One-pot solvothermal synthesis and characterization of UiO-66/HKUST-1 composites

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Abstract. Metal-organic frameworks (MOFs) are promising crystalline materials for various application due to their controllable porous structure and large specific surface area. Their properties can be further improved by several means, such as making a binary MOF comprising of two different MOFs. In this research, UiO-66/HKUST-1 composites have been synthesized by solvothermal method, in which the UiO-66 was prepared at 120 °C for 24 h in N,N-dimethylformamide (DMF) prior to preparation of HKUST-1 at 100 °C for 10 h in solvent mixture of DMF, ethanol and water. Amounts of Zr2+ for the synthesis of UiO-66 added during the synthesis process were varied at 5, 10 and 20% toward the amount of Cu2+ for synthesis of HKUST-1. Diffractogram patterns of the obtained composites showed dominant characteristic peaks, similar to that reported for HKUST-1. Furthermore, FTIR spectra of all solids showed absorption bands at the same wavenumbers as reported for HKUST-1. Transmission Electron Microscopy (TEM) images showed the spread of Zr metal evenly on the pore of composites.

1. Introduction
Metal Organic Framework (MOF) is a group of porous materials that are unique and superior compared to other porous materials. The presence of metals and organic ligands makes MOF become an efficient adsorbent in which the size and volume of the pore of the MOF can be adjusted with the material to be adsorbed [1]. MOF has been widely used as catalysts, adsorbent, drug delivery, and material templates [2]. MOF has several sub-groups including IRMOF, ZIF, HKUST-1, and UiO-66.

One type of MOF that is often studied is HKUST-1 or commonly known as Cu-BTC. MOF type HKUST-1 was first synthesized by Chui et al., by use of cupric nitrate trihydrate and trimesic acid ligands. HKUST-1 has a characteristic surface area of 692.2 m²/g, pore size and pore volume of 0.9 nm and 0.33 cm³/g, respectively, with thermal stability of 240 °C [3]. Besides having advantages, the HKUST-1 also has disadvantages, namely the low thermal stability and micro pore characteristics that limit the application performance [4]. The low thermal stability of MOF is caused by the bond between metals and their organic ligands [5].

Several methods have been carried out to improve the thermal stability of MOF including the addition of metals or other compounds [6]. Several previous studies have introduced MOF in its composite form. Furtado et al. has introduced the synthesis of HKUST-1 with addition of MCM-41 support [7]. Kondo et al. have successfully reported the preparation of HKUST-1/SBA-15 composite and its application as ethanol adsorption [8]. Liu et al. reported that performance of H₆P₂W₁₈O₆₄@Cu-
BTC composite increased in dye adsorption applications [9]. However, some of these materials are expensive if applied on a large scale. Recently, there is an innovation to increase the thermal stability of the MOF by synthesis of binary MOF. UiO-66 is one type of MOF which has high thermal stability up to 540 °C [10]. Besides, some interesting properties are shown by UiO-66, namely a large surface area and high porosity and stable in water media. The composting of the two types of MOF is expected to be able to cover the shortcomings of one of the MOF properties so as to improve its performance in certain applications.

2. Experimental

2.1. Materials

All chemicals used in this study, namely copper(II)nitrate trihydrate [Cu(NO₃)₂·3H₂O, 99%], zirconium tetrachloride (ZrCl₄, 99.0%), benzene-1,3,5-tricarboxylic acid (H₃BTC, 98%), and benzene-1,4-dicarboxylic acid (H₂BDC, 98.9%), were obtained from Sigma Aldrich. Ethanol (EtOH, 99.8%), methanol (MeOH, 99.8%), chloroform (CHCl₃, 99.9%) and N,N- Dimethylformamide (DMF, 99.88%) were purchased from Merck and aqua demineralized (aqua DM).

2.2. Synthesis HKUST-1

HKUST-1 was synthesized using the procedure reported by Chowdury et al. [11]. First, 2.077 g of Cu(NO₃)₂·3H₂O was dissolved in 15 mL of aqua DM, while 1 g of H₃BTC was dissolved in 30 mL solvent mixture of ethanol and DMF (v:v = 1:1). The reaction mixture was then stirred with magnetic stirrer for 30 min, followed by heating process in oven at 100 °C for 10 h. The reaction mixture was allowed to cool at room temperature in two days. The solid was then separated from solvent by decantation. The solid was washed by adding 40 mL of DMF, soaked overnight, and the solvent was removed by decantation. The washing process was repeated by adding 60 mL of methanol and placed in oil bath at range temperature of about 40 °C. The resulting powder was dried in oven at 55 °C for 4 hours.

2.3. Synthesis UiO-66

UiO-66 was synthesized using a procedure reported by Rahmawati and Ediati [12], in which 0.3496 g of ZrCl₄ and 0.2492 g H₂BDC were dissolved in 30 mL DMF, then solution was stirred with magnetic stirrer for 30 min in a vial bottle. The reaction mixture was then placed in oven at 120 °C for 24 h. The reaction mixture was allowed to cool at room temperature overnight. The solid was then separated by decantation, washed with 40 mL of DMF and 30 mL chloroform, respectively. The obtained powder was dried in oven at 60 °C for 4 hours.

2.4. Synthesis UiO-66/HKUST-1 Composites

The method for synthesis of binery MOFs of UiO-66/HKUST-1 is the same as for synthesis of HKUST-1 and UiO-66. UiO-66 was first synthesis by solvothermal method at 120 °C for 24 h in DMF solvent, so that a mixture of solid in solvent was obtained. The reaction mixture was then added to solution for HKUST-1 synthesis. The reaction mixture was then treated as for HKUST-1 synthesis, i.e. heated in oven at 100 °C for 10 h. In this study, the amount of UiO-66 added was varied at 5, 10 and 20 (w/w %) in order to determine the effect of UiO-66 addition on HKUST-1 crystal formation. The obtained solids were labelled as U/H(X) where X was the amount of UiO-66 added.

2.5. Characterization

The crystallinity of the obtained solid was examined using X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), and angle range of 3 - 50°. Determination of functional groups was carried out using FTIR instrument in the wavenumber of 400 - 4000 cm⁻¹. TEM images were obtained using a JEOL JEM1400 transmission electron microscope at an accelerating voltage of 200 kV. The thermal gravimetric analysis was recorded in the temperature range of 30 – 900 °C under air flow with heating rate of 10°/min.
3. Results and Discussion

3.1. X-ray diffraction (XRD) analysis

The XRD patterns of the obtained solids are shown in Figure 1. The formation of HKUST-1 structure was confirmed by the appearance of characteristic peaks at 2θ of 6.7, 9.5, 11.6, 13.8 and 17.0°, respectively, as reported by Lin et al. [2]. Likewise, the UiO-66 showed characteristic peaks at 2θ of 7.3° with the highest intensity and at 2θ of 8.5° with lower intensity, which are similar to that reported by Gokpinar et al. [13] for UiO-66. The XRD patterns of the composite with 5% w/w UiO-66 was dominated by the characteristic peaks of HKUST-1. When the amount of UiO-66 was increased, however, the characteristic peak of UiO-66 was seen at 2θ of 8.5°. These results indicated that the UiO-66 structure in the composites remained unchanged, even though the existence of UiO-66 in the composites decreased the intensity of characteristic peaks of HKUST-1.

![XRD pattern of HKUST-1, UiO-66 and Composites.](image)

3.2. The Fourier transform infrared (FT-IR)

The FTIR spectra of all solids are shown in Figure 2. As can be seen, the HKUST-1, UiO-66 and all UiO-66/HKUST-1 composites show absorption bands at wavenumber similar to that of binary MOF of UiO-66 and HKUST-1, as reported by Azhar et al. [14]. Absorption bands appeared in the wavenumber ranging of 1450 - 1650 cm⁻¹ indicated the presence of C = C groups of aromatic groups. The presence of C-O stretching carboxylic groups was shown by absorption bands at around 1300-1400 cm⁻¹. The absorption bands at around 3200 - 3600 cm⁻¹ indicated the presence of O-H groups. The finger print absorption bands of about 700 cm⁻¹, showed the presence of bonds between Cu-O and...
Zr-O in all the obtained solids [15][16]. In general, there has been no significant difference between FTIR spectra of the HKUST-1, UiO-66 and binary MOFs.

Figure 2. FT-IR spectra of HKUST-1, UiO-66 and Composites.

3.3. Transmission Electron Microscope (TEM)
TEM analysis was carried out to determine the pore morphological characteristics of a material. In this study TEM analysis was performed on composite samples U/H(20) and HKUST-1 as a comparison. As is shown in Figure 3, the pure HKUST-1 exhibited more uniform pore morphology when compared to composite U/H(20). Furthermore, the composite U/H(20) showed the spread of black dots which might indicate the spread of Zr atoms in HKUST-1 pores.
3.4. Thermal Gravimetric Analysis

The results of thermal gravimetric analysis of the obtained HKUST-1, UiO-66 and U/H(20) composite are shown in Figure 4. It can be seen that the thermal stability of the HKUST-1 reached a temperature of 292 °C with two stages of mass reduction [17]. A high thermal stability of 510 °C was exhibited by UiO-66. The thermal stability of the U/H(20) composite, however, was lower than those of HKUST-1 and UiO-66. The decrease in the value of thermal stability of the composite U/H(20) may be as a result of crystal growth disturbance of the HKUST-1 due to the presence of UiO-66 in the reaction mixture of composite synthesis.

Figure 4. The thermal gravimetric analysis of materials synthesized.
4. Conclusion
In this study, the UiO-66/HKUST-1 composite was successfully synthesized by the solvothermal method with a one-step synthesis. The results of XRD analysis showed that the addition of UiO-66 during the synthesis of HKUST-1 did not change the crystal structure of either HKUST-1 or UiO-66, significantly. The results of FTIR analysis showed that the composites exhibited absorption bands at same wavenumber to those of HKUST-1 or UiO-66. The thermal stability of the U/H(20) composite, however, was lower when compared to those of HKUST-1 and UiO-66.

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