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Synthesis, characterization and hydrogen adsorption on metal-organic frameworks Al, Cr, Fe and Ga-BTB

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ABSTRACT

Benzenetribenzoate (BTB) ligand is combined with four trivalent metals, Al, Cr, Fe and Ga by solvothermal synthesis to form four different metal-organic frameworks (MOFs), abbreviated as M-BTB, where M stands for the metal. Each of the MOFs is characterized with pore texture, scanning electron microscopic images (SEM), X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Pore texture reveals the highest BET surface area belongs to Al-BTB (1045 m^2/g) and decreases in the order of Cr > Fe > Ga. Hydrogen adsorption at 77 K and up to ambient pressure indicates that Al-BTB adsorbs highest amount of H_2 (0.98 wt.%) and decreases in the same order as the specific surface areas. High pressure H_2 adsorption at room temperature (298 K) and pressure up to 80 bar reveals that Fe-BTB adsorbs highest amount of hydrogen (0.51 wt.% or 2.75 $g\,L^{-1}$, absolute) and the adsorption amount decreases in the order of Cr > Al > Ga.

1. Introduction

Metal-organic frameworks (MOFs) are highly promising adsorbents because of their very high specific surface area, tunable pore size and case-specific tailoring of basic molecular architecture leading to the large and selective adsorption capacities of several gas molecules. A large volume of MOFs has been reported in the literature; most of them were synthesized and decorated accordingly with an aim towards gas storage [1–3], separation [4], heterogeneous catalysis [5], drug delivery [6] or molecular sensing [7]. Topologically, all the MOFs consist of metal centers, more precisely known as secondary building units (SBUs) connected with each other by the organic molecules, commonly known as organic linkers [8]. Different types of metals have been employed and examined for the structure forming capacity of MOFs; typical examples are zinc [9–15,28], copper [16,17], chromium [18–20], aluminum [21,22], iron [23,24], scandium [25], manganese [26], zirconium [27], vanadium [29] or cadmium [42].

Organic linker is probably the far most important part in tailoring the architecture of metal-organic frameworks. The linker molecule plays the role to tune the pore size and specific surface area of the MOFs. Most versatile usages of different organic molecules as linkers were noticed in synthesizing different species of IRMOFs where zinc was employed as part of secondary building units [8,28]. Benzenedicarboxylic acid (BDC) or terephthalic acid is most common in synthesizing different species of MOFs, including MOF-5 [9,13,28], MIL-53 (Cr, Al or Fe) [19,29] or MIL-101 [20,30,31]. However, the reported large surface area and the maximum gas (H_2 and CO_2) uptake is observed for benzenetribenzoic acid (BTB) as organic linker that formed metal-organic framework, MOF-177 with zinc as SBU former [10–12,14,15,33–35]. Besides hydrogen and carbon dioxide, methane [36], nitrous oxide [36] and carbon monoxide [37] adsorption was also examined on MOF-177. In recent time, Furukawa et al. incorporated few other ligands, like 4,4′,4″-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate (BTE), 4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate (BBC) or biphenyl-4,4′-dicarboxylate (BPDC) that demonstrated even larger surface area than BTB containing ligands [38]. Apart from the usage of pure or only one type of ligand, employing more than one ligand to form a single MOF was reported recently. Koh et al. [39] combined BDC and BTB ligands in different proportions to form different species of MOFs and it was reported that between the ratio of 6:4 and 5:5 of BDC over BTB, a new type of mesoporous MOF was generated and has been named as UMCM-1. Saha and Deng [40] also generated two types of hybrid MOFs consisting of BDC and BTB by employing two different solvents, DMF (N,N, dimethylformaide) and DEF (N,N, diethylformaide). In other work, Koh et al. [41], synthesized the hybrid MOF (UMCM-2) with the combination of BTB and thieno[3,2-b]thiophene-2,5-dicarboxylate (T^2DC) in 1:1 ratio, that possesses the BET surface area of more than 5000 m^2/g. Klein et al. [43] synthesized the hybrid mesoporous MOF DUT-6 with BTB and NDC (2,6-naphthalenedicarboxylate) in 3:2 mole ratio that possesses high pore volume of 2.02 cm^3/g. Despite the ubiquitous

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Table 1
Synthesis conditions of the metal-organic frameworks.

MOF identity	Metal salts	Salts amount (g)	BTB amount (g)	Thermal conditions
Al-BTB	$Al(NO_3)_3{\cdot}9H_2O$	0.171	0.2	90 °C, 24 h
Cr-BTB	$Cr(NO_3)_3{\cdot}9H_2O$	0.182	0.2	90 °C, 24 h
Fe-BTB	$Fe(NO_3)_3{\cdot}9H_2O$	0.270	0.2	80 °C, 3 days
Ga-BTB	$Ga(NO_3)_3{\cdot}xH_2O$	0.255	0.2	100 °C, 24 h

evidence that BTB ligand could provide high surface area and gas adsorption properties, it was not employed to form MOFs with any other metal, till today.

In this work, we combined BTB ligand with four different trivalent metals, aluminium, chromium, iron and gallium to form four types of metal-organic frameworks. Each type of MOF was performed materials characterization with pore texture, density measurement, scanning electron microscopy (SEM), Fourier-transform infra-red (FT-IR) spectra, thermogravimetric analysis (TGA) and X-ray diffraction to reveal the identity of the crystals. Hydrogen adsorption measurement was performed at 77 K and room temperature to examine the hydrogen sorption capacity of those MOFs.

2. Experimental methods

2.1. Synthesis of Al, Cr, Fe and Ga-BTB

All metal-organic frameworks of this present work were synthesized by solvothermal technique. In general, the corresponding metal salts or the metal precursors were dissolved in 25 mL ethanol, where as the BTB ligand was dissolved in 10 mL N,N-dimethylformamide (DMF) followed by mixing the two solutions and subjecting to thermal treatment. For Ga-BTB, both the precursor and the ligand were dissolved in 35 mL of DMF as the Ga precursor was sparingly soluble in ethanol. The exact identity of metal precursor, amounts of reagents and the thermal conditions are revealed in details in Table 1. After the thermal treatment, the crystals were separated from the solution and washed twice with DMF in order to remove any unreacted reagent. Finally, the DMF treated samples were washed several times with chloroform minimize the DMF level within the crystals and stored inside glovebox under argon atmosphere in closed container.

2.2. Materials characterizations

The materials characterizations techniques employed for each sample include pore textural properties, density measurement, Fourier-transform infra-red spectroscopy (FT-IR), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction technique.

The pore textural properties were calculated by nitrogen adsorption–desorption study at liquid nitrogen temperature (77 K) and pressure up to 1 bar in *Micromeritics* ASAP 2020 instrument. The pore textural properties BET surface area and pore size distribution by density functional theory (DFT) were obtained by analyzing the nitrogen adsorption and desorption isotherms with the built-in software in the ASAP 2020 surface area and porosity analyzer. The adsorbent samples were degassed *ex-situ* at 373 K for 24 h to

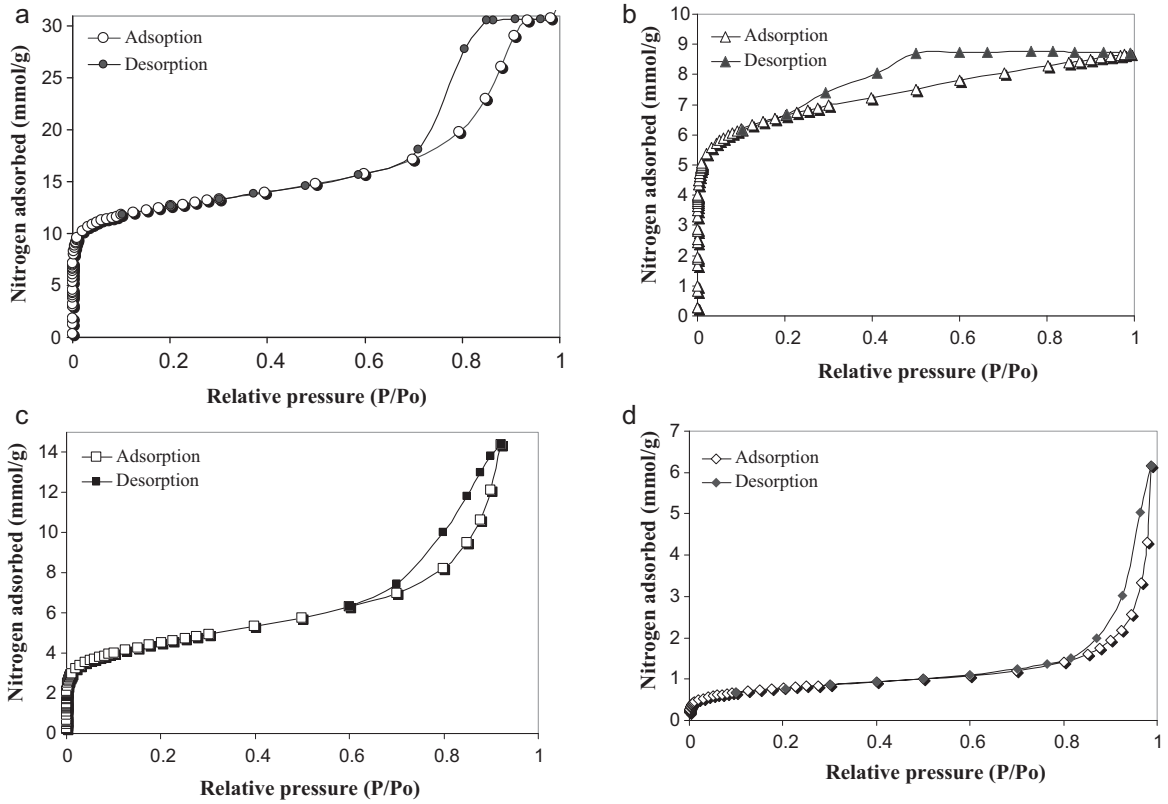

Fig. 1. N_2 adsorption–desorption plot of Al-BTB (a), Cr-BTB (b), Fe-BTB (c), Ga-BTB (d).