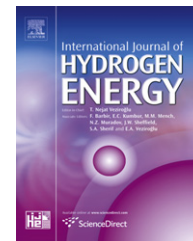


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Synthesis, characterization and hydrogen adsorption properties of metal–organic framework Al-TCBPB

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ABSTRACT

In this work, a new metal–organic framework (MOF) was synthesized by using a large organic ligand 1,3,5-tris[4'-carboxy(1,1'-biphenyl)-4-yl] benzene (abbreviated as TCBPB) and aluminum as the metal that forms the secondary building unit (SBU) by solvothermal method. The MOF, named as Al-TCBPB, was characterized with pore textural properties, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Raman and FT-IR spectroscopy. Hydrogen adsorption was measured volumetrically at ambient pressure and temperatures of 77, 88 and 298 K and at high pressure (up to 9 MPa) for temperatures 77 and 298 K. Pore textural properties revealed a high BET surface area of 2311 m²/g, narrow bimodal pore widths of 11.8 Å and 20 Å and a total pore volume of 0.80 cm³/g. PXRD identified the crystal structure as monoclinic with space group *c2/m*. This MOF adsorbs 1.53 and 0.83 wt.% of hydrogen at 77 and 88 K, respectively, and pressures up to ambient conditions. At higher pressure of 9 MPa, it demonstrated an excess adsorption of 4.8 and 1.4 wt.% at 77 and 298 K, respectively; these high-pressure data fit well with modified Dubinin–Astakov (D–A) analytical model. The heat of adsorption values of Al-TCBPB vary between 5.9 and 4.9 kJ/mol for the hydrogen adsorption loading of 0.1–0.8 wt.% and decreases monotonically to approximately 2 kJ/mol when the adsorption loading becomes 4.8 wt%.

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1. Introduction

Metal–organic frameworks (MOFs) are potential adsorbents for today's technology which can be attributed to their high specific surface area, controllable pore size and need-based tailoring of structural architecture leading to the large and selective gas adsorption capacities. Topologically, all MOFs consist of two structure building components: the metal ion coordinated with the oxygen atoms, known as secondary building units (SBUs) and the organic ligands that connect the SBUs to form the three or two-dimensional networks [1]. Till

today, a large number of MOFs have been reported in literature with the variation of metal center and organic ligands [2–10] and a large portion of these MOFs has been examined for their hydrogen adsorption capacities with an aim to contribute to the adsorptive hydrogen storage research program.

Use of aluminum in the secondary building units resulted in largest varieties of metal–organic frameworks after zinc, reported till today. MIL-53(Al) (MIL stands for Materials Institute of Lavoisier) is the first member of Al-based MOF series with 1,4-benzenedicarboxylic acid as the organic ligand

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[11–14]. It has a BET surface area of $\sim 1100 \text{ m}^2/\text{g}$ with H_2 adsorption capacity in the order of 3.8 wt.% at 77 K and 1.8 MPa with a hysteresis loop generated from the structural breathing effect from the crystal architecture. MIL-120(Al) [15] is composed of 1,2,4,5-benzenetetracarboxylic acid as the organic ligand. It possesses the BET and Langmuir specific surface areas of $308 \text{ m}^2/\text{g}$ and $432 \text{ m}^2/\text{g}$, respectively, and a hydrogen adsorption capacity of 1.3 wt.% at 77 K and 2 MPa. MIL-96(Al) [16,17] included trimesic acid as the organic ligand that resulted in BET and Langmuir surface area of $532 \text{ m}^2/\text{g}$ and $700 \text{ m}^2/\text{g}$, respectively. MIL-100(Al) [18] employed trimethyl-1,3,5-benzenetricarboxylate as the organic ligand to generate a MOF that bears largest specific surface area amongst any type of aluminum-based MOF (BET: $2152 \text{ m}^2/\text{g}$, Langmuir: $2919 \text{ m}^2/\text{g}$). MIL-100(Al) also possesses a DR-micropore volume of $0.79 \text{ cm}^3/\text{g}$ within the crystal size of 0.5 to $2 \mu\text{m}/\text{g}$. (It has a slightly high micropore volume of $0.82 \text{ cm}^3/\text{g}$ when determined using t-plot method.) MIL-69(Al) [19], MIL-118(Al) [20] and MIL-122(Al) [21] are the other Al-based MOFs that have been reported to contain 2,6-naphthalenedicarboxylic, pyromellitic and 1,4,5,8-naphthalenetetracarboxylic acids as the organic ligands, respectively. However, detailed pore textural and adsorption capacities of these MOFs were not reported.

Apart from the MIL series, Senkowska et al. [22] synthesized two other Al-based MOFs and named as DUT-4 and DUT-5 [22] (DUT stands for Dresden University of Technology) containing 2,6-naphthalenedicarboxylic acid and 4,4'-biphenyldicarboxylic acid respectively, as the organic ligands. DUT-4 has a pore volume of $0.68 \text{ cm}^3/\text{g}$ and exhibits hydrogen adsorption capacity of 2.1 wt.% at 77 K and 3 MPa, whereas DUT-5 has a the higher pore volume of $0.81 \text{ cm}^3/\text{g}$ with elevated hydrogen capacity of 3.3 wt.% under the same conditions.

Organic ligand molecules play a vital role in tuning the pore texture of the metal–organic frameworks. 1,4-Benzenedicarboxylate (BDC) is the most common organic ligand used for synthesizing different species of MOFs, including MOF-5 [2,4], MIL-53 (Cr, Al or Fe) [11–14,23] or MIL-101(Cr) [24,25]. However, the reported largest surface area and the maximum gas (H_2 and CO_2) uptake is observed for MOF-177, a MOF formed using benzenetribenzoate (BTB) as ligand and zinc as SBU former [3,5,8–10,26–30]. It has a BET specific surface area of approximately $3100 \text{ m}^2/\text{g}$ (determined using P/P_0 between 0.03 and 0.07) and a pore volume of $1.56 \text{ cm}^3/\text{g}$. The higher analog of benzenetribenzoic acid is 1,3,5-tris(4'-carboxy(1,1'-biphenyl)-4-yl) benzene (abbreviated as TCBPB, Fig. 1) where three additional benzene rings attached with phenyl rings and carboxylic groups of BTB giving rise to the ligand expansion with a possibility of greater surface area and pore volume. Daofeng et al. [31] reported a Zn-MOF and TCBPB with pyridine as deprotonation agent. However, they could not generate larger surface area because of loss of porosity owing to the inherent framework collapse upon removal of coordinated pyridine and water molecules. Therefore for the first time, we attempted to investigate the synthesis and hydrogen adsorption properties of an Al-based MOF generated by TCBPB as ligand.

The MOF was synthesized by solvothermal method. We performed materials characterization with pore texture, density measurement, scanning electron microscopy (SEM), Fourier-transform infra-red (FT-IR) and Raman spectroscopy,

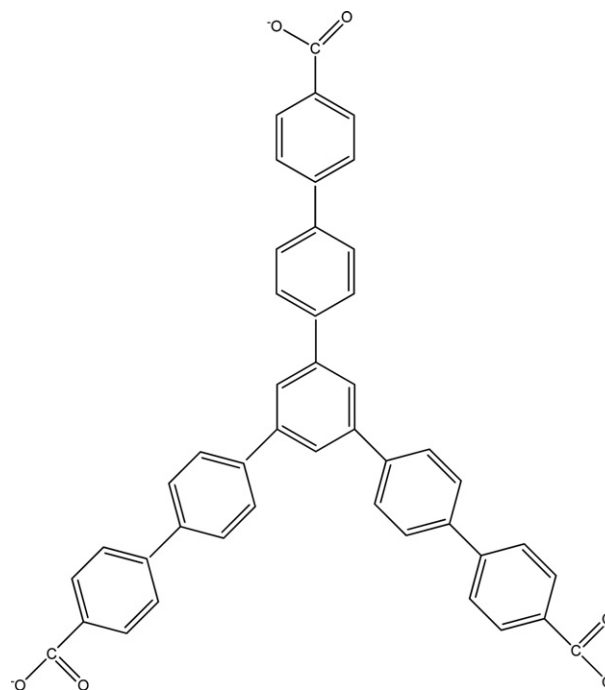


Fig. 1 – Molecular structure of 1,3,5-tris[4'-carboxy(1,1'-biphenyl)-4-yl] benzene (TCBPB).

thermogravimetric analysis (TGA) and X-ray diffraction to reveal the identity of the MOF crystals. Hydrogen adsorption was measured at ambient pressure and temperature at 77, 88 and 298 K and at higher pressures up to 9 MPa at 77 and 298 K.

2. Experimental methods

2.1. Synthesis of Al-TCBPB

Al-TCBPB was synthesized by solvothermal method. In a typical run, 0.40 g of aluminum nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma–Aldrich) and 0.11 g of TCBPB (Sigma–Aldrich) were dissolved in 30 ml of *N,N*-dimethylformamide (DMF) and transferred to an air-tight reaction vial. The vial was then transferred to an oven at $75 \text{ }^\circ\text{C}$, for 5 days. After the thermal treatment, the generated crystals were separated from the solution by filtration and washed thrice with DMF in order to remove any unreacted reagent. Finally, the DMF treated samples were washed several times with chloroform to exchange the DMF within the crystals and upon drying stored inside glovebox under argon atmosphere in closed container.

2.2. Materials characterizations

The bulk density was measured following the ASTM standard D 2854-96 whereas the skeleton density was measured by helium expansion experiment at ambient temperature and pressures less than 2 MPa. The pore textural properties were measured by nitrogen adsorption and desorption at liquid

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