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2016 IOP Conf. Ser.: Mater. Sci. Eng. 107 012030

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Solvothermal and electrochemical synthetic method of HKUST-1 and its methane storage capacity

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Abstract. A comparison synthetic strategy of Metal-Organic Frameworks, namely, Hongkong University of Technology-1 {HKUST-1[Cu₃(BTC)]₂} (BTC = 1,3,5-benzene-tri-carboxylate) through solvothermal and electrochemical method in ethanol:water (1:1) has been conducted. The obtained material was analyzed using powder X-ray diffraction, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermo-Gravimetric Analysis (TGA) and Surface Area Analysis (SAA). While the voltage in the electrochemical method are varied, ranging from 12 to 15 Volt. The results show that at 15 V the texture of the material has the best degree of crystallinity and comparable with solvothermal product. This indicated from XRD data and supported by the SEM image to view the morphology. The thermal stability of the synthesized compounds is up to 320 °C. The shape of the nitrogen sorption isotherm of the compound corresponds to type I of the IUPAC adsorption isotherm classification for microporous materials with BET surface area of 629.2 and 324.3 m²/g (for solvothermal and electrochemical product respectively) and promising for gas storage application. Herein, the methane storage capacities of these compounds are also tested.

1. Introduction

Methane is an abundant and renewable fuel potentially developed in Indonesia [1]. In addition, it is environmentally friendly due to the cleaner burning than gasoline [2]. This gas can also be locally produced from biogas and biomass. The development and usage of methane is also based on sustainability and social economy to support the governmental programs towards energy self-sufficient community. Meanwhile, the success in the discovery of renewable energy should be supported by efficient energy storage systems [3].

Very recently the U.S. Dept. of Energy has started a new methane storage program [4] with the following targets: 0.5 g (CH₄) per g (sorbent) for gravimetric capacity and $r = 0.188$ g/cc (11.741 mmol/cc) for volumetric capacity, which corresponds to the density of compressed natural gas (CNG) at 250 bar and 298 K. The new volumetric target is equal to 263 cc (STP: 273.15 K, 1 atm) per cc, which is significantly higher than the previous target of 180 cc (STP) per cc at 35 bar [5].



So far, methane is typically compressed in a pressure containment vessel at ca. 250 bar and room temperature for on-board vehicle applications. At such high pressures, cost issues and volume effectiveness of the fuel tank remain as major concerns. To address these technical challenges, intense research efforts have been carried out to find suitable porous materials to help store methane. However, two major classes of porous materials that are available commercially, such as activated carbon and zeolites, do not have sufficiently high storage capacities and, to date, no suitable material has been commercialized [6]. In response to this important technological challenge, the scientists have recently reported many novel porous materials especially for use in natural gas vehicles (NGVs) with ever increasing methane storage capacities [7, 8, 9]. Many of these materials belong to a versatile class of porous hybrid materials known as metal-organic frameworks (MOFs) that are synthesized by the self-assembly of modular molecular “building blocks” into stable, highly porous crystals [10, 11].

On the other hand, the importance of discovering “green” methods for synthesizing compounds and materials have highlighted due to the rising concerns about the energy efficiency, toxicity and environmental impact of chemical processes. The “green” perspective of research and development in inorganic and metal-organic synthesis has traditionally focused on developing materials for applications recognized as green and environmentally-friendly, such as energy storage, for specific as methane storage. In this contribution, we aim to present an innovative electrochemical synthetic approach, as applied to the synthesis of HKUST-1 [12], the most explored owing the high stability of metal-organic frameworks (MOFs). With this electrochemical method, MOFs have opened a route to metal-organic materials and their syntheses on large industrial scales [13]; environmentally friendly, sustainable and commercially viable synthesis. As comparison, the solvothermal synthetic approach [14] will also be discussed and the methane storage capacity via gravimetric method will be presented.

2. Experimental

2.1. Materials and methods

Cu-plates with 99.9% purity are used as electrode material. 1, 3, 5- benzene tricarboxylic acid (BTC) and tetrabutyl-ammonium-tetrafluoroborate (TBATFB) were purchased from ABCR, Germany and used without further purification. Analytical grade, ethanol HPLC grade was used as received from Merck. Before used, the electrode was activated by immersing in 100 mL HNO₃ (1 M) and scrub with sand-paper until shiny. Methane gas (purity > 98%) which used during gravimetric measurement was supplied from PT. Samator Gas Industry, Tangerang, Indonesia.

2.2. Preparation of HKUST-1 [Cu₃(BTC)₂]

The electrochemical method in synthesizing HKUST-1 [Cu₃(BTC)₂] was conducted according to literature procedure [15] with slightly modification in the used solvent (water:ethanol, ratio 1:1, with totally 50 ml). The solution was then placed in the electrolysis cell and stirred for 15 min for complete dispersion. Electrolysis was carried out in an electrochemical cell under constant voltage electrolysis (with keeping current varying to make voltage constant) for ca. 2 h to complete the reaction. Finally the sky blue color precipitate of [Cu₃(BTC)₂] was collected from the electrolysis cell and allowed to dry at room temperature and then activated at 200 °C for 2 h. The sky blue color which appeared initially was changed to dark blue after activation, i.e., change in color indicates that the co-ordination number of Cu in the complex state is changed from six to four [16]. Further optimization of experimental parameters like, applied voltage ranging from 12 to 15 Volt and reaction temperature were carried out in order to get good yield and highly crystalline [Cu₃(BTC)₂]. As comparison, the solvothermal synthetic method of HKUST-1 in solvent mixture water: ethanol (1:1) was also carried out according to Schlichte et al. [14b] The yield of the product corresponding to the amount of weight loss in the copper anode (for electrochemical method) is ranging from 16 to 52%, while the solvothermal method reached until 99% as shown in Table 1.

Table 1. The yield of HKUST-1 synthesized by electrochemical (with voltage and temperature variations) compared to solvothermal method

Voltage variation (V)	Yield in (%) at various temperature condition			
	RT	40 °C	60 °C	80 °C
12	23.8	18.911	26.952	28.962
13	46.4	16.068	12.894	30.284
14	20.0	19.506	17.787	17.919
15	52.4	19.047	31.673	30.416
Solvothermal (120 °C)	99,2			

2.3. Characterization

The synthesized product was characterized by Powder X-Ray diffraction using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), with the voltage and current were held at 40 kV and 30 mA ($2\theta = 5\text{--}50^\circ$) at a scan rate of $1^\circ/\text{min}$. SEM data of samples were collected using FEI type Inspect S50 to confirm their surface morphology. Fourier Transform Infrared spectrum has been recorded on a FT-IR-8201 PC using KBr pellet in the range of $400\text{--}4000 \text{ cm}^{-1}$. The surface area and pore volume of the $[\text{Cu}_3(\text{BTC})_2]$ are determined from BET adsorption isotherms of nitrogen at 77 K using a static volumetric apparatus Micrometrics, NOVA 1200e. Thermogravimetric analysis was performed using a Q 500 instrument manufactured by TA Instruments and experiments were conducted with a constant heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

2.4. Gravimetric measurements

The methane uptake experiment was performed at room temperature condition ($25\text{--}30 \text{ }^\circ\text{C}$) and at relatively low pressure (20 psi). Prior to the measurement, the sample HKUST-1 (ca 5 gram) was degassed at $200 \text{ }^\circ\text{C}$ to remove undesired gases. The sample was then loaded into a sample holder which it was connected to an analytical balance's hook. The mass of the sample after degassing was recorded as the initial mass before methane uptake measurement.

Methane was then flown through the sample at $15 \text{ ml}/\text{min}$ after which its methane storage capacity was measured using the gravimetric method by observing changes of its weight. Methane storage capacity test was performed until mass of the sample saturated. The mass of the sample was observed every 5-10 minutes and collected by Mettler Toledo MS 4002 SDR analytical balance. The amount of methane uptake capacity was evaluated using Equation (1)

$$\% \text{CH}_4 = \left(\frac{m_1 - m_0}{m_0} \right) \times 100\% \quad (1)$$

where m_0 is the initial mass of the sample, m_1 is the mass of the sample after the methane uptake test and $\% \text{CH}_4$ is the amount of the CH_4 adsorbed on HKUST-1 (%wt.).

3. Results and discussion

3.1. Structural study of HKUST-1

HKUST-1 is one of the MOFs material that are widely studied due to its structural stability and various potential applications, such as in catalysis [14], gas separation [18] and gas storage [19, 20]. The specific advantage of HKUST-1 is having structural features such as an open metal coordination sites [3]. The compound has a bimodal pore size distribution, the larger pores are approximately 9 \AA in diameter and the smaller pockets have openings approximately 3.5 \AA in diameter [21].

Single X-ray analysis revealed that HKUST-1 has dimeric unit of copper-tetracarboxylic (Figure 1) with Cu-Cu bond length of $2.628(2) \text{ \AA}$. This framework is electrically neutral. Twelve carboxylate oxygen atoms of two ligands 1,3,5-benzene tri-carboxylate (BTC) bind to the four coordination site for

each of the three Cu^{2+} ions of the formula unit. Each metal completes its pseudo-octahedral coordination sphere with an axial aqua ligand opposite to the Cu-Cu vector [12]. The interconnection of Cu-paddle wheel unit with the tridentate BTC linker bond is repeated so that infinitely cubic frameworks are formed.

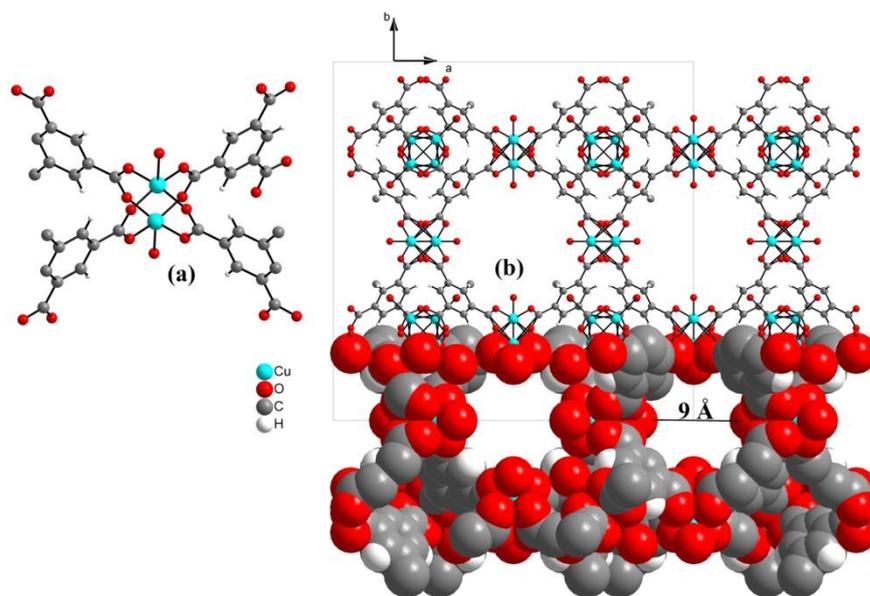
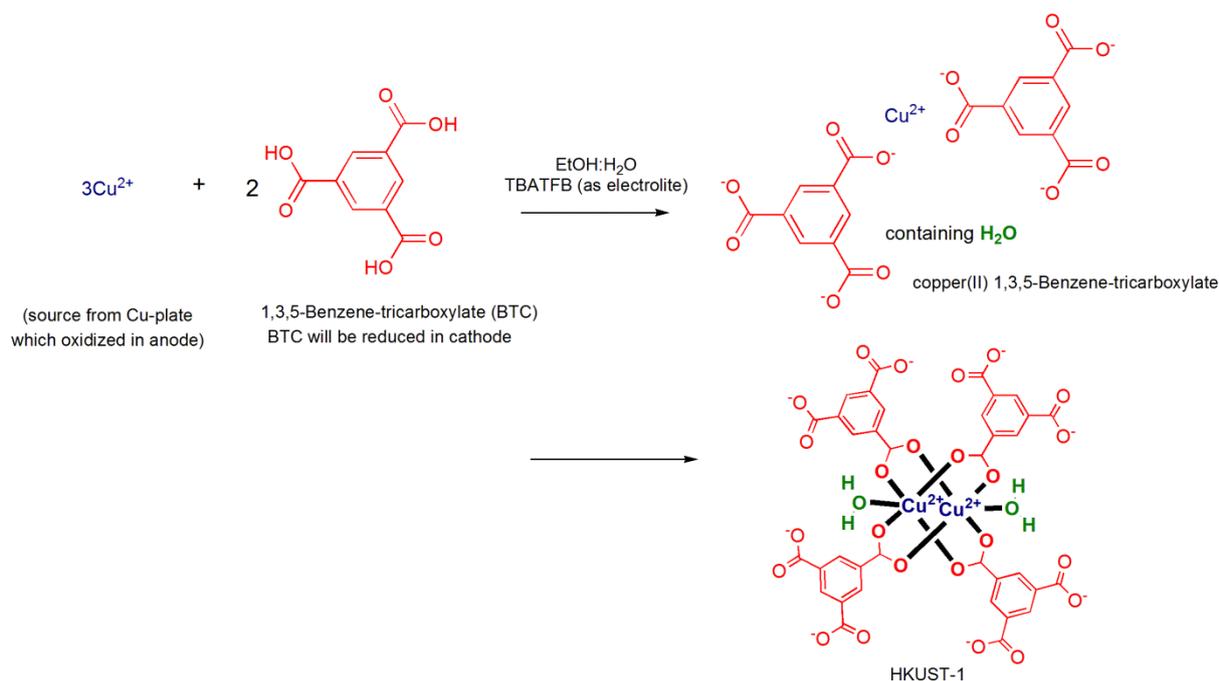


Figure 1. (a) Molecular structure of HKUST-1 with dicopper(II) tetracarboxylate as the basic framework (b) Frameworks of HKUST-1 $[\text{Cu}_3(\text{BTC})_2 \cdot (\text{H}_2\text{O})_3]_n$ with orientation [100] and shows nanometer-sized channel.

3.2. Comparison of solvothermal and electrochemical methods

Synthesis of HKUST-1 was firstly reported by Cui et al. [12] through solvothermal for 12 hours at a temperature of 180 °C. However, these reaction conditions lead to the formation of impurities in the form of CuO due to the influence of a high reaction temperature. Schlichte et al. [14b] had optimized the solvothermal reaction in order to get purer crystal of HKUST-1 from Cu_2O impurity by conducting in the solvent mixture water: ethanol (1:1) with a source of Cu^{2+} in the form of salts, for example $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ but using a lower reaction temperature of about 120 °C. The result is a bluish-green crystal which was then washed with ethanol and dried at room temperature with stable frameworks after the drying process and activation. However, the used Cu^{2+} salt led to the formation of acidic by-product that is certainly not environmentally friendly. Reaction time of 12 hours is also considered ineffective, therefore efficient and environmentally friendly synthetic method that is required. In this paper we have tried to use innovation and green synthetic method by electrolysis and then we have compared to solvothermal product. In the electrochemical method, the source of metal salt is from the metal electrode itself; in this case is the copper-plate. The reaction is supported by the presence of the electrolyte, TBATFB. The general reaction scheme of the electrolysis process to synthesize HKUST-1 is depicted in Scheme 1.



Scheme 1. Synthetic reaction to generate HKUST-1 by electrolysis method.

3.3. Material Characterization

The bulk product either from electrolysis and solvothermal product were characterized by powder X-ray diffraction in order to ensure a high purity of the crystalline phases. The X-ray diffractograms are identical to those calculated from single crystal analysis data reported in literature [12,14b] and the amount of side products is below the limit of detection by means of powder X-ray diffraction (Figure 2). The final results obtained greenish-blue powder which is dried at room temperature. Activation till 200 °C for 2 h lead to the purer and sharper peak of intensity and change to the color from light blue to dark blue indicates the release of coordinated water from copper(II). Temperature variations from RT to 80 °C, however, tend to produce lower yield. The sharper peaks in the range area of 2θ from 20 to 30° assumed represent the peak of the coordinated and or uncoordinated solvent (Figure 3). This can be observed after the activation at 200 °C these peaks are decreased as observed in Figure 2. However, these kind of peaks do not imply the significant impurities and found also in some referred literatures [15,22]. Additionally, it is remarkable that the synthesized $[\text{Cu}_3(\text{BTC})_2]$ does not exhibit any peaks corresponding to CuO ($2\theta = 35.5^\circ$ and 38.7°) or Cu_2O ($2\theta = 36.43^\circ$) and also in particular no significant impurities peak at $2\theta = 11.0^\circ$ as observed by Hartmann et al. [23] who synthesized $[\text{Cu}_3(\text{BTC})_2]$ by hydrothermal method which confirms that higher purity $[\text{Cu}_3(\text{BTC})_2]$ was obtained from this electrochemical method.

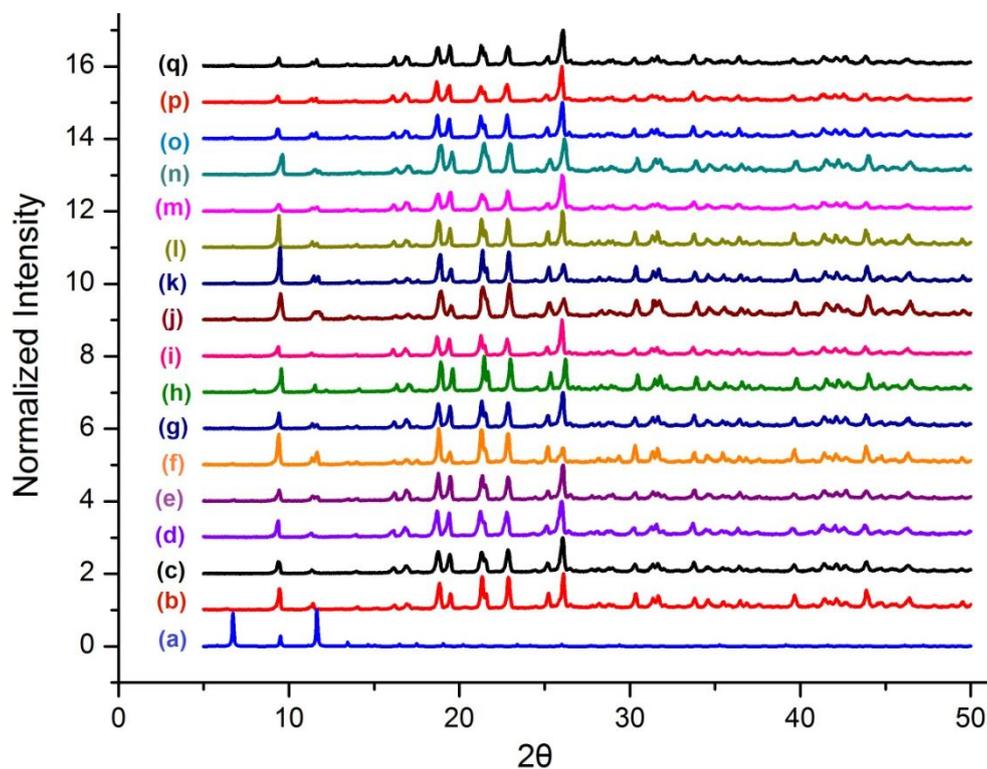


Figure 3. PXRD diffractograms of synthesized HKUST-1 by electrochemical method at 15 V (RT, 40, 60 and 80 °C ; b, c, d, e), 14 V (RT, 40, 60 and 80 °C ; f, g, h, i) , 13 V (RT, 40, 60 and 80 °C ; j, k, l, m) and 12 V (RT, 40, 60 and 80 °C ; n, o, p, q) compared to simulated pattern (a).

3.4. Thermal stability

The thermal stability of the resulting material was tested by thermo-gravimetric analysis (TGA). The electrochemically synthesized HKUST-1 at 15 V that only dried at room temperature indicates a change in the mass of nearly 20% at a temperature of 100-150 °C. This peak indicates the loss of water that fills the pores of HKUST-1. The next mass change of 5% at a temperature of 150-300 °C, these changes indicate a loss of water coordinated to Cu which serves as a node (node) at HKUST-1. Naturally, the higher temperatures required to break bonds of coordinated water with copper(II) rather than to release the water from the pore of HKUST-1. Then frameworks and ligand began to collapse at a temperature of 320 to 400 °C (Figure 4) to a perfect transformed into CO₂ and Cu₂O or metal Cu⁰ [14b].

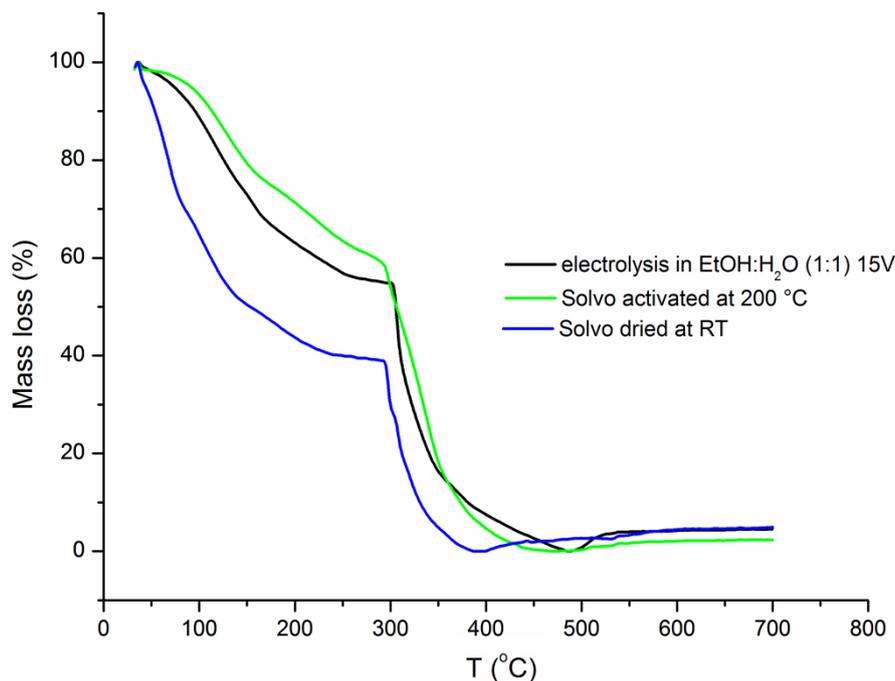


Figure 4. Thermogravimetric analysis of synthesized HKUST-1 either through solvothermal and electrolysis method.

As has been previously mentioned, the chemical and physical bonding of water molecules in HKUST-1 easily removed by heating the material. Dehydration makes part of the coordination of Cu can be accessed by other molecules that may play a role in the process of catalysis and gas storage [14]. The release of water molecules can be seen from the color of HKUST-1 after a synthesis that is turquoise and after drying to dark blue as shown in Figure 5.

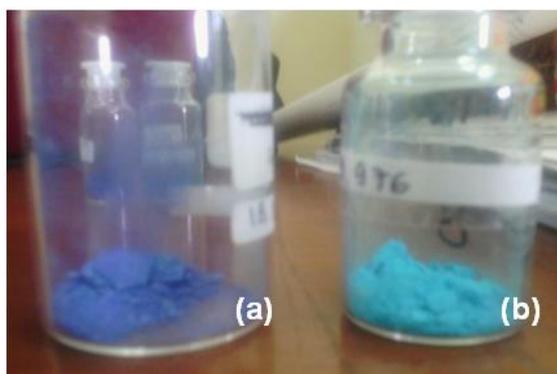


Figure 5. (a) HKUST-1 after being dried at a temperature of 200 °C, (b) HKUST-1 was dried at room temperature.

3.5. Porosity and Surface Area Analysis

To determine the surface area and porosity of HKUST-1 analysis using surface area analysis (SAA) and pore analysis at a temperature of 77 K were performed. The samples were previously activated at

200 °C for 12 hours. Based on this analysis, the synthesized HKUST-1 either by solvothermal or by electrolysis method at a voltage of 15 Volt shows the type I of the nitrogen adsorption isotherms which typical for MOFs and can be categorized as micro-porous material (Figure 6) according to IUPAC (1985) [24]. The synthesized HKUST-1

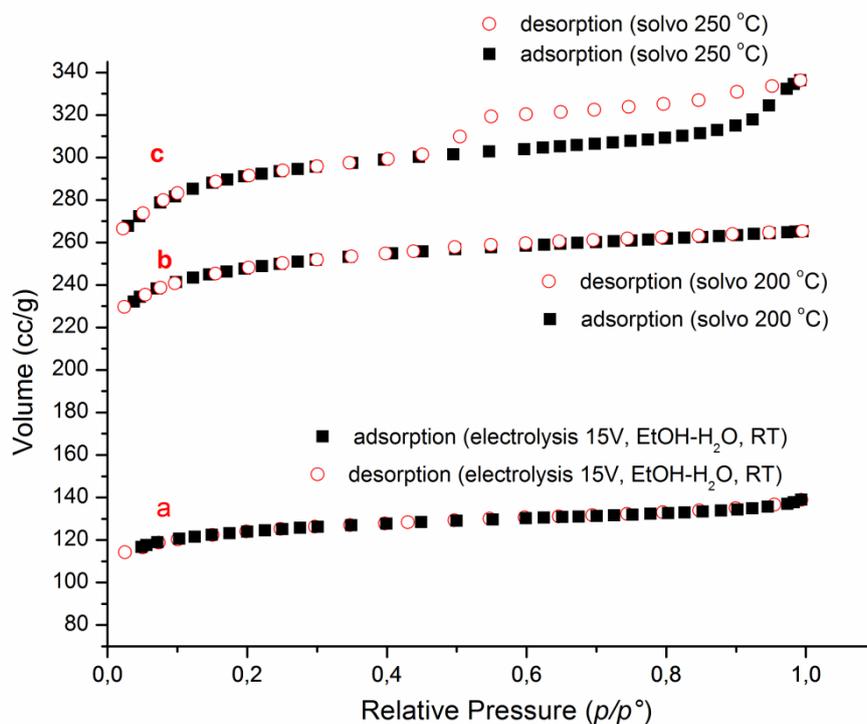


Figure 6. Nitrogen adsorption isotherm of the obtained HKUST-1 which synthesized through electrolysis (a) and solvothermal (b and c)

HKUST-1 by electrolysis at 15 Volt (RT) was obtained BET surface area of 324.331 m²/g with a pore volume of 0.1902 cc/g and a pore diameter average size of 11.73 Å. While the model of Horvath and Kawazoe (HK method) defined pore size of 1.838 Å. Solvothermally synthesized HKUST-1 showed BET surface area of 635.637 m²/g with a total size of the pore volume of 0.3531 cc/g and an average size of 11.11 Å pore diameter measured by the HK method. Thus, solvothermal method is capable of producing HKUST-1 with a surface area and pore volume two times larger than the electrolysis method. Nitrogen adsorption isotherm measurement synthesized HKUST-1 via solvothermal method after activation at a temperature of 250 °C showed the BET surface area and pore volume greater than at the time of activation at 200 °C, respectively, the value was 629.2 m²/g and 0.3777 cc/g with average pore size diameter of about 12 Å (Figure 6).

3.6. Morphological analysis of HKUST-1

The morphology of HKUST-1 was identified by scanning electron microscopic analysis (SEM). Based on Figure 7, it can be seen that the results of the synthesized of HKUST-1 through solvothermal method produce larger material size than the synthesis using electrolysis at a voltage of 15V in solvent combination ethanol: water (1:1). The HKUST-1 morphology with these two methods is solid dark blue with octahedral crystals form with the size of 0.5-5 μm. These results are comparable with the results Mueller et al. (2006).

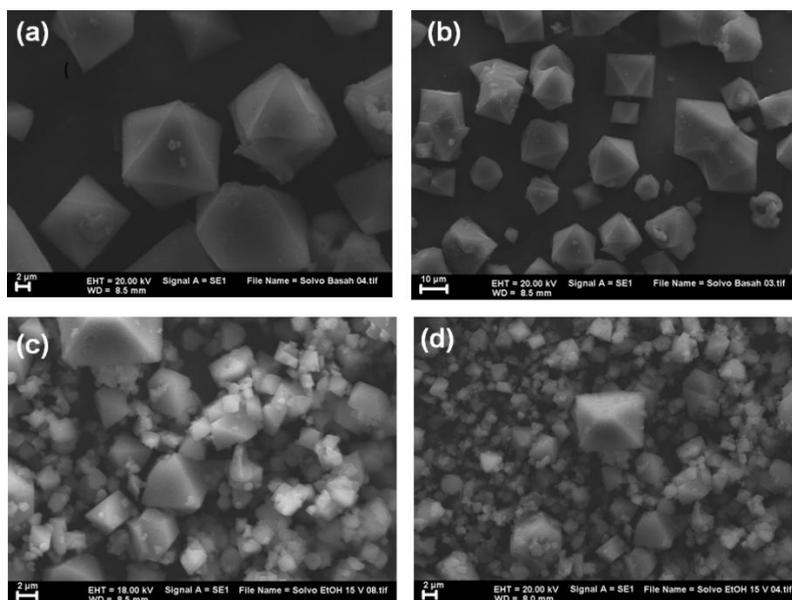


Figure 7. The morphology of HKUST-1 corresponding SEM analysis (a, b). Synthesis results under solvothermal condition; and (c, d) under electrochemical synthetic method at 15 Volt.

3.7. Infra-Red Measurement

Infrared (IR) analysis is used to determine the functional groups in the BTC ligand and the changes that occur when a BTC ligand coordinated with the copper ion and formed HKUST-1 which mainly changes in absorption of carboxyl groups possessed by BTC ligand. Absorptions around 1715 cm^{-1} corresponds to stretching vibration of C=O acid ligands shown in BTC which after forming HKUST-1 shifted to 1665 cm^{-1} , indicating the deprotonation process occurred in C=O bond. This shift proved that the carboxylate ion participate in the complex formation. Absorption peaks at 410, 500, 610 and 615 cm^{-1} indicating that the synthesis product free of CuO and Cu₂O [25] during the formation of HKUST-1. Moreover, the vibration characteristics of the 714 cm^{-1} may be a Cu-O stretching vibration in which the oxygen atom coordinated with Cu²⁺. Wide peak at $2500\text{-}3300\text{ cm}^{-1}$ correspond to OH stretching absorption of carboxyl group and shifted from 3100 to 3600 at HKUST-1, which indicates the presence of water molecules bond loss at HKUST-1. FTIR comparisons between pure ligand BTC, HKUST-1 were synthesized solvothermal or by electrolysis can be seen in Figure 8.

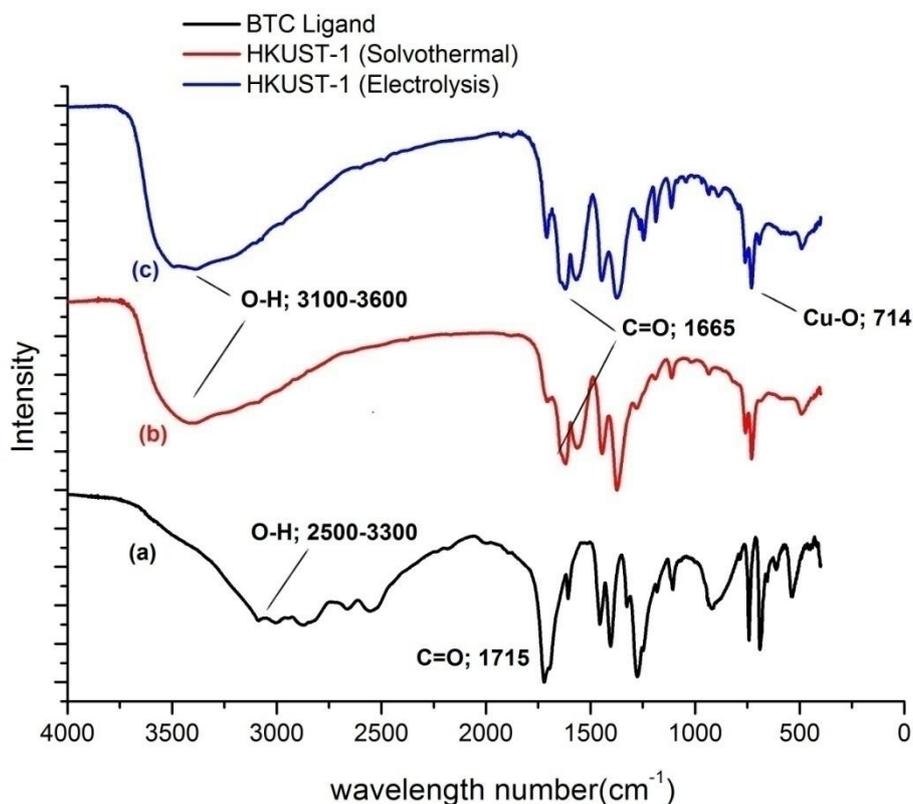


Figure 8. FT-IR spectra of (a) 1,3,5-benzene tricarboxylic acid and (b and c) $[\text{Cu}_3(\text{BTC})_2]$ synthesized under solvothermal and electrolysis method.

3.8. Methane Storage Measurement

The synthesized HKUST-1 either by solvothermal or electrochemical method especially the optimum yield produced at 15 V at room temperature were examined for its methane uptake capacities using gravimetric method at relatively low pressure (20 psi \sim 1.38 Bar) following equation (1). Figure 9 shows the methane storage capacities of the HKUST-1. The capacity of electrochemically synthesized HKUST-1 continuously increases even up to 250 minutes with the average ultra high pure (UHP) methane uptake capacities of the HKUST-1 after several measurements was ranging from 7 to 11 %wt. This result is significantly higher than the reported methane storage over HKUST-1 synthesized by solvothermal method by Kaskel and co-worker [14a]. In contrast, the gravimetric measurement of the sample toward mixed gases containing only 5% methane shows lower capacity, although the trend of storage measurement tend to increase till 120 minutes then decrease afterward. This condition indicate. This condition indicates that the presence of gases other than methane (for instance nitrogen) can disturb and compete the methane storage itself. The gravimetric methane storage measurement over the solvothermal product in this case also tend to decrease and only show maximum capacity ca. 6 %wt., which however this condition still need to be optimized.

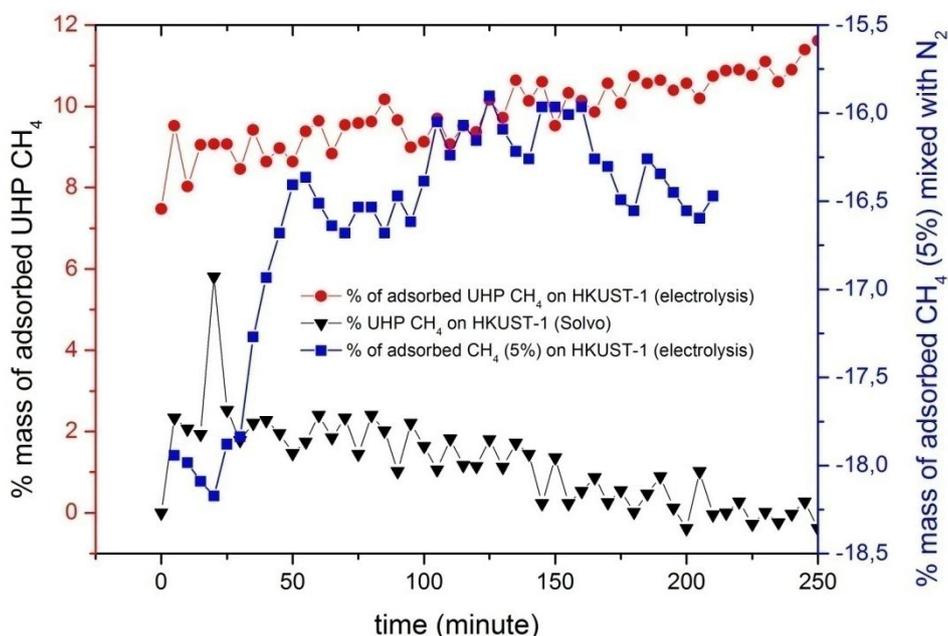


Figure 9. Methane storage by gravimetric analysis of HKUST-1 synthesized by electrolysis and solvothermal method.

The larger capacity of HKUST-1 synthesized by electrochemical method as compared to the solvothermal product can be attributed to the presence of the HKUST-1 synthesized by electrochemical method have relatively high surface area and well-developed pore characteristics. Besides that the method is also suitable to produce large scale of HKUST-1 or MOFs material which applied to industrial scale due to time and cost efficient, environmentally friendly synthesis and support the sustainable development toward the renewable energy.

4. Conclusions

HKUST-1 has been successfully synthesized through an efficient and environmentally friendly electrochemical method. Methane uptake experiment of the corresponding product (at 15 V, RT in the solvent mixture EtOH: H₂O /1:1) showed higher capacity than the solvothermal product and reached up to 11 %wt at 20 Psi (1,38 Bar) according to gravimetric analysis.

Acknowledgement

We gratefully acknowledge financial support by the research grant Doktor Baru and Hibah Mandatory PNPB Sebelas Maret University (UNS). We thank MSc. Wahyu Prasetyo Utomo from ITS Surabaya for conducting the gravimetric measurements.

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