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Use of waste TPA in the synthesis of a metal organic framework (MOF) for use in hydrogen storage

DOAN VAN HUAN[1], **VALESKA TING**[2]

[1]Hanoi University of Mining and Geology, [2]University of Bath

Abstract

The need to reduce global reliance on fossil fuels by the use of alternative technologies has pushed hydrogen to the forefront of gas storage applications. This research is focused on a metal organic framework material, MOF-5, which has appealed to a number of scientists for application in hydrogen storage. However, MOF synthesis often requires expensive starting materials. Cheaper sources of starting materials need to be identified if economical large-scale use of MOFs is to become practically feasible. In this research, MOF-5 was prepared by solvothermal method and using spent terephthalic acid (TPA) waste from PetroVietnam Petrochemical and Textile Fiber Joint Stock Company (PVTex) as a starting material. Products in this research were then characterized by X-Ray diffraction (XRD), Infrared Spectroscopy (IR), Thermogravimetric analysis (TGA), Scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area analysis. The results showed typical cubic crystals from SEM analysis, and XRD analysis of the synthesized sample showed peaks consistent with the published structure of MOF-5. In addition, with the high porosity and high thermal stability, this material will have prospective application in hydrogen storage, demonstrating that waste TPA has potential for use as a sustainable starting material for synthesis of MOFs for gas storage.

Keywords: hydrogen storage, storage capacity, metal organic framework, MOF

1. Introduction

It is true that humans nowadays encounter numerous problems caused by our heavy reliance of fossil fuels, such as the limited supply and climate change caused by the build-up of carbon dioxide and other greenhouse gases. This led to the need for sustainable energy which has attracted extensive attention from scientists in recent years. Of investigated energies, hydrogen is considered a promising energy carrier in future energy systems [1]. However, one of the key challenges for the commercialization of hydrogen energy is the development of appropriate onboard hydrogen storage systems, capable of storing, charging and discharging large quantities of hydrogen with fast enough kinetics to meet commercial requirements [2, 3].

Adsorbing hydrogen onto a high-surface area material is one of the most attractive solutions for a number of reasons. For example, adsorptive storage is fully reversible and the hydrogen maintains its molecular form, and while there is a minor drawback of low interaction energies meaning cryogenic temperatures are required, the operating temperatures and pressures required for adsorptive storage are less extreme than those required for storage of hydrogen as a cryogenic liquid or high pressure gas, respectively. In addition, adsorptive storage can increase the volumetric density of the stored hydrogen, making it more appropriate for on-board energy storage in vehicles [4, 5].

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[1] Tel: +84988668120
Email: doanvanhuan@humg.edu.vn

Examples of high-surface area materials which can be used in hydrogen storage include porous activated carbons, zeolites, porous polymers and metal organic framework (MOF) materials. MOFs are a relatively new class of materials that have attracted widespread attention because of their potential in a variety of applications. Application of MOFs in fuel storage (e.g. as methane or hydrogen) has recently become a popular research topic [6, 7]. MOF-5 [8] with high porous cubic structure and high thermal stability (over 250 ^{o}C) is an isoreticular MOF (IRMOF) which is has been investigated for its potential as a hydrogen storage material. However, it is well-known that gas adsorption measurements can be greatly dependent on sample preparation and activation procedures used [9]. In addition, while MOF materials can display promising hydrogen sorption capacities, they typically necessitate expensive starting materials to produce. Exploring new and cheaper sources of starting materials for production of MOFs is necessary for the large scale production of MOF materials. Here we report the attempted synthesis of the archetypical MOF (MOF-5) from waste TPA starting material.

TPA also known as terephthalic acid was used principally as a precursor to the polyester PET. Following development of the chemical industry in Vietnam, the first Vietnamese polyester manufacturing plant was built on 22 March, 2008. This led to a huge amount of TPA being produced annually. Meanwhile, the majority of this substance is wasted, in the absence of a recycling process. The purpose of this research was to make use of this resource and therefore reduce the cost of MOF synthesis.

2. Experimental

The synthesis of MOF-5 followed the solvothermal procedure published by Yaghi *et al*. [8]. 1,4-benzenedicarboxylic acid (H2BDC) used in this research was gathered from PVTex as a solid industrial waste, spent TPA. This spent acid was recrystallized at 300 ^{o}C - the melting point of H2BDC to obtain the pure acid.

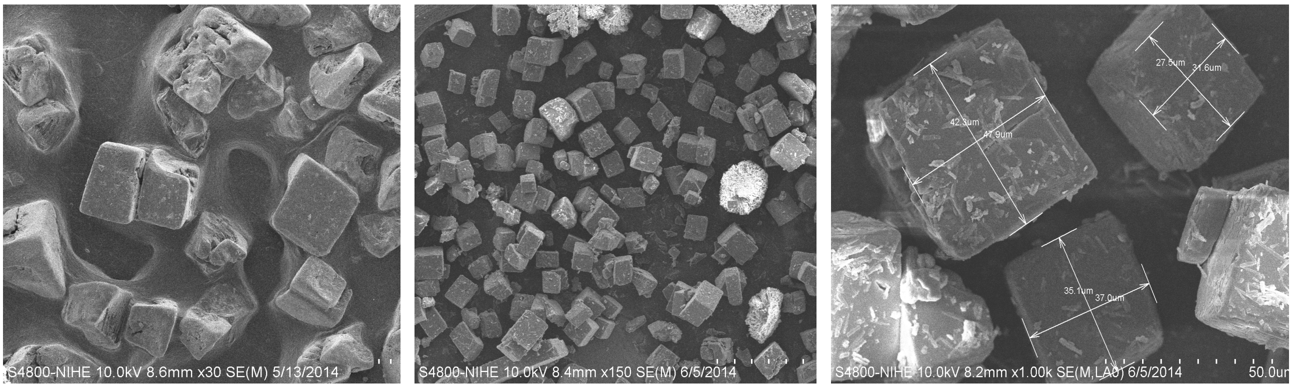
To synthesize MOF-5, 476 mg, 1.60 mmol of $Zn(NO_3)_2.6H_2O$ and 66.5 mg, 0.4 mmol of H2BDC were dissolved in 10 ml dimethylformamide (DMF). The product of this reaction was tempered in a Teflon container at 100 °C over 48 h. Then this mixture was cooled to room temperature before the crystals were recovered by filtration. The obtained white crystals were washed threefold with 10 ml DMF, then were stored in anhydrous DMF solution.

The products were tested by modern chemical analysis methods including XRD, IR, TGA and SEM. The result of surface area measurements for the different samples analyzed by BET method will be reported in further research with the investigation of the effects of solvents and acids in the optimization of MOFs structure.

3. Results and discussion

3.1. SEM analysis

SEM images of the clear synthesized materials (Fig. 1) showed that while some of the synthesized crystals were irregularly shaped, the majority had the cubic shape typical of MOF-5, with crystals ~20-50 μm in size.

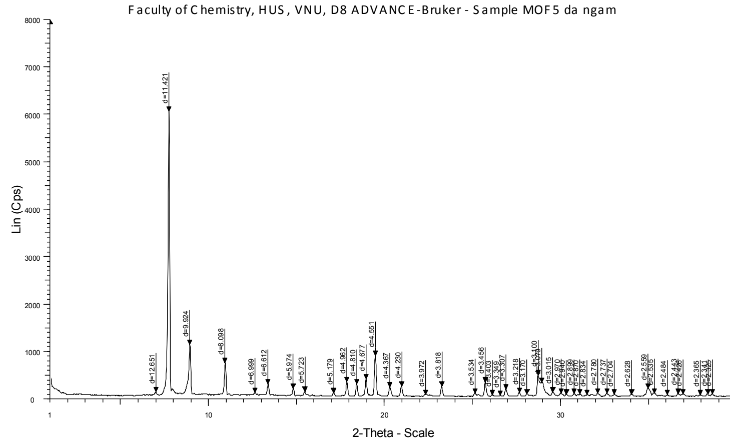


a) 30 times magnification b) 150 times magnification c. 1000 times magnification

Figure 1. SEM images of synthesized MOF-5

3.2. XRD analysis

Powder X-ray diffraction was used to determine the structure of the cubic materials synthesized from $Zn(NO_3)_2.6H_2O$ and H2BDC in the ratio of 4:1 in DMF solvent. From the previous research, MOF-5 has intense peaks in the range of 2θ from 10-40. In our research, the results of powder XRD analysis for the MOF-5 sample showed sharp and narrow diffraction peaks (see Fig. 2). This indicated the formation of a crystalline structure during the synthesis process. From the spectra below, there are peaks at 6.8°, 9.7°, 14° and 15.8° in 2θ, which can also be seen in published MOF-5 spectra in Yaghi's research (Fig. 3) [8]. Note that the presence of other small diffraction peaks from 17° onwards is because solvent was not eliminated from MOF-5 completely prior to XRD analysis.



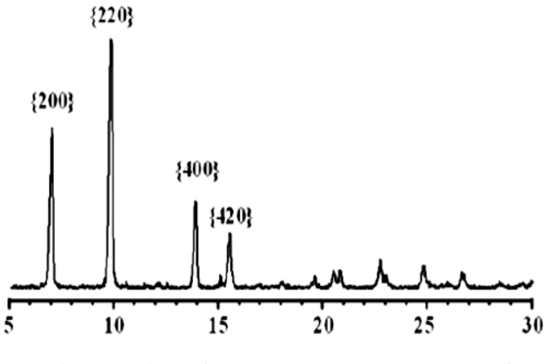


Figure 2. The X-Ray spectrum of synthesized crystal

Figure 3. The X-Ray spectrum of MOF-5 synthesized by Yaghi et al. [8]

3.3. IR analysis

IR spectroscopy helps to identify specific functional groups in organic compounds. The IR spectrum of synthesized MOF-5 (Fig. 4) has a high intense peak at 1568 cm^{-1} which is characteristic of the C=O group of carboxylate. The position of this peak has a small difference with that of H2BDC (peak at 1663 cm^{-1}), thus we predicted that there was a reaction between carboxylic acid and Zn^{2+} which shifts this C=O linkage in acid. In this spectrum, the peak at 1567 cm^{-1} was characteristic of the structure of an aromatic group, the peak at 730 cm^{-1} and 901 cm^{-1} were H atom in benzene. The wide range of peaks from 2937 cm^{-1} to 3547 cm^{-1} showed the presence of H_2O which indicated that the moisture was not fully eliminated from the sample.

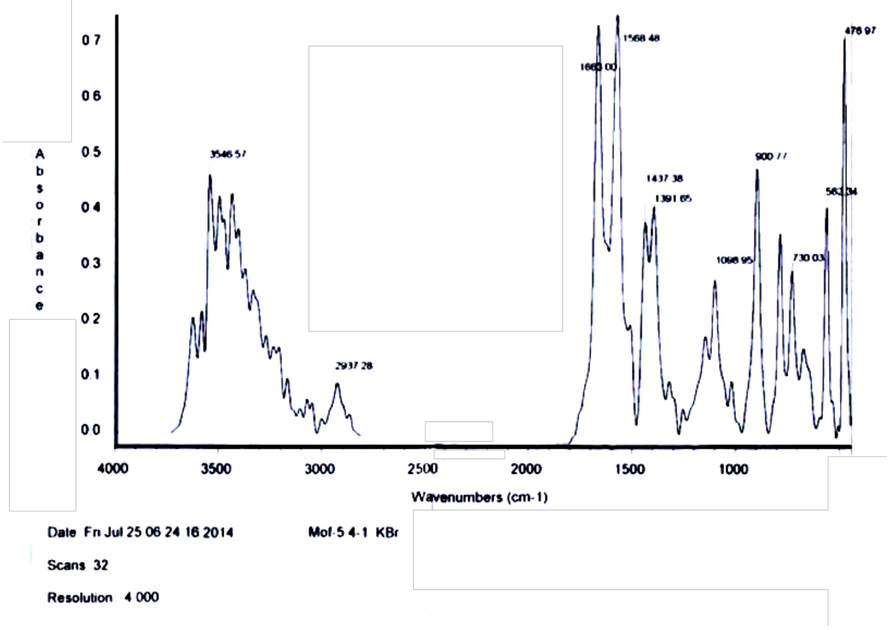


Figure 4. IR spectrum of the synthesized sample

3.4. TGA analysis

The thermal stability of MOF-5 was tested by thermogravimetric analysis (TGA). A 23 mg sample of MOF-5 was run on a TGA Q500 themogravimetric analyzer over a temperature range from 25 – 800 °C (ramp rate = 5 deg min^{-1}) under a flow of nitrogen. In the spectrum (Fig. 5), a small weight loss of 2.6% at ~285 °C is caused by the amount of solvent or moisture in the sample. From 285 °C to 450 °C, there was an extreme change, with ~68% of mass reduction. This is because the organic compounds in the sample decomposed, in other words, the sample became an inorganic material. A slow mass reduction of the sample from 450 °C to 800 °C was due to the decomposition of inorganic components. So, the MOF-5 is thermally stable up to ~285 °C. This helps this material to have a wide range of applications.

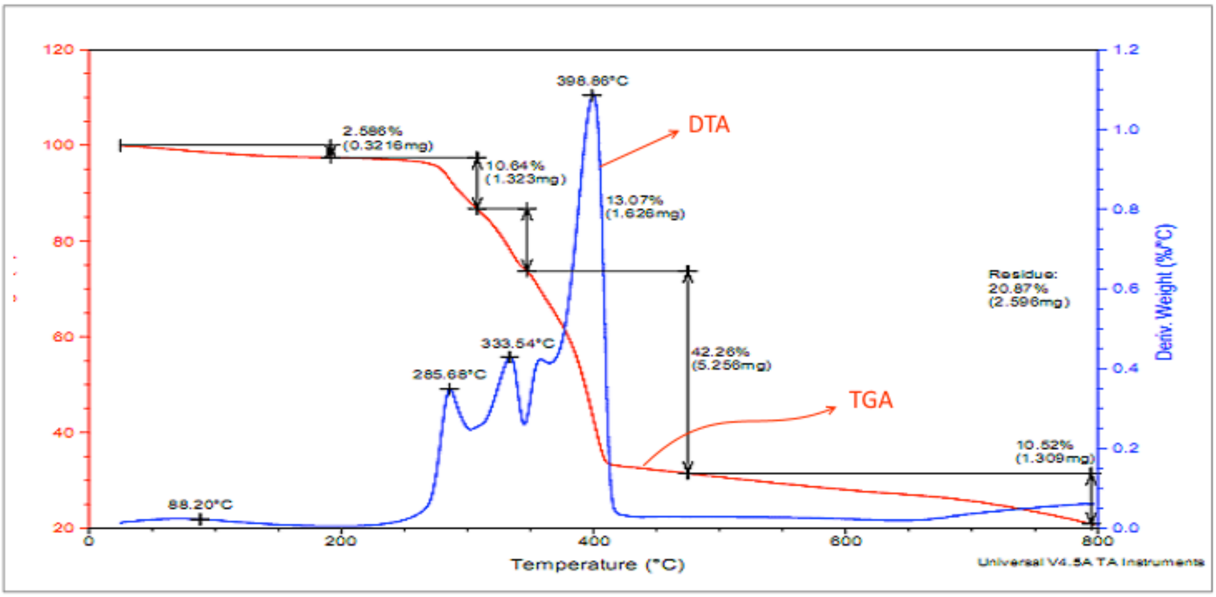


Figure 5. TGA of synthesized MOF-5

3.5. BET analysis

The surface area of these samples was obtained using the BET method, as applied to nitrogen sorption analysis with 5 points P/P_o from 0.05 to 0.3 at -196.15 ^oC (77 K) on a Quantachrome NOVA 2200e. The sample was degassed under high vacuum at a temperature of 170 ^oC for 4 h prior to analysis. The surface area calculated by Quantachrome^{TM} Novawin software was 1424 m^2 g^{-1}, far below the reported value of 2900 m^2 g^{-1} by Yaghi *et al.* [8]. This figure indicates that the material is likely to be microporous. However, this will be optimized in future work.

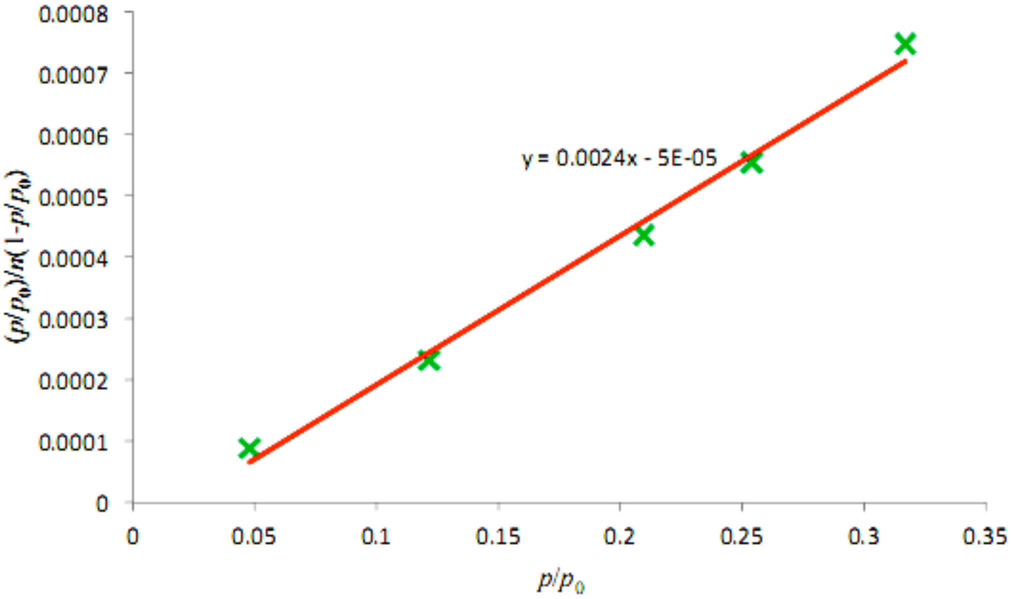


Figure 6. The BET plot from the synthesized MOF

4. Conclusions

Synthesis of the material MOF-5 using TPA from spent industrial waste was attempted by solvothermal method. The resulting crystalline solid was characterized by modern chemical analysis methods including IR, XRD, SEM, TGA and BET. The results showed that crystalline MOF samples synthesized from waste TPA starting material were able to produce cubic crystals with high surface area and high thermal stability.

References

1. Ulrich Eberle, Michael Felderhoff, and Ferdi Schuth, Chemical and Physical Solutions for Hydrogen Storage, *Angewandte Chemie International Edition.* (2009), **48**, 6608 – 6630.

2. Deborah Durbin, Cecile Malardier-Jugroot, Review of hydrogen storage techniques for on board vehicle applications, *International Journal of Hydrogen Energy* (2013), **38**, 14595-14617

3. U.S. Department of Energy, Targets for onboard hydrogen storage systems for light-duty vehicles. http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targetsonboardhydrostorageexplanation.pdf (Accessed July 2014)

4. Andreas Züttel, Arndt Remhof, Andreas Borgschulte and Oliver Friedrichs, Hydrogen: the future energy carrier, *Philosophical Transactions A.* (2010), **368,** 3329–3342.

5. Nuno Bimbo, Valeska P. Ting, Jessica E. Sharpe, Timothy J. Mays, Analysis of optimal conditions for adsorptive hydrogen storage in microporous solids, *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* (2013), **437**, 113-119

6. Bo Xiao, Qingchun Yuan, Nanoporous metal organic framework materials for hydrogen storage, *Particuology.* (2009), **7**, 129-140.

7. Tina Düren, Lev Sarkisov, Omar M. Yaghi and Randall Q. Snurr, Design of new materials for methane storage. *Langmuir.* (2004), **20**(7), 2683–2689.

8. Hailian Li, Mohamed Eddaoudi, Michael O'Keeffe, Omar M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nature*. (1999), **402,** 276.

9. Michel Latroche, Suzy Surblé, Christian Serre, Caroline Mellot-Draznieks, Philip L. Llewellyn, Jin-Ho Lee, Jong-San Chang, Sung Hwa Jhung and Gérard Férey, Hydrogen Storage in the Giant-Pore Metal–Organic Frameworks MIL-100 and MIL-101, *Angewandte Chemie International Edition.* (2006), **45**, 8227–8231.