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A study on metal organic framework (MOF-177) synthesis, characterization and hydrogen adsorption -desorption cycles

V.Viditha[1], M.Venkateswer Rao[1], K.Srilatha1[1], V.Himabindu[1], Anjaneyulu Yerramilli[2]

[1] Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad-500 085, A.P, India.
[2] Director, TLGVRC, JSU Box 18739, JSU, Jackson, MS32917-0939, USA.

Abstract
Hydrogen has long been considered to be an ideal alternative to fossil-fuel systems and much work has now been done on its storage. There are four main methods of hydrogen storage: as a liquid; as compressed hydrogen; in the form of metal hydrides; and by physisorption. Among all the materials metal organic frameworks (MOFs) are considered to have desirable properties like high porosity, pore volume and high thermal stability. MOF-177 is considered to be an ideal storage material. In this paper we study about its synthesis and hydrogen storage capacities of MOF-177 at different pressures ranging from 25, 50, 75 and 100 bar respectively. The obtained samples are characterized by XRD, BET and SEM. The recorded results show that the obtained hydrogen capacity is 1.1, 2.20, 2.4 and 2.80 wt%. The desorption capacity is 0.9, 2.1, 2.37 and 2.7 wt% at certain temperatures like 373 K.

Keywords: Hydrogen storage; MOF-177; Metal organic framework; Adsorption; Hydrogen.

1. Introduction

Hydrogen is considered as the fuel of future since it is environmental clean, abundant in nature and the most probable successor of conventional fuels. One problem that still must be solved is the storage of the hydrogen gas [1].
There are four main possibilities to store hydrogen

1) As a liquid
2) As a compressed gas
3) To split hydrogen molecules into atoms which form strong chemical bound with solids (chemisorption)
4) To bound molecular hydrogen to a sorbent with high specific surface area through the weak van der waals force (physisorption).

Hydrogen storage is considered to be the biggest challenge in a new hydrogen economy and is used in fuel cell application and mobile applications. The study of hydrogen storage materials is still being carried on in order to meet the requirements of the U.S. Department of Energy (DOE) as it suggested that an adsorbent should store 6.5 wt% of hydrogen or 62.5 kg m^{-3} for actual automotive fuel cell applications [2]. Most studies are going on materials like metal hydrides, alanates, and carbon materials to fulfill above requirements but unfortunately none of them could show satisfactory performance for commercial

vehicular applications [3] MOFs show a promising way to solve the hydrogen storage problem for vehicular applications because of its high specific surface area and thermal stability. MOFs are a rapidly growing class of micro porous materials. MOF-177 is a porous crystalline material that consists of $[Zn_4O]^{+}$ units connected with benzene tribenzoate (BTB) ligands [4]. MOFs do not need high temperature or pressure changes to store and retrieve the hydrogen. Much work on MOF-177 has been done by various groups like Rowsell, Li and Yang, David J et al, Yingwei and Ralph et al, Dipendu saha et al, Hiroyasu Furukawa et al and they carried out hydrogen storage studies at various temperatures ranging from 77 K, 298 K, 323 K, 194 K and obtained around 1.45 wt%, 1.36 wt %, 0.92 wt%, 1.25 wt %. In this paper we discuss about the hydrogen storage results obtained for MOF-177. The adsorption capacity is around 2.8 wt % at 100 bar. Synthesized MOF-177 was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET. One of the promising ways of increasing the hydrogen adsorption capacity is to intercalate the adsorbent with transition metals like lithium, palladium, vanadium and some researchers are trying to improve the hydrogen adsorption capacity.

2. Materials and methods

2.1 Materials

All the chemicals used for MOF-177 synthesis in this work are purchased from M/s. Sigma Aldrich India Pvt. Ltd and are of highest purity. Benzene tribenzoic acid, Zinc acetate dihydrate, Diethyl form amide and Chloroform.

2.2 Synthesis of MOF- 177

The MOF-177 is synthesized at room temperature. A known amount of benzene tribenzoic acid (626 mg) and Zinc acetate dihydrate (2.51 g) were stirred with a known volume of diethyl formamide for 3 h, forming a powder of MOF-177. The product was collected by filtration and immersed in 40 mL of chloroform to remove the impurities. The MOF-177 sample is activated under vacuum at $120\ ^{0}$C for 12 h and the product was collected [5].

2.3 Hydrogen adsorption unit

The high-pressure hydrogen adsorption/desorption experimental setup as given in (Figure 1) consists of two adsorber assembly units (AAU). Each AAU consists of measuring section, heater and sample cell assembly. The measuring section is attached to the main frame unit used to monitor the hydrogen pressure is connected to the pressure transducers of range (0 – 148 bar) procured from Keller, USA. A heater attached to the main frame to remove any undissolved gases and for the activation of the pores of the sample taken in the quartz tube is provided with water circulation to avoid the O- ring from over heating. Sample cell assembly comprises of a cylindrical outer SS-block into which a cylindrical copper block is fitted. To allow the sample to be placed inside the copper block, it has a drill with 10 mm diameter. The sample is taken in a quartz tube of 6 mm inner diameter, which is inserted into the sample cell. The sample cell is kept inside a vertical tube furnace for studying the hydrogen storage properties at different Pressures. The main frame consists of stainless steel tubes, tees, elbow joints and needle valves are procured from Swagelok USA which can withstand up to a maximum pressure of 350 bar. It also consists of piping and reference vessels which are used for passage of gas and calibration purposes. A turbo molecular pump attached to the main frame is used for complete evacuation of the system up to 10^{-9} mbar. A K-type thermocouple is introduced into the AAU to monitor the temperature of the furnace. The unit is tested for leaks at high pressures using nitrogen and leaks were arrested by tightening the bolts [6].

3. Hydrogen – storage measurement

The specific surface area and pore volume are two factors that govern the hydrogen storage in MOF materials [7]. Before we start our experiments the leaks should be arrested by carrying out the leak test with gases and the bolts were tightened. The experiments are performed using a volumetric setup that had been tested for leaks. Initially, a known volume of hydrogen gas is inserted and it is taken as initial pressure (P1) for regular interval of time the pressure drop is noted and at a certain point the pressure gets stable it is noted down as (P2). Hydrogen adsorption and desorption studies are carried out at 25, 50, 75, 100 bar respectively. The hydrogen adsorption capacity is expressed in terms of wt%. For the calculation of hydrogen concentration present in the material, the Vander Waals equation of state is used. It is defined as:

$$W_t\% = \frac{\text{Weight of the hydrogen molecules}}{\text{Weight of the material}} \times 100$$

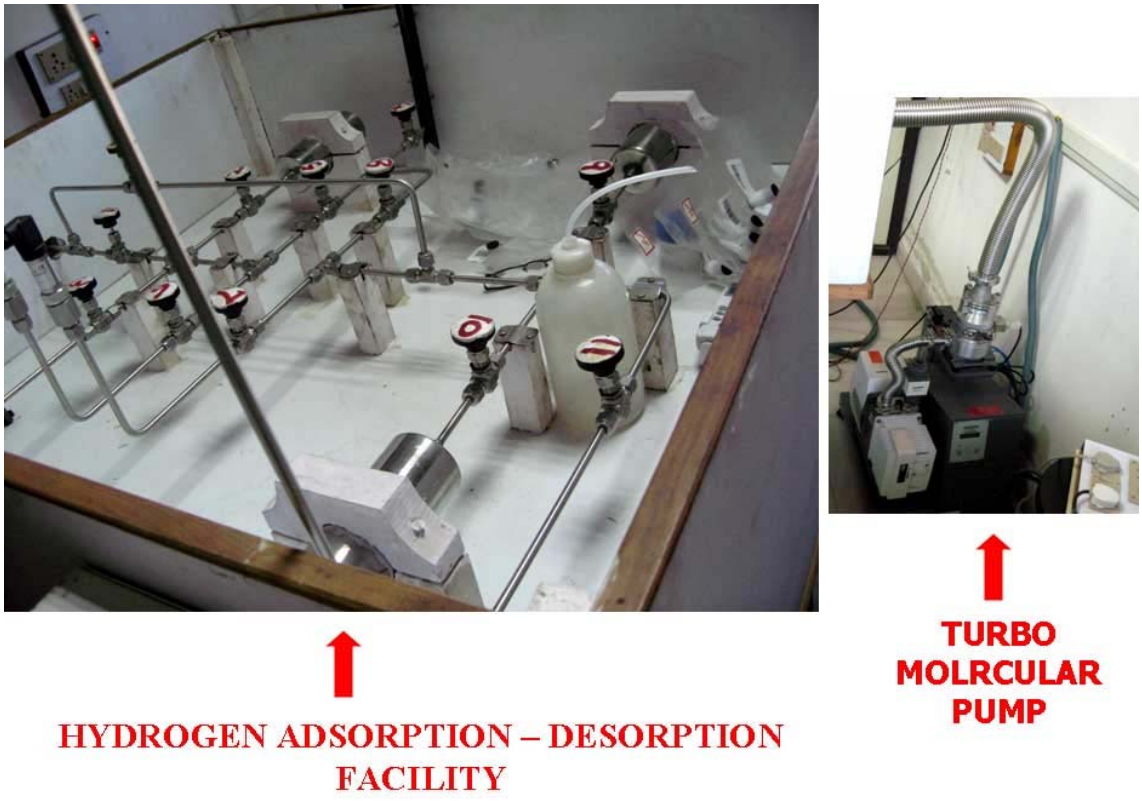


Figure 1. Hydrogen adsorption unit

4. Results and discussions

4.1 SEM studies

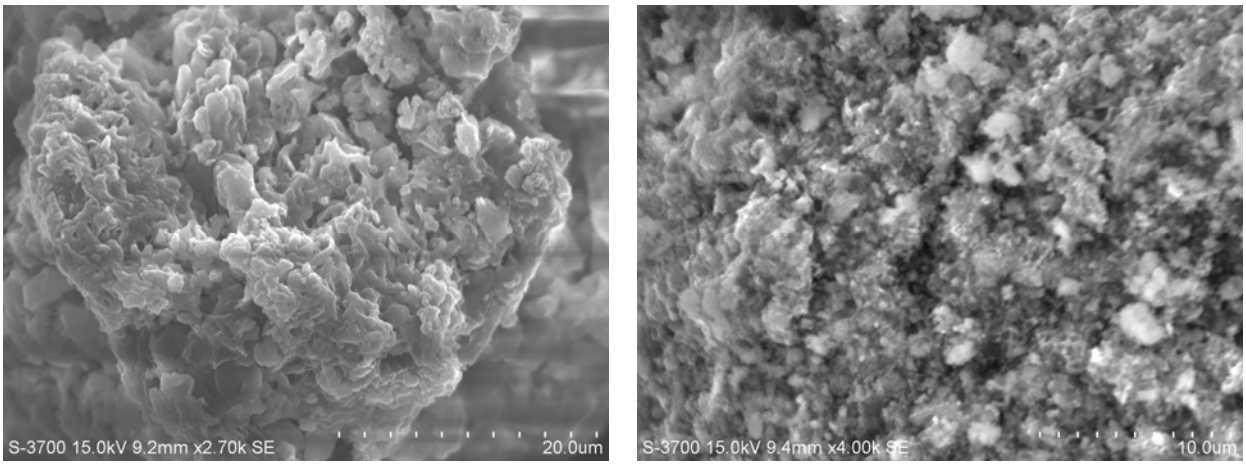
The morphologies of the material were observed with SEM method. The SEM images of MOF-177 are enclosed in Figure 2 that appeared is carried out using Hitachi S-3700 variable vacuum SEM at an accession voltage of 15.0 KV, using a carbon conducting tape adhered on aluminum stub. The definite crystal shape is not observed, most probably due to the polycrystalline agglomerate nature. The images of MOF-177 show a high surface area and porosity. The MOF-177 is a cream color powdery material. The high crystallinity of MOF-177 leads to higher specific surface area and probably better adsorbent for hydrogen storage [8].

4.2 XRD studies

The powder XRD patterns of the dried samples are recorded on a Shimadzu XRD-7000 X-ray diffractometer using CuKα1 radiation and operating at 40 kV and 30 m A. Using ICDD PDF2 release library, the three major strongest peaks 2θ = 36.2966, 2 θ = 31.7593 and 2 θ = 34.5600 are well identified and show the crystalline nature of the material in the enclosed Figure 3. The major peaks in the XRD patterns of MOF-177 reported in different publications are quite consistent. However, the peak positions and the location of the strongest peak are shifted to a small extent. The pore size mainly determines the interaction between hydrogen and the metal-organic frameworks [9]. The high surface area confirms the formation of MOF-177 structure.

4.3 FT-IR

Figure 4 shows the IR spectrum of as synthesized MOF-177. The observation of the strong broad bands between 2496.7 and 3566.9 cm -1 confirms the presence of carboxyl groups. The presence of characteristic bands of the framework – (o-c-o) – groups around 1424.5 and 1383.5 cm -1 indicate the presence of the dicarboxylate within the MOF-177 sample. The strong peak at 1594.9 was the characteristic peak for DEF (C=O) solvent.



(a) (b)

Figure 2. SEM image of MOF-177

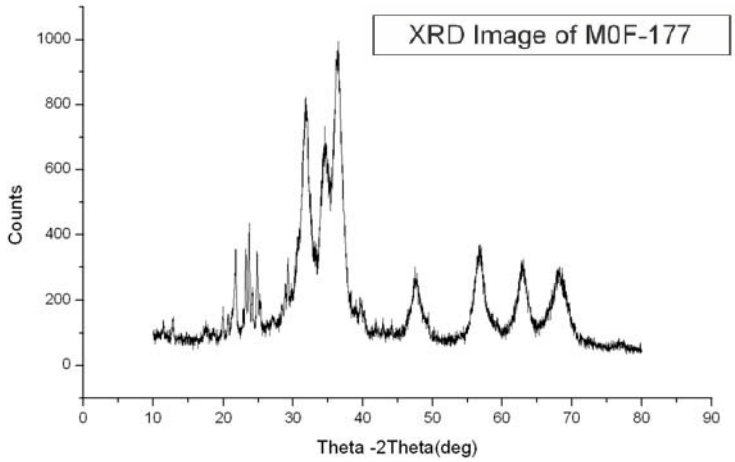


Figure 3. XRD image of MOF-177

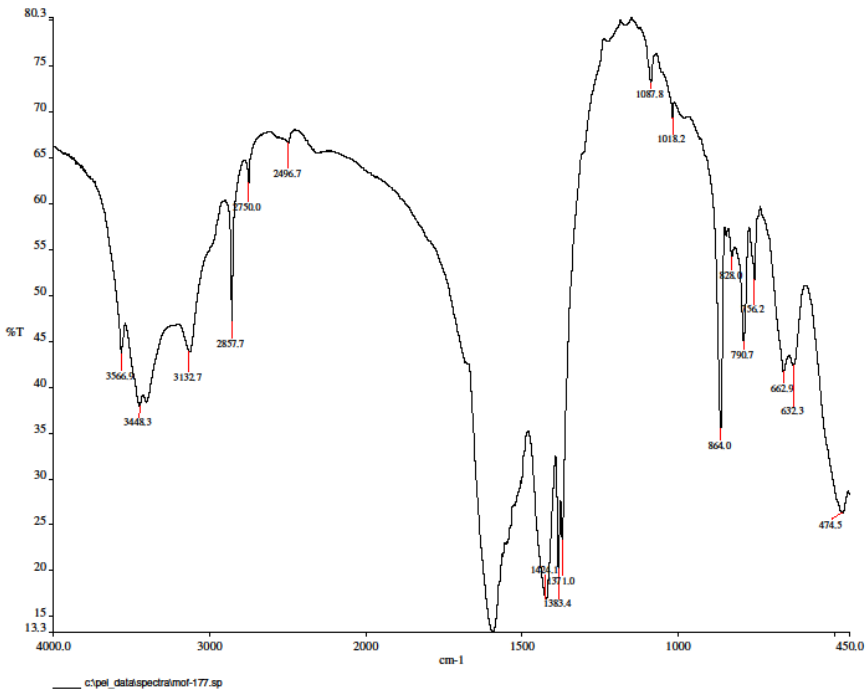


Figure 4. FT-IR spectra of MOF-177

4.4 Nitrogen sorption measurements

The BET (Brunauer, Emmett, and Teller) measurements from these crystals yield a surface area of 2500 m2 /g and a pore size of 1.3 m^3/g. The pore size mainly determines the interaction between hydrogen and the metal-organic frameworks. The high surface area confirms the formation of MOF-177 structure.

5. Hydrogen storage results

The hydrogen adsorption and desorption graph is given in Figure 5. In order to meet the DOE, USA targets several novel hydrogen storage materials have been introduced and much research is going on with alanates, amides, MOFs and amino borane. Among these all the MOFs are considered to be the best adsorbents as they have got more advantages than other materials. Much theoretical work is going on with materials like alanates and around 5.6 wt % at 77 K for 1 bar. The hydrogen adsorption on MOF-177 were studied in the ambient temperature region and at four different pressures like 25, 50, 75, 100 bar. The recorded results show that the obtained hydrogen capacity is 1.1, 2.20, 2.4 and 2.80 wt%. The desorption capacity is 0.9, 2.1, 2.37 and 2.7 wt% at certain temperatures like 373 K.

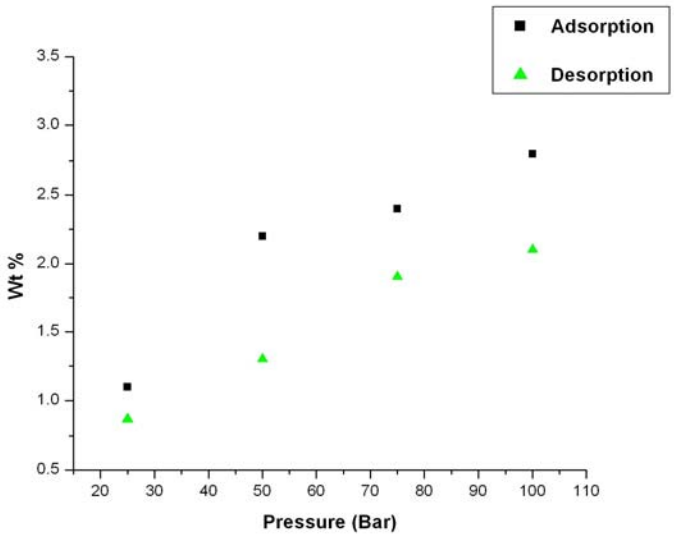


Figure 5. Adsorption and Desorption Isotherm of MOF-177

5.1 Hydrogen adsorption –desorption cycling studies

The hydrogen adsorption – desorption cycling induced by pressure change in a closed system were carried out with MOF-5. The half capacity life of MOF-5 can be projected as 3 cycles for room temperature pressure cycling. In a closed system the impurity level of hydrogen gas is extremely low compared with that of open system where a new hydrogen gas of 99.99% purity is dosed for every cycle [10].

6. Conclusion

In conclusion we can assume that MOF-177 is a good material for hydrogen storage. Among the hydrogen adsorbent materials like metal hydrides, zeolites and carbon materials even though they got better surface area and better adsorption capacity they also got disadvantages like heavy weight hydrides, high gravimetric density and requires high temperature for desorption. Moreover, to overcome these drawbacks materials like MOFs are considered as compatible hydrogen adsorbent because of very low density, high surface area, and large porous volume. The present study discusses about the synthesized MOFs at room temperature, the morphology and hydrogen adsorption capacity. The hydrogen adsorption capacities of MOF-177 are 1.1, 2.22, 2.40 and 2.8 wt% at 297 K and at 25, 50, 75 and 100 bar results in using MOF-177 as a good hydrogen storage material for mobile applications.

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V. Viditha completed his Masters Degree in chemistry, Acharya Nagarjuna University, Guntur, Andhra Pradesh, India, at present he is working as a research scholar on Hydrogen storage on metal hydrides.

M. Venkateswer Rao He has completed his master's degree in industrial chemistry from Jawaharlal Nehru Technological University Hyderabad. He is working on flame synthesis.

K. Srilatha She has completed his master's degree in industrial chemistry from Jawaharlal Nehru Technological University Hyderabad. she is working on thermo catalytic decomposition of hydrocarbons.

V. Himabindu She has completed her masters in environmental chemistry from SV university and Ph.D from JNT University. She is working as Associate professor in the Centre for Environmental sciences, JNTU. She has 30 peer reviewed journals.
E-mail address: drvhimabindu@gmail.com (or) viditha.v@gmail.com; Tel: +91-040-23156133 Fax: +91-040-23156133

Anjaneyulu Yerramilli has completed her masters in chemistry from Andhra University and Ph.D from Andhra University. He was working as Director, TLGVRC, JSU, Jackson, USA. He is having 50 peer reviewed journals.

