Study the Influence of Solvothermal Conditions Changing On UiO-66

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ABSTRACT

Metal Organic framework UiO-66 considered to have significant physicochemical characteristics with great potential for various applications. Nevertheless obtaining high porous prosperities by optimization the synthesizing method remained challenge. In this study, a solvothermal method has been used to synthesis the UiO-66 with different synthesis time (12, 24, 48, 72 and 96 hours) and different heated (80, 100, 120, and 140 °C). By changing the temperature up to 140 and synthesis time 24 h the main peak intensity increased. The XRD and SEM analysis showed that by increasing the synthesis temperature the degree of crystallinity increased and cubic shape crystals was obtained. The XRD characterization analysis for UiO-66 showed the white powdered obtained at 12 h reaction time and 140 °C synthesis temperatures was the highest XRD intensity at 7.3°, 8.4°, 25.6° and 30.6° 2Theta. When changing the synthesis time for 48 h or longer, XRD diffractograms revealed phase change and that the intensity at 7.3° 2Theta was lower than the intensity at 8.5° 2Theta, with new peaks appeared. SEM analysis confirmed the phase change after synthesis time 48h, by changing the crystals square clusters shape to the needle-like shape.

Key words: UiO-66, Zr-MOFs, reaction times, and heating

الخلاصة

يعتبر الأطر المعدني العضوي UiO66 ذو خصائص فضية كبيرة وكمية كبيرة مع امكانات كبيرة ل مختلف التطبيقات. UiO66 محدود من ذلك هناك تحديات كبيرة في السيطرة على ظروف تصنيع هذه المادة. في هذه الدراسة تم استخدام مетод solvethemal لتصنيع UiO-66 ودراسة تأثير كل من زمن التصنيع ودرجة الحرارة. حيث تم اولا تغير درجة الحرارة من 80 إلى 140 م درجات م ويتفصل خلال 24 ساعة. ثم تم تثبيت درجة حرارة التصنيع على 140 م وتغير زمن التفاعل من 12 إلى 96 ساعة. لوحظ بعد تغير درجة الحرارة وتبني زمن التصنيع على 24 ساعة ارتفاع درجة XRD و SEM عن إجراء الدراسات ب درجة الحرارة.

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البلورة وتكون بلورات مكعبة وتكون مسحوق أبيض. أما عند إجراء الفحوصات للمماذج التي تم فيها تثبيت درجة حرارة التصنيع على 140 °C، وتغيير الوقت فقد لوحظ أنه هناك تغيير بالطريقة بالإضافة إلى تغيير في شكل البلورات المتكونة من الشكل المكعب إلى الشكل الأبري عند زيادة وقت التصنيع أكثر من 48 ساعة. حيث كان وقت التصنيع الأقل هو 12 ساعة واتجاه مادة ذو درجة تبلور عالية وذات بلورات مكعبة و زمن التفاعل و التسخين.

الكلمات الرئيسية: Uio-66, Zr-MOFs, زمن التفاعل والتسخين.

1. INTRODUCTION

MOFs are considered as new kinds of materials that could be tailored by a number of ligand/metal combinations with a huge diversity in pore sizes and shapes, functional groups, and structures Kareem, et al., 2019, Alrubaye, et al., 2019. MOFs reveal great potential applications in the separation of, catalysts, and gas storage Cavka, et al., 2008. The stability of MOF framework is depending on the strength of the chemical bonds between the inorganic metal and linker, for example thermal stability temperature up to 280°C HKUST-1, and 300°C for MOF-5. A research group at University of Oslo-66 reported synthesis MOF for first time using 1,4-benzendikarboxilsat acid (BDC) and zirconium (Zr) and called it as Uio-66. The thermal stability temperature of Uio-66 was 540°C with good chemical stability and 1187m2/g and cubic crystals Abid, et al., 2012. The zirconium organic frameworks was prepared by solvothermal process for 24 hours at 120°C. Since 2008, when university of University of Oslo introduced Uio-66, the solvothermal method has been the most successful method to synthesis this MOF at temperatures in the range of 80 - 120 °C for 24 h or more. The researchers investigated the factors that affecting the synthesis process (time and temperature of solvothermal) and reflect on the produced MOFs. It was found that by increasing the synthesis temperature, quicker crystallization occurs and less reaction time will be required. Numerous Uio-66 synthesis methods have been applied that involve synthesis temperatures in the range of 80 to 120 °C, over 24 hours and more Eddaoudi, et al., 2001, Sumida, et al., 2011, Rallen, et al., 2015, and Alrubaye, et al, 2018. This study has introduced a fast solvothermal synthesis method that took only 12 h at 140 °C to produce the Uio-66 molecules. Furthermore, the effects of varying the temperature of the reaction and synthesis time on synthesis of the Uio-66 have been addressed. The investigation of the Uio-66 crystallization at specific reaction time and 140°C temperature revealed a rapid synthesis time and high crystallinity degree.

2. EXPERIMENTAL WORK

The Two sets of experiments were carried out in this study to understanding the influence of the changing the temperature and time of the synthesis on the characterization physical prosperity of the Uio-66. All the samples prepared for the first set were synthesis at 24 h with different synthesis temperatures (80, 100, 120 and 140 °C), and the optimum synthesis temperature was chosen to applied for the synthesis Uio-66 samples for the second set. The second set samples were prepared by carrying out the solvothermal process at 140 oC for different synthesis time (12, 24, 48, 72 and 96 hours). The Uio-66 samples preparation (Cavka, et al., 2008) were achieved (by mixing 1,5 mmol of ZrCl4 (Zirconium tetraclorida, Sigma-Aldrich, 99,0%) with 1,5 mmol of BDC (Benzene-1,4-dicarboxylic acid, Sigma-Aldrich, 98,9%) and poured into flask contained 30 mL of DMF (Dimethylformamide, Merck, 99%), the prepared mixture was stirred for 30 minutes with magnetic stirrer. Then, The mixture was transferred to Teflon-lined stainless-steel autoclave and heated at the specific synthesis temperature (80, 100, 120 and 140 °C) for specific synthesis time (12, 24, 48, 72 and 96 hours). The produced solid was collected, filtered and washed by 30 mL DMF and left overnight. The solid was washed twice further with chloroform (CHCl3, Merck,
99.9%) as the solvent. Finally, the collected powder was then dried at 60-70 °C under vacuum using rotary evaporator.

3. CHARACTERIZATION

All samples for the first and the second set were analysis using the X-ray powder diffraction (XRD) patterns that were obtained using a Rigaku Miniflex diffractometer (CuKα radiation, k = 1.5406 Å, 30 kV, 15 mA,) using a 0.05° step-scan with a range of 5° < 2θ < 45°. UiO-66 samples morphology were analysis with Quanta200 FEI to investigate the morphologies of the UiO-66 crystalline. The N2 adsorption-desorption isotherms at 77K were measured with a ASAP2000 instrument. The Brunauer-Emmet-Teller (BET) surface area was calculated using the BET model in the linear region and pore size distributions were calculated.

4. RESULTS AND DISCUSSIONS

4.1 INFLUENCE OF THE SYNTHESIS TEMPERATURE ON THE PREPARED UIO-66

The XRD analysis of UiO-66 samples synthesized with varying the solvothermal temperatures showed at Fig 1. The XRD results reveal that all prepared samples showed the formation of the UiO-66, however the crystalline peak intensities (the UiO-66 characteristic peaks at 2θ of 7.4°, 8.5° and 25.5°) were different depending on the varying of the synthesis time. The intensity of the characteristic peak for the samples increased with rising synthesis temperature up to 140 °C. The higher intensity was at 140°C synthesis temperature. This result is in a good agreement with Abid, et.al. 2012 results, which was showed increasing of the crystallinity degree by increasing synthesis temperature

Fig. 2 showed the SEM images of UiO-66 samples prepared with various synthesis temperatures. SEM analysis showed that by increasing the temperature (80- 140 °C) the particles size increased and the particles shape was good formed. Moreover, the distribution of pore size of the UiO-66 samples at different synthesis temperatures showed in Fig. 3. At 140°C synthesis temperature, the distribution of pore size was the narrowest and that was the consistent with the crystallinity level in the XRD analysis. From the characterization analysis of the samples prepared with various synthesis temperatures, it was found that the UiO-66 prepared at 140°C has better-characterized physical prosperities.

4.2 INFLUENCE OF THE SYNTHESIS TIME ON THE PREPARED UIO-66

All the UiO-66 samples prepared with solvothermal methods at various reaction time (12, 24, 48, 72 and 96 hours) was heated synthesis temperature 140°C, to understanding the effect of the reaction time on the UiO-66 proprieties.

The XRD analysis of all the prepared samples of UiO-66 with a different reaction time up to 96 hours at 140°C revealed variation in the characteristic peaks intensities (Fig 4). The peak intensity for UiO-66 at 8.5° and 25.6° showed that the area under the curve for the main peaks (at 2 theta 7.3°) and characteristic peaks (at 2 theta 8.5° and 25.6°) for the synthesized UiO-66 sample at a 12 h has the largest area under the characteristic peaks compared to the other sampled synthesized at different temperature. Therefore, the UiO-66 synthesized sample at 140° C for 12 h has the highest crystallinity degree, which was a good comparison to the standard crystallinity Abid, et al., 2012. The crystallinity results of UiO-66 synthesized sampled are listed in Table 1.

At 12 h the UiO-66 is formed quickly and produces with the highest intensity Sumida, et al., 2011. At 24 h, the characteristics peaks intensity was lower than 12 h. By increasing reaction
time up to 24 h, the main peak intensity declined while the intensity at 2 theta 8.5° increased slightly. The decreasing in the main peaks intensity could be attributed to the MOFs phase change and that clearly showed by characteristic peaks shifted at 24 h synthesis time. When increasing synthesis time up to 96 h, the XRD patterns have been changed, the intensity at 2 theta 7.3° and at 2 theta 8.5° and 25.6 showed new generated peaks and decline at 2 theta 7.3° intensity and an increase at 2 theta 8.5° intensity. This founded has been supported by SEM analysis for the UiO-66 synthesized samples at various reaction time (12, 24, 48, 72 and 96 hours) and 140°C synthesis temperature.

The SEM images of UiO-66 synthesized samples (Fig.5) revealed the morphology change of UiO-66 synthesized samples by increasing synthesis time. At 12 h, the UiO-66 synthesized samples demonstrated a cubic crystals shape. This is agreed with the results of XRD patterns and the standard UiO-66 (Fig 4 (12h)). By increasing synthesis time beyond 48 h the MOF morphology was changed to needles-like and that was consistent with the XRD analysis results. The XRD diffractogram and SEM results of crystal analysis was confirmed that the optimum time to prepared UiO-66 was 12 h at 140°C.

5. CONCLUSION
This study represents an investigation to the solvothermal synthesis of UiO-66 temperature and synthesis time effect on the physical characteristic of the synthesis MOFs. It was found that the best synthesis temperature was 140°C. By increasing synthesis temperature up to 140°C, for the samples prepared at 24 h, the crystallinity increased and the MOF morphology showed a typical UiO-66 crystal shape. Furthermore, XRD pattern and SEM image analysis showed that increasing synthesis (+72h) time led to the UiO-66 Phase change. Therefore, the optimum synthesis conditions for synthesis UiO-66 for this study were 12h and 140°C.

![Figure 1. UiO-66 synthesized with different temperature at 24 h XRD analysis.](image-url)
Figure 2. UiO-66 synthesized at 24 h with different temperature. SEM IMAGES (a) 80 °C, (b) 100 °C, (c) 120 °C, and (d) 140 °C.

Figure 3. UiO-66 synthesized with different temperature at 24 h Pore size distribution.
Figure 4. UiO-66 synthesized at 140°C with different synthesis time XRD analysis and standard XRD for UiO-66.

Figure 5. UiO-66 at 140°C, for different synthesis time SEM analysis (a) 12 h and (b) 96 h.

Table 1. UiO-66 crystallinity for crystals synthesized with different of synthesis time.

| Synthesis time (h) | 2θ(°) | area under the curve | Crystllinity degree(%) |
|-------------------|-------|----------------------|------------------------|
| 12 h              | 7,39; | 8,53; 2670           | 100                    |
|                   |       | 25,76                |                        |
| 24 h              | 7,39; | 8,54; 5600           | 45                     |
|                   |       | 25,78                |                        |
| 48 h              | 7,38; | 8,73; 4000           | 32                     |
|                   |       | 25,79                |                        |
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|---|---|---|
| 72 h | 7,43; |  |
|  | 8,72; | 6960 55 |
|  | 24,71 |  |
| 96 h | 7,48; |  |
|  | 8,78; | 8490 70 |
|  | 25,84 |  |