



# Study of structural, surface and hydrogen storage properties of boric acid mediated metal (sodium)-organic frameworks

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## ARTICLE INFO

### Article history:

Received 16 October 2017

Received in revised form

15 December 2017

Accepted 18 December 2017

Available online 18 December 2017

### Keywords:

Sodium

B-MOF

Succinic acid

Fumaric acid

Acetylene dicarboxylic acid

Hydrogen storage

## ABSTRACT

Three boric acid mediated metal organic frameworks were synthesized by solution method with using succinic acid, fumaric acid and acetylene dicarboxylic acid as a ligand source and sodium as a metal source. The complexes were characterized by FT-IR, powder XRD, elemental analyses and single crystal measurements. The complexes with the formula,  $C_4H_{18}B_2Na_2O_{14}$ ,  $C_4H_{16}B_2Na_2O_{14}$  and  $C_4H_{14}B_2Na_2O_{14}$  were successfully obtained. BET surface area of complexes were calculated and found as 13.474 m<sup>2</sup>/g for catena-(tetrakis(μ<sub>2</sub>-hydroxo)-(μ<sub>2</sub>-trihydrogen borate)-(μ<sub>2</sub>-succinato)-di-sodium boric acid solvate), 1.692 m<sup>2</sup>/g for catena-(tetrakis(μ<sub>2</sub>-hydroxo)-(μ<sub>2</sub>-trihydrogen borate)-(μ<sub>2</sub>-fumarato)-di-sodium boric acid solvate) and 5.600 m<sup>2</sup>/g for catena-(tetrakis(μ<sub>2</sub>-hydroxo)-(μ<sub>2</sub>-trihydrogen borate)-(μ<sub>2</sub>-acetylenedicarboxylato)-di-sodium boric acid solvate). Hydrogen storage capacities of the complexes were also studied at 77 K 1 bar pressure and found as 0.108%, 0.033%, 0.021% by mass. When different ligands were used, the pore volume, pore width and surface area of the obtained complexes were changed. As a consequence, hydrogen storage capacities also changed.

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## 1. Introduction

Hydrogen is one of the most rewarding energy source because of the decreasing fossil fuel supply. Effective separation and storage of hydrogen are becoming significant [1]. Metal hydrides [2], carbohydrides [3], clathrates [4] and nanotubes [5,6] are used as hydrogen storage materials. In recent years, hydrogen storage in metal-organic frameworks have attracted considerable interest because of structural diversity and changeable surface properties [7]. Metal-organic frameworks consist of metal centers or clusters and organic ligands to form one, two or three dimensional coordination network. Soluble nitrate, sulphate and acetate salts use as metal source. Organic molecules which contain alcohols, aldehydes, carboxylic acids, nitriles and thiols as a functional group use as ligand [8]. Carboxylic acid ligands are the most preferred ligands due to their thermal stability and chemical durability. Physical properties of ligands influence pore size, surface area and surface properties of frameworks [9].

Boron containing metal organic framework was first synthesized by El-Kaderi et al., in 2007 [10]. Boronic acid [10], carboranes [11], organoborons [12] and borax [13] were used as boron source. Boric acid mediated metal(sodium)-organic frameworks were synthesized by our groups with using trimelic acid and terephthalic acid as ligand [14]. Boron compounds were used for living, energy, electronics [15] and hydrogen storage [16]. Boron containing frameworks were expended as catalyst [17], methane storage [18], hydrogen storage [19], antimicrobial [20], chiral [21] and luminescent material [22].

In the present study, we chose three different aliphatic dicarboxylic acid ligands which were fumaric acid, succinic acid and acetylenedicarboxylic acid to prepare three boron containing metal organic frameworks. The structural properties of complexes were characterized by elemental analyses, FT-IR, powder XRD and single crystal XRD. Surface properties of complexes were investigated by BET technique. Hydrogen storage capacities of complexes were also calculated and compared.

## 2. Materials and methods

Sodium bicarbonate (NaHCO<sub>3</sub>) (Merck, 99.5%) was used as a

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sodium source. Boric acid ( $\text{H}_3\text{BO}_3$ ) (Sigma, 99.5%) was used as a boron source. Succinic acid ( $\text{C}_4\text{H}_6\text{O}_4$ ) (Aldrich, 98%), fumaric acid ( $\text{C}_4\text{H}_4\text{O}_4$ ) (Sigma, 99%) and acetylene dicarboxylic acid ( $\text{C}_4\text{H}_2\text{O}_4$ ) (Aldrich, 95%) were used as ligand source. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) (Sigma, 99.8%), ethyl acetate ( $\text{C}_4\text{H}_8\text{O}_2$ ) (Sigma, 99.7%) and deionized water were used as solvent.

#### 2.1. Synthesis of sodium succinate-boron complex (catena-(tetrakis( $\mu$ 2-hydroxo)-( $\mu$ 2-trihydrogen borate)-( $\mu$ 2-succinato)-di-sodium boric acid solvate))

1 mmol (0.118 g) of succinic acid was dissolved in 20 mL deionized water. 2 mmol (0.168 g) of sodium bicarbonate were added to form the sodium salt of succinic acid. Boric acid (2 mmol) was added to solution and completely dissolved. The mixture was stirred at 90 °C. 20 mL of ethyl acetate were added to crystallize. White crystals were obtained from the crystallizing solution 8 days later.

#### 2.2. Synthesis of sodium fumarate-boron complex (catena-(tetrakis( $\mu$ 2-hydroxo)-( $\mu$ 2-trihydrogen borate)-( $\mu$ 2-fumarato)-di-sodium boric acid solvate))

1 mmol (0.116 g) of fumaric acid was dissolved in 20 mL of deionized water. 2 mmol (0.168 g) of sodium bicarbonate were added to form sodium fumarate. 2 mmol of boric acid were added and stirred at 90 °C until dissolved. 20 mL of ethanol were added. White crystals were obtained after 11 days.

#### 2.3. Synthesis of sodium acetylenedicarboxylate-boron complex (catena-(tetrakis( $\mu$ 2-hydroxo)-( $\mu$ 2-trihydrogen borate)-( $\mu$ 2-acetylenedicarboxylato)-di-sodium boric acid solvate))

1 mmol (0.114 g) of acetylenedicarboxylic acid was dissolved in 20 mL deionized water. 2 mmol (0.168 g) of sodium bicarbonate and 2 mmol boric acid were added and stirred at 90 °C. White crystals were obtained after 18 days in water-ethanol solution.

#### 2.4. Characterization of complexes

C, H contents were determined by CHNS-932 LECO model elemental analysis instrument. Na and B contents were determined by Perkin Elmer DRC II model ICP-MS instrument. Thermal behavior were performed by Shimadzu DTG-60H system. FT-IR spectra were recorded in 4000–400  $\text{cm}^{-1}$  range with Perkin-Elmer Spectrum One instrument by KBr pellet technique. Surface area measurements and hydrogen storage capacity were recorded by Quantachrome Autosorb IQ. Suitable crystal was selected for data collection which was performed on a Bruker APEX-II diffractometer equipped with a graphite-monochromatic Mo-K $\alpha$  radiation at 296 K. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F2 using SHELXL-97 [23] from within the WINGX [24] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93 Å. All other H atoms were located in a difference map refined subject to a DFIX restraint. Molecular diagrams were created using MERCURY (Mercury) [25]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [26].

### 3. Results and discussion

#### 3.1. Elemental analysis

The amounts of carbon and hydrogen were examined using elemental analysis device and the sodium and boron amounts were determined by ICP-MS. The obtained results are shown in Table 1. Experimental results have similarity with the calculated results of C, H, B and Na amounts from single crystal measurement.

#### 3.2. FTIR analysis

The FT-IR peaks values of starting materials, sodium salts and sodium-boron complexes are summarized in Table 2. The most important peaks (O–H, asymmetric –COO, symmetric –COO, C=O and BOH) are compared. As shown in Table 2, there are band shifts

**Table 1**  
Chemical composition of the complexes.

Complex	MW g/mol	Chemical Composition Calc. (Exp.) (%)			
		C	H	Na	B
$\text{C}_4\text{H}_{18}\text{B}_2\text{Na}_2\text{O}_{14}$ (Succinate complex)	357.78	13.43(13.83)	5.07(4.87)	12.85(12.90)	6.04(5.80)
$\text{C}_4\text{H}_{16}\text{B}_2\text{Na}_2\text{O}_{14}$ (Fumarate complex)	355.77	13.50(13.73)	4.53(4.47)	12.92(12.65)	6.07(5.74)
$\text{C}_4\text{H}_{14}\text{B}_2\text{Na}_2\text{O}_{14}$ (Acetylenedicarboxylate complex)	353.75	13.58(13.33)	3.99(3.96)	6.11(6.12)	12.99(13.03)

**Table 2**  
The FT-IR peaks values of starting materials, sodium salts and sodium-boron complexes.

Compound	$\nu_{\text{O-H}}$	$\nu_{\text{as-COO}}$	$\nu_{\text{s-COO}}$	$\nu_{\text{C=O}}$	$\nu_{\text{BOH}}$
Succinate complex	3690–3000	1621–1582	1418–1394	–	1204
Sodium succinate	3720–3150	1561	1470–1391	1685	–
Succinic acid	3530–3000	1570	1415	1700	–
Fumarate complex	3700–3000	1627–1591	1421–1382	–	1185
Sodium fumarate	3653–3300	1597	1412–1385	1722	–
Fumaric acid	3500–3000	1527	1321	1679	–
Acetylenedicarboxylate complex	3660–3000	1637–1609	1418–1355	–	1173
Sodium acetylenedicarboxylate	3680–3270	1631–1594	1409–1361	–	–
Acetylenedicarboxylic acid	3650–3000	–	1422–1273	1709	–
Boric acid	3500–3100	–	–	–	1191

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