

SYNTHESIS AND CHARACTERIZATION OF COPPER TEREPHTHALATE

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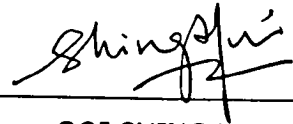
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A handwritten signature in black ink, appearing to read 'Zuripulic', written above a horizontal line.

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ABSTRACT

Copper terephthalate, with its high pore volume, high surface area and large number of open metal sites, is one of the well-known metal-organic framework materials. It was synthesized by mixing copper (II) nitrate trihydrate and 1,4-benzenedicarboxylic acid in *N,N*-dimethylformamide solution through sonication method. The light blue product was identified as pure copper terephthalate crystals. Besides, copper terephthalate is cubic crystal with minimum particle diameter of 2 μm . Thermal stability analysis showed that the copper terephthalate crystal was able to withstand temperature up to 360 $^{\circ}\text{C}$. Chemical stability experiment revealed that copper terephthalate is stable in water, methanol and ethanol for at least 7 days.

SINTESIS DAN PENCIRIAN KUPRUM TEREPHTHALATE

ABSTRAK

Kuprum terephthalate, dengan isipadu liang yang tinggi, luas permukaan yang tinggi dan tapak logam terbuka yang banyak, adalah salah satu bahan rangka kerja logam organic yang paling terkenal. Kuprum terephthalate telah disintesis dengan mencampurkan kuprum (II) nitrat-trihydrate dan asid 1,4-benzenedicarboxylic dalam larutan N,N-dimetilformamid melalui tindakan sonik. Produk biru muda telah dikenalpasti sebagai hablur kuprum terephthalate yang tulen. Selain itu, hablur kuprum terephthalate berbentuk kiub dengan diameter minima sebanyak 2 μm . Analisis kestabilan terma menunjukkan bahawa hablur kuprum terephthalate mampu menahan suhu sehingga 360 °C. Eksperimen kestabilan kimia mendedahkan bahawa kuprum terephthalate adalah stabil dalam air, metanol dan etanol sekurang-kurangnya 7 hari.

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LIST OF SYMBOLS AND ABBREVIATIONS

CO ₂	Carbon dioxide
CSD	Cambridge Structural Database
Cu(NO ₃) ₂ •3H ₂ O	Copper nitrate trihydrate
D	Domain size
DMF	N,N-dimethylformamide
DSC	Differential scanning calorimeter
H ₂ BDC	1,4-benzenedicarboxylic acid
IUPAC	International Union of Pure and Applied Chemistry
LPG	Liquefied petroleum gas
MOFs	Metal organic frameworks
NO	Nitrogen monoxide
SEM	Scanning electron microscope
SO ₂	Sulphur dioxide
TGA	Thermogravimetric analyzer
TPA	Terephthalic acid
XRD	X-ray diffractometer
VOCs	Volatile organic compounds

CHAPTER 1

INTRODUCTION

1.1 Metal Organic Frameworks (MOFs)

Metal organic frameworks (MOFs) are subclass of hybrid porous solid which are built up by metal atoms linked together by multifunctional organic ligands (Leus *et al.*, 2012). Rapidly emerging as a new class of nanoporous material, MOFs have attracted tremendous research in the academic community over the past decade (Hu *et al.*, 2009). The research results in thousands of different MOFs structures have been synthesized and categorized in Cambridge Structural Database (CSD) today (Keskin and Kizilel, 2011). These large number of structures are due to the large variety in possible combinations of organic and inorganic subunits of MOFs (Ghysels *et al.*, 2013).

Compared to other porous materials, MOFs have gained massive interest due to their distinct features of high porosity, low density and large surface area. Modulated pore sizes of MOFs range from microporous (less than 2 nm) to macroporous (more than 50 nm), endowing them in enormous high surface area of more than 3000 m²g⁻¹ (Jiang and Xu, 2011). Besides, MOFs have flexible structure that can adjust themselves to accommodate incoming gases or liquids. MOFs can be obtained in high yield and low cost as they can be synthesized using hydrothermal, solvothermal, ionothermal and microwave method (Chang, 2008).

MOFs have a series of functional groups that can be grafted onto linker, giving perspectives of different applications such as hydrogen storage, gas separation, catalysis and drug delivery (Gu *et al.*, 2012). Furthermore, MOFs display



excellent properties in sensing and imaging device due to their high porosity and high surface area (Li and Xu, 2013). Recently, MOFs have been suggested as separating materials and proton conducting materials that allow protons to be transported at high temperature and relatively low-humidity environments in fuel cell technology (Paesani, 2013).

1.2 Copper Terephthalate

MOFs incorporating terephthalic acid (TPA) have been known since 1967. Nickel terephthalate compound was synthesized by Acheson and Galwey (1967) while other hydrated metal terephthalate compounds such as iron, chromium, cobalt, copper, silver, manganese, lanthanum terephthalate were synthesized by Sherif (1970). Compared to other terephthalate series such as cobalt, nickel and zinc terephthalate, copper terephthalate, with lamellar geometry structure occupies a prominent position because of its high pore volume, high surface area and large number of open metal sites (Figure 1.1) (Anbia and Sheykhi, 2012). The first copper terephthalate with large surface area was reported by Mori *et al.* (1997).

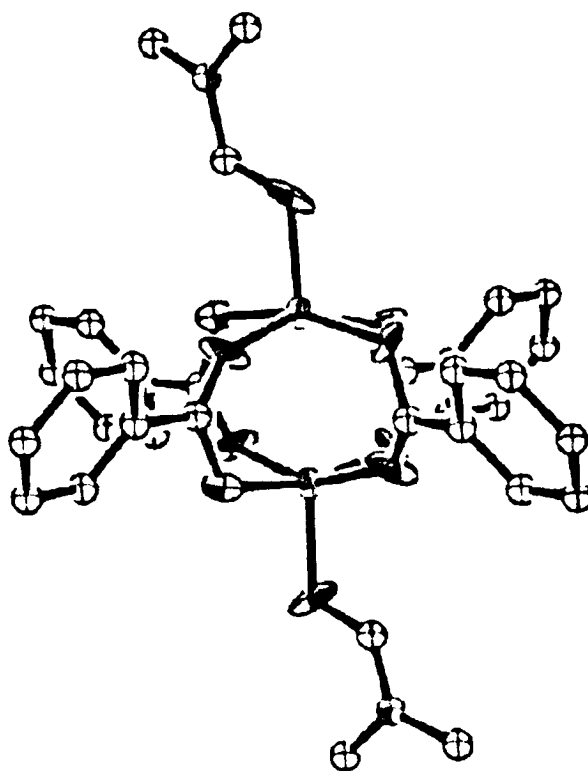


Figure 1.1: Open metal sites of copper terephthalate (Carson *et al.*, 2009).

Copper terephthalate, with open coordination sites, has the potential to perform both homogeneous and heterogeneous catalytic behaviour. Compare to zeolite, copper terephthalate has the advantage in its ability to be 'tuned' to reactions of delicate molecules (Alaerts *et al.*, 2006). Besides, copper terephthalate exhibits a markedly higher surface area, making it a superior material for gas separation and sieving application such as removal of sulphur dioxide, nitrogen monoxide and volatile organic compounds emission (Panasyuk *et al.*, 2007).

Metal organic frameworks connected by rigid or semi-rigid organic linkers are fascinating candidates that can provide very high surface area and controllable pore sizes for energy storage. The tuning of the pore size and enhancement of micropore volume in copper terephthalate enable it to have the potential to store sufficient methane gas (Prasanth *et al.*, 2011). This potential application is very helpful especially in energy storage development as natural gas has a significant advantage over conventional fossil fuels from an environmental viewpoint and the natural abundance and resources (Anbia and Sheykhi, 2012).

1.3 Objectives of Study

The objectives of this study are:

- i. to synthesis copper terephthalate by sonication method,
- ii. to characterize copper terephthalate using XRD, SEM, TGA and DSC,
- iii. to examine the chemical stability of copper terephthalate in water, methanol and ethanol.

1.4 Scope of Study

This study focused on synthesis and characterization of copper terephthalate. During the synthesis process, copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, 1,4-benzenedicarboxylic acid (H_2BDC) and N,N-dimethylformamide (DMF) were reacted and sonicated for 2 hours. The suspension was cooled to room temperature before centrifugation was carried out for 30 minutes. Then, the suspension was further washed with DMF and was dried in oven at $150\text{ }^\circ\text{C}$ for 20 minutes. The precipitate was cooled under room temperature for overnight.

Copper terephthalate was characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). Identification of copper terephthalate was done using XRD while thermal stability of copper terephthalate was examined using TGA and DSC. Surface morphology of copper terephthalate was determined using SEM. Lastly, chemical stability of copper terephthalate was also examined in water, methanol and ethanol.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanoporous Materials

Nanomaterials have been a primary focus of nanoscience and nanotechnology in which both field develop multidisciplinary field of study attracting great investment, interest and effort in research and growth around the world. As a subset of nanomaterials, nanoporous materials are either an organic and/or inorganic framework which retaining a porous structure with a typically huge surface area. The word 'porous' origins from the Greek word 'πορος' (porous) that means 'passage' (Logar and Kaucic, 2006). Nanoporous materials possess unique structural, surface and bulk properties, making them important in various fields such as separation, ion exchange, sensor, catalysis, bio-molecular isolation and purification (Zhang *et al.*, 2010). They provide new chances for preparing nanoparticles, nanowires and other quantum nanostructures in area of chemistry, guest-host synthesis, molecular reactions and manipulation in nanoscale (Lu and Zhao, 2001).

According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be classified based on their pore diameters. Micropores are smaller than 2 nm in diameter, mesopores have pore diameter between 2 nm and 50 nm while macropores have pore diameters greater than 50 nm. Nanoporous materials have pore diameters between 1-100 nm and porosity (volume ratio of pore space to the total volume of the material) greater than 0.4 (Lu and Zhao, 2001). Pores in porous materials can be classified into two types which are open pore and close pore. Open pores connect to the surface of the material whereas close pores isolate from the outside (Logar and Kaucic, 2006). Open pores are required for

separation, catalysis and sensing while close pores are useful in sonic and thermal insulation (Lu and Zhao, 2001). Basically, there are four types of porous structures (Figure 2.1). Firstly, zero-dimensional cavities with nanosized pores that are isolated and do not connect with the surface of the material. Second type is one-dimensional space, with pores that are seen in a variety of compounds and are useful transport channels from the surface to the inner porosity. Thirdly, two-dimensional space with pores cut through the structure and create layers connected together by Van der Waals forces or interactions with guest molecules. Lastly, three-dimensional space which contains three dimensional interesting channels constructed from several one dimensional channels that run in different directions.

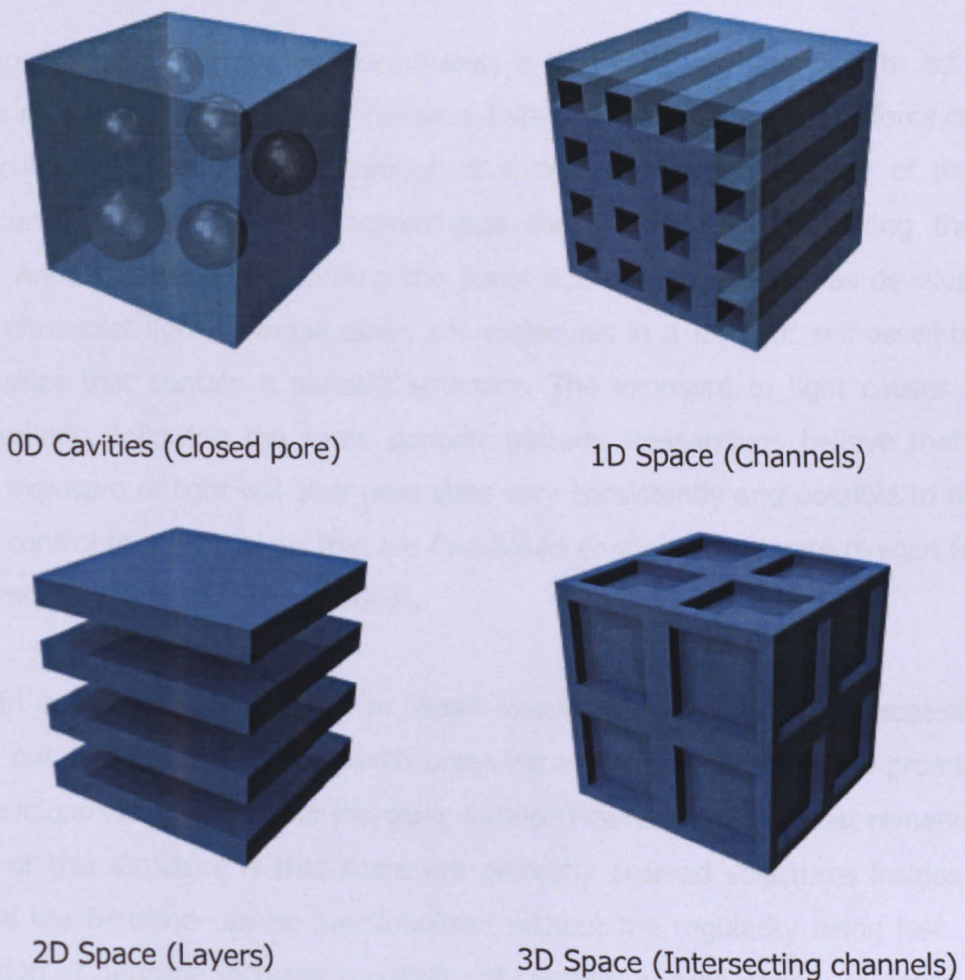


Figure 2.1: Pore Types (Beretta, 2009).

2.1.1 Types of Nanoporous Materials

There are many ways to make nanoporous materials whereby some have been used industrially for a long time. It is most strikingly that the production of a large variety of membranes where control over pore size is increasing drastically. Substances in the nanoporous membranes can be selectively escaped out of a solid by leaving pores in their place or combinations of polymers can be made to form into nanoporous solids by heating so that one polymer degrades and able to be escaped. One of the methods involves the combination of polymers and inorganic materials, such as silica is by using sol-gel method. This method can be used to make gel-based materials such as aerogels. During the process, a gas is dispersed in a gel, producing a very light solid where only four times as dense as air (Holister *et al.*, 2003).

Application of nanoporous membranes is the ability of nanopores to act as permeable membrane selector to let certain substances pass through or to force only one molecule like DNA to diffuse through at a time. Controlling the size of these pores accurately is one of the technological challenges faced in making these materials. Another approach to control the pores size in membranes was developed by using ultraviolet light to break down the molecules in a layer of self-assembled thin film silica that contain a periodic structure. The exposure to light causes the silica to solidify, following the same periodic pattern. Researchers believe that by changing exposure of light will alter pore sizes very consistently and possible to have sufficient control to create pores that are fine-tuned enough to separate oxygen from nitrogen molecules (Hamon *et al.*, 2009).

In early 2002, researchers in Japan managed to produce a self-assembled structure out of silica and benzene with pores between 3 and 5 nm which promising recent development in organic or inorganic hybrid (Figure 2.2). The most remarkable property of this structure is that there are perfectly ordered structures inside the pores and the benzene can be functionalized without the regularity being lost. This modification of benzene increase possibility of creating a large variety of pores with internal structures that are precisely engineered at molecular scales (Sun *et al.*, 2010).

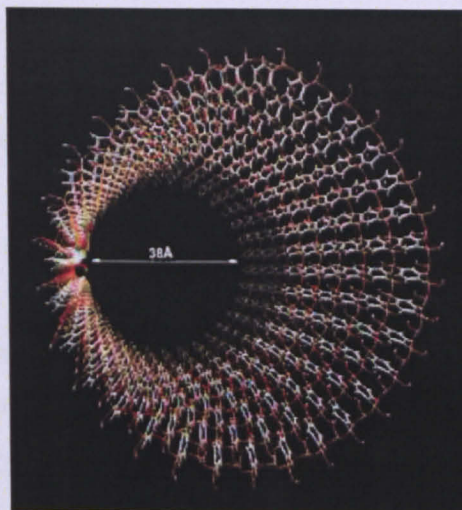


Figure 2.2: Ordered mesoporous organosilica hybrid material with a crystal-like wall structure (Holister *et al.*, 2003).

Second type of nanoporous material is bulk nanoporous materials which can better to be pictured as small sponge-like substances. Bulk nanoporous materials show catalytic properties because the properties of materials tend to change in different ways when they are held inside nanopores. Although bulk nanoporous materials are less exciting in term of range of possibilities and excellent level of control but they offer new applications on industrial scale. The adsorbent and absorbent of bulk nanoporous materials offer potential properties in environmental remediation by eliminating heavy metals of arsenic or mercury (Lu and Zhao, 2001).

The two examples of bulk nanoporous materials are activated carbon and zeolites. Activated carbon has been produced by a very large number of companies for a long time. Researchers in Korea have created activated carbon with uniform 8 nm and 12 nm pore sizes using silica nanoparticles that showed an adsorption greater than 10 times compared to commercial activated carbon. The removal of metal ions from a crystalline matrix which containing both metal and carbon allows the creation of various nanoporous carbon materials depending on the process condition. This approach is being commercialized by the Swiss company Skeleton Technologies (Holister *et al.*, 2003). Zeolites are microporous minerals that are widely used in water purification industry. Applications for zeolites cover a broad range of areas such as catalysis, separation, ion exchange, sensing and advanced optoelectronics (Valtchev, 2002). Later on, a modified zeolite (electrides) was shown to be one of the interesting class of materials. Electrides are positive charged

structure with charge being balanced in the form of an electron gas in the pores. In addition, electrides are stable at room temperature and have interesting electrical, magnetic and optical properties (Xu *et al.*, 2012).

2.1.2 Classification of Nanoporous Materials

Nanoporous materials such as polymer, carbon, glass, alumina-silicate, oxides and metal can be categorized based on their materials constituents and their properties (pore size, surface area, permeability, strength, thermal stability, chemical stability, cost and life) (Table 2.1).

Table 2.1: Classification of nanoporous materials (Lu and Zhao, 2001).

	Polymeric	Carbon	Glass	Alumino-silicate	Oxides	Metal
Pore size	Meso-macro	Micro-meso	Meso-macro	Micro-meso	Micro-meso	Meso-macro
Surface area/Porosity	Low >0.6	High 0.3-0.6	Low 0.3-0.6	High 0.3-0.7	Medium 0.3-0.6	Low 0.1-0.7
Permeability	Low-medium	Low-medium	High	Low	Low-medium	High
Strength	Medium	Low	Strong	Weak	Weak-medium	Strong
Thermal stability	Low	High	Good	Medium-high	Medium-high	High
Chemical stability	Low-medium	High	High	High	Very high	High
Cost	Low	High	High	Low-medium	Medium	Medium
Life	Short	Long	Long	Medium-long	Long	Long

2.1.3 Properties of Nanoporous Materials

The unique properties of nanoporous materials include large surface area and uniform pore distribution, high selectivity, high adsorption capacity, excellent mechanical stability and good stability and durability (Dai and Ju, 2012). The large surface area and the uniform pores distribution can provide more catalytic sites for the loading of a large amount of catalyst and thus making it high sensitivity in detection (Ju *et al.*, 2011). Surface area is important as it can affect the behaviour of nanoporous materials in processes which include activity of catalysts, water detoxification and purification of hydrocarbons. Particle size distribution is an important physical characteristic influencing the behaviour during storage and processing. The great porosity and uniform structure of nanoporous materials facilitate the fast transport of the analytes to active sites in the nanopores (Dai and Ju, 2012).

Selectivity is highly desired for separation in multi-component mixture of nanoporous materials. The selectivity of an adsorbent depends on the pore size, shape, pore size distribution and the nature of the adsorbate components. Modification surface of nanoporous adsorbent by organic materials have been developed in order to increase selectivity to target metals of nanoporous materials. Selection of the organic materials are made in such a way that one side of the molecules should contain charges or polar groups that can interact preferentially with metal ions while another side should be atoms or molecules that have ability to connect to the surface of nanoporous materials (Wongsakulphasatch, 2012). Furthermore, nanoporous materials also possess high adsorption capacity. Fundamental properties that affect this parameter are specific surface area, pore size and surface chemical nature. These parameters indicate how much adsorbates can be accumulated by per unit mass of adsorbates. Large surface area will give high adsorption capacity of nanoporous materials (Xia *et al.*, 2011).

Next, nanoporous materials have excellent mechanical properties that depend on its porosity and sizes of microstructure. Surface stress has great impact on the mechanical and physical properties of nanoporous materials. Hence, adsorbents need to be mechanically strong to support friction, corrosion and crushing in adsorption columns or vessels. Elastic constants of nanoporous materials can be

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