacking open metal coordination sites [26]. Interaction of hydrogen with the framework is characterized by an enhanced electrostatic interaction with the exposed metals in the framework, and has been characterized by gas adsorption isotherms, powder neutron diffraction, inelastic neutron scattering, theoretical calculation and optical spectroscopies. These studies indicate a strong adsorption primarily at the metal center, followed by adsorption associated with the organic framework oxygen and carbon atoms that are weaker and more van der Waals in nature [27–34].

Here, we expand these data to include the Ni₂(dobdc) member of the series, which exhibits the strongest enthalpy for hydrogen adsorption and the shortest interaction distance from metal to deuterium. Using inelastic neutron scattering as a probe of the rotational potential, and hence the hydrogen–metal interaction, is complicated due to local magnetic ion fluctuations interconverting *para*- and *ortho*-hydrogen that contains a spectrum composed of rotations and rotation-phonon combination bands. However, by using D₂ we were able to mask the signal coming from the different site and therefore assign the observed features in the spectra.

2. Experimental

Ni₂(dobdc) was synthesized using published procedures [9]. The material was characterized using powder X-ray diffraction to

* Corresponding author at: National Institute of Standards and Technology, Center for Neutron Research, Gaithersburg, MD 20899, USA. Tel.: +1 3019755134.

E-mail address: craig.brown@nist.gov (C.M. Brown).

¹ Current address: GE Global Research, Niskayuna, NY 12309, USA.

ensure the framework structure was correct and prior to data collection the samples were activated to remove residual guests from the pores of the solid. This is best done in a two stage process; first the materials are placed under vacuum to remove loosely held guests before heating carefully to 110 °C under dynamic vacuum for 36 h to ensure all coordinated water molecules are removed [35,36].

The BT-1 high-resolution neutron powder diffractometer at the National Institute of Standards and Technology Center for Neutron Research (NCNR) was used to perform neutron powder diffraction (NPD) experiments on 1.075 g of activated Ni₂(dobdc). Data were collected using a Ge(311) monochromator with an in-pile 60' collimator resulting in a wavelength of 2.0782 Å. The sample in a vanadium cell was mounted with gas loading lines onto a closed-cycle refrigerator and data were collected on the bare framework at 4 K. For D₂ loading, the sample was heated to 77 K, exposed to a specified amount of D₂, and subsequently cooled back to 4 K for data measurement. Data were collected at loadings of 0.5 and 1.5 D₂ molecules per nickel. NPD data were analyzed using the Rietveld method as implemented in EXPGUI/GSAS [37,38]. Adsorbed atoms were located using Fourier techniques and subsequently added to the Rietveld model and refined as single atoms of D with double occupancy due to the quantum mechanical rotational that average their positions [28].

Inelastic neutron scattering (INS) experiments were performed on the Filter Analyzer Neutron Spectrometer (FANS) at the NCNR [39] and with improved resolution on the TOSCA [40] neutron spectrometer located at the ISIS facility of the Rutherford Appleton Laboratories. When operated with one proton pulse removed for use on the second target station, the instrument accesses energy transfers between −3 meV and 500 meV with a resolution of ≈2% ΔE/E on the sample energy gain (positive) side of the spectrum. The same sample used for diffraction was loaded into a vanadium cell (1.024 g) in a helium glovebox and attached to a gas loading stick for a top-loading closed-cycle refrigerator that is installed in the spectrometer. The spectrum of the activated, bare, sample was measured at base temperature at ~12 K. Calibrated volumes were used to dose known amounts of *n*-H₂ and *p*-H₂ at 35 K and the spectra were recorded at ~12 K.

Spectra on FANS were obtained using a 20' collimated and monochromatic (PG(002)) neutron beam. After the scattered neutrons are passed through a low energy band-pass filter consisting of Bi, Be, and graphite, the energy transfer of the scattered neutrons is determined at a bank of ³He detectors. Data were collected on the bare framework, and with loadings of 1 *p*-H₂ and 2 *p*-H₂ per Ni²⁺. An additional loading with 1 D₂ saturating the strongest adsorption site followed by a further 1 *p*-H₂ per Ni²⁺ was measured. The smaller zero-point motion of the D₂ molecule ensures that it is adsorbed at the strongest binding site, thus saturating the metal with the much weaker scattering D₂, and allows for easier discrimination of the weaker sites that adsorb H₂ [19]. While both spectrometers probe similar ranges in momentum transfer (Q), FANS measures intensities proportional to the densities-of-states and TOSCA measures the scattering function, S(Q, ω). This effectively gives the FANS spectra an intensity boost that goes as the square of the energy transfer, ω. Upon hydrogen adsorption the framework modes are apparently not significantly perturbed and a direct subtraction of the bare framework spectra results in the rotation-vibration spectra of the adsorbed hydrogen. Data were analyzed using the DAVE software suite [41].

3. Result and discussion

Rietveld refinement of the neutron powder diffraction (NPD) data measured on the activated Ni₂(dobdc) material was performed using an isostructural refinement previously determined

Table 1

Comparison of unit cell dimensions of M₂(dobdc) series studied using neutron diffraction.

M ²⁺ cation:	<i>a</i> (Å)	<i>c</i> (Å)
Ni (this work)	<i>a</i> = 25.797(1)	<i>c</i> = 6.7505(4)
Mg [18]	<i>a</i> = 25.861(3)	<i>c</i> = 6.9143(8)
Zn [29]	<i>a</i> = 25.887(3)	<i>c</i> = 6.816(1)
Co [42]	<i>a</i> = 25.9067(9)	<i>c</i> = 6.8548(5)
Fe [19]	<i>a</i> = 26.0983(5)	<i>c</i> = 6.8512(2)
Mn [42]	<i>a</i> = 26.331(2)	<i>c</i> = 7.0472(5)

as an initial model [29]. The data is consistent with the structure conforming to a R-3 space group and unit cell parameters of *a* = 25.797(1) Å and *c* = 6.7505(4) Å. The unit cell dimensions are the smallest compared to those determined for Zn [29], Mg [18], Fe [19,43], Co and Mn [42] variants from NPD data under similar conditions (Table 1). Fig. 1 indicates that the model provides an excellent fit to the data, with structural parameters detailed in Table 2.

NPD experiments with Ni₂(dobdc) dosed with approximately 0.5 D₂/Ni²⁺, indicate population of a single adsorption site, site-I, located close to the open metal center. The data can be well fit using an isotropic atomic displacement parameter, yet this can be improved on by allowing anisotropic parameters for the deuterium binding at the Ni²⁺ site (Table 3, Fig 1.). This is unlike the case for other MOFs with open metal sites studied by neutron diffraction [18,21,22,24,44,45] where the interaction is more isotropic for these necessarily time-averaged measurements. Density functional theory applied to calculating the rotational potential at the copper site in HKUST-1 indicated that the potential is expected to be anisotropic, and we would anticipate that it is more anisotropic in this case with a much stronger/shorter H₂–Ni²⁺ interaction [28]. The oblateness of the site I deuterium here, results in a very close interaction distance of 2.20(1) Å. The short distance

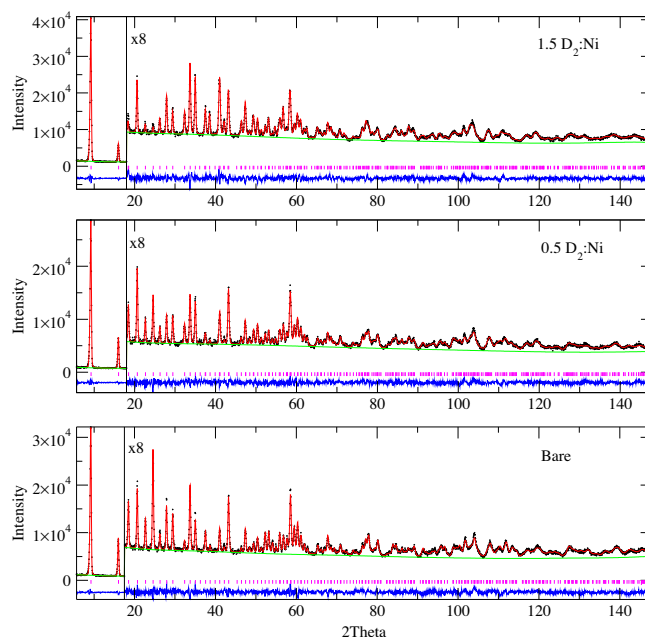


Fig. 1. Rietveld refinement of neutron powder diffraction data for Ni₂(dobdc) measured at 4 K. Bottom, middle and top panel are for the bare, 0.5 D₂:Ni and 1.5 D₂:Ni loadings, respectively. Green lines, crosses, and red lines represent the background, experimental, and calculated diffraction patterns, respectively. The blue line represents the difference between experimental and calculated patterns, with allowed reflections as pink tick marks. The data are scaled by a factor of 8 above ~17° to highlight the high Q region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/5373695>

Download Persian Version:

<https://daneshyari.com/article/5373695>

[Daneshyari.com](https://daneshyari.com)