The effect of solvent and temperature in the synthesis of CPO-27-Ni by reflux

Joan Guasch a, Pascal D.C. Dietzel b, Paul Collier c, Nadia Acerbi c,*

a Universitat Rovira i Virgili, Campus Sescelades, Marcelli Domingo, s/n, 43007 Tarragona, Spain
b University of Bergen, P.O. Box 7803, 5020 Bergen, Norway
c Johnson Matthey Technology Centre, Blount’s Court, Sonning Common, Reading RG4 9NH, UK

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A B S T R A C T
CPO-27-Ni was synthesized by reflux at temperatures up to 110 °C by using different organic solvent/water mixture and only water. Depending on the solvent(s) used, properties comparable to the material prepared by solvothermal synthesis were achieved typically at lower temperature. It has been demonstrated that the solvent has an effect on crystal growth, this latter influencing size and morphology of the crystal. Also a temperature effect on crystallization and crystal morphology was observed when using the same organic solvent/water mixture at different temperatures. Finally neither the structure nor the stability suffers relevant changes due to solvent modification. The reflux method is a viable route to be used for large scale synthesis of this MOF.

1. Introduction

Metal–Organic Frameworks (MOFs, also known as coordination polymers) are porous solid materials built up of two and three-dimensional frameworks whose skeleton contains both organic and inorganic moieties linked by coordination bonds [1]. The ligands act as spacers, creating an open porous three-dimensional structure, with very high pore volumes and surface areas. There is much interest in tailoring MOFs properties, for instance by combining of metal salts with organic linkers of prescribed chain length and branching characteristics [2]. MOFs with sufficiently rigid frameworks demonstrate permanent porosity, i.e. the ability to maintain the porosity after solvent removal. The most influential parameters in determining the structure – and consequently the properties – of the MOF is the stereochemical directionality of the constituent secondary building units (SBU). In addition, important parameters that influence how the SBUs assemble are reagent concentration, pH, nature of the solvent and temperature [1]. The solvent molecules play an essential role in the properties of MOFs since it is believed that it acts as a template for the framework [3]. Moreover, it has been observed that the polarity of the solution where the reaction takes place also is a parameter that has an effect on the final product, and this can be tuned easily playing with the solvent and mixtures of solvents [4]. Nevertheless, there is a lack of a systematic investigation in the literature about discussion on the effect of the nature of solvent on MOFs properties.

Herein, we present an investigation on the influence of different mixtures of organic solvent/water and temperature on the properties of a nickel based Metal–Organic Framework, CPO-27-Ni. CPO-27-Ni was first synthesised by Dietzel et al. [5] and consists on a three-dimensional honeycomb-like framework with large one-dimensional pores of ~11–12 Å diameter. Its composition is Ni2(2,5-dioxidoterephtalate) (H2O)2/8H2O. It is a member of an isostructural series of MOFs with various divalent cations (Zn, Co, Ni, Mg, Mn, Fe, Cu), alternatively also called MOF-74, M2(dhtp) or M2(dobdc) [2,5–9]. The solvent contained in the channels after the synthesis is easily removed by thermal treatment, resulting in an activated stable framework structure. A characteristic feature of the structure of activated CPO-27-Ni is the presence of a high concentration of coordinatively unsaturated metal cations. This vacant coordination site at the metal ion is the primary coordination site for the guest molecules [10].

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CPO-27-Ni has been synthesised using a mixture of THF and water following the procedure reported by Dietzel et al. [5] and, alternatively, in a mixture of DMF/water/2-propanol [8] under solvothermal conditions or by microwave heating [14]. The synthesis procedures [5,11] were performed using the solvothermal method leading to a crystalline solid with a determined BET surface area of typically 1200 m$^2$/g and a pore volume of ~0.47 cm$^3$/g [2,5,11,15]. In this work, CPO-27-Ni has been synthesised under reflux conditions in different mixtures of organic solvent/water and only water. The organic solvents used were tetrahydrofuran (THF), 2-butanone, hexanol, n-butanol, ethylene glycol and glycerol. An alternative route to make CPO-27-Ni, such as the reflux used in this work, is a more attractive synthesis procedure to be implemented at industrial large scale. A material is obtained with properties comparable to the solvothermally synthesized material at a reduced temperature, typically not higher than 100 °C, while the solvothermal process requires temperature between 105 and 130 °C. Our results show that CPO-27-Ni crystal growth and morphology are dependent on the solvent mixture used, with the most polar solvents promoting the best crystal growth. A temperature effect on crystal morphology was also observed when the same organic solvent/water at different temperatures was used.

2. Experimental

2.1. Synthesis of materials

The CPO-27-Ni material was prepared from nickel(II) acetate tetrahydrate and 2,5-dihydroxyterephthalic acid in an organic solvent–water mixture 50:50 by volume. A solution of 2,5-dihydroxyterephthalic acid (Alfa Aesar, 98%) (0.596 g, 3 mmol) in organic solvent (or water) (20 ml) and a solution of nickel(II) acetate tetrahydrate (Aldrich, 98%) (1.492 g, 6 mmol) in water (20 ml) were prepared separately and then combined in a 100 ml round bottom flask attached to a reflux condenser and reacted under stirring for 24 h at a determinate temperature. Further preparation details are shown in Table 1. Once the reaction was completed, the final product was cleaned three times with distilled water (500 ml) for 20 min each time and next dried on air for overnight and subsequently under vacuum at 80 °C for 24 h. The dried product consisted of crystallites between yellow and ochre color.

The system chosen for the temperature study was the synthesis of CPO-27-Ni in a mixture of ethylene glycol and water. In order to compare the temperature study with the solvent one, temperatures chosen were 110, 94 and 67 °C. 110 °C was chosen as the boiling point of the ethylene glycol/water (50 vol%) azeotrope, 94 °C and 67 °C were the temperatures used in the solvent study for ethylene glycol/water and THF/water, respectively. The procedure details and the scale are the same than the used in the solvent comparison. The difference was that, in this case, the organic solvent was a fixed parameter, and the only variable was the temperature.

2.2. Characterization

Adsorption measurements were performed with an Autosorb 1, Quantachrome Corp. equipment using nitrogen sorption at 77 K. The synthesised CPO-27-Ni was pretreated by heating at 363 K for 24 h in a vacuum oven and degassed for 22 h at 150 °C connected to the adsorption instrument. Additional adsorption measurements were carried out with a Quantachrome Autosorb 1 using nitrogen sorption at 77 K and desagassing temperatures of 200 °C for 24 h for the entire series of samples and 220 °C for samples synthetized in glycerol/water and only water.

Thermogravimetric analysis was used to analyze the stability in air of each MOF (Diamond TG/DTA from PerkinElmer). The program used in this work was the same for all the samples and consisting of heating from 35 °C to 600 °C under air (200 ml min$^{-1}$) at a heating rate of 10 °C min$^{-1}$. Phase identification and crystallite size were obtained from X-ray diffraction using a Bruker AXS D8 with 90 position sample changer (Diffractometer D8 Lynxeye) with a cathode of copper.

The crystallite size of the observed phase was estimated by Pawley analysis [16].

The morphology of crystals from the different MOF samples were determined by SEM analysis using a Zeiss Ultra 55. Yields were calculated on a nickel basis, using nickel assays determined by ICP-ES analysis.

3. Results and discussion

3.1. Effect of solvent in the synthesis of CPO-27-Ni by reflux in a mixture of organic solvent/water

<table>
<thead>
<tr>
<th>Code</th>
<th>Organic solvent</th>
<th>$T$ experiment (°C)</th>
<th>Yield (%)</th>
<th>Crystallite size (nm)</th>
<th>$T$ start decomposition (°C)</th>
<th>$T$ total decomposition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPTHF</td>
<td>THF (Sigma Aldrich, 99.9%)</td>
<td>67</td>
<td>71.0</td>
<td>33</td>
<td>220.0</td>
<td>256.0</td>
</tr>
<tr>
<td>CPMEK</td>
<td>2-Butanone (Alfa Aesar, 99.5%)</td>
<td>75</td>
<td>75.9</td>
<td>88</td>
<td>254.5</td>
<td>278.0</td>
</tr>
<tr>
<td>CPHEX</td>
<td>Hexanol (Aldrich, 98%)</td>
<td>100</td>
<td>69.9</td>
<td>96</td>
<td>262.2</td>
<td>277.2</td>
</tr>
<tr>
<td>CPBUT</td>
<td>1-Butanol (BDH, 99.9%)</td>
<td>94</td>
<td>84.2</td>
<td>56.4</td>
<td>248.6</td>
<td>263.0</td>
</tr>
<tr>
<td>CPET54</td>
<td>Ethylene glycol (Alfa Aesar, 99%)</td>
<td>94</td>
<td>86.2</td>
<td>120</td>
<td>278.1</td>
<td>282.1</td>
</tr>
<tr>
<td>CPGLY</td>
<td>Glycerol (BDH, 99.5%)</td>
<td>94</td>
<td>65.2*</td>
<td>107</td>
<td>249.9</td>
<td>270.5</td>
</tr>
<tr>
<td>CPWAT</td>
<td>–</td>
<td>100</td>
<td>80.0</td>
<td>106</td>
<td>265.4</td>
<td>288.0</td>
</tr>
</tbody>
</table>

* Part of the product was lost accidentally during the synthesis, so the real yield should be higher.
Fig. 1. Comparison of the peak position between the samples done with different solvent and with solvothermal reference. (a) The solvothermal reference DHTP99 (0.3 mm diameter capillary), (b) CPTFH, (c) CPHEX, (d) CPET94, (e) CPMEK, (f) CPWAT, (g) CPGLY and (h) CPBUT.

Fig. 2. Plot representing the weight loss depending on the temperature for the samples done in different water and organic solvent mixtures. (TGA in air of CPO-27-Ni prepared solvothermally can be found in Ref. [5].)

Fig. 3. Plot representing the relation between stability and crystallite size.
Fig. 4. Full adsorption and desorption isotherms for samples CPTHF (aged and re-activated sample), CPMEK, CPHEX, CPBUT, CPET94, CPGLY and CPWAT. All samples have been degassed at 200 °C apart from differently stated.

Table 2
Values of the surface area when samples were degas at 150 and 200 °C; pore volume when degassing was carried out at 200 °C for each sample of the solvent screened. DHTP673 is the solvothermal reference.

<table>
<thead>
<tr>
<th>Code</th>
<th>Surface area (m²/g) 150 °C deg</th>
<th>Surface area (m²/g) 200 °C deg</th>
<th>Pore volume (cc/g) 200 °C deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPTHF</td>
<td>468, 1081a (pore volume: 0.43 cc/g)</td>
<td>69b</td>
<td>0.27</td>
</tr>
<tr>
<td>CPMEK</td>
<td>1207</td>
<td>1008</td>
<td>0.4</td>
</tr>
<tr>
<td>CPHEX</td>
<td>912</td>
<td>1272</td>
<td>0.34</td>
</tr>
<tr>
<td>CPBUT</td>
<td>1306</td>
<td>946</td>
<td>0.425</td>
</tr>
<tr>
<td>CPET94</td>
<td>1103</td>
<td>1024</td>
<td>0.43</td>
</tr>
<tr>
<td>CPGLY</td>
<td>240</td>
<td>827</td>
<td>0.34</td>
</tr>
<tr>
<td>CPWAT</td>
<td>122</td>
<td>1025</td>
<td>0.41</td>
</tr>
<tr>
<td>DHTP673</td>
<td>–</td>
<td>1218</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Note that CPGLY after degassing at 220 °C exhibits a surface area of 1370 m²/g.

a BET surface area obtained on the aged sample re-activated in an autoclave half-filled with water heated at 110 °C for 24 h, filtered and washed with methanol.

b BET surface area obtained on the aged samples.
The TGA plots of CPO-27-Ni prepared by different water/solvent mixtures are displayed in Fig. 2. This plot shows that all the samples follow a similar weight loss/temperature curve. It is worth to point out that CPTHF exhibits a more gradual weight loss due to sample total decomposition in comparison with the other samples. The reason of this difference is unknown at this stage. However, it can be clearly seen that the most stable samples, exhibiting the highest decomposition temperature, are those made using water and ethylene glycol, respectively. On the other hand, the least stable, with the lowest decomposition temperature, is that synthesised with THF. This may be a purely kinetic effect caused by difference in crystallite size (see Fig. 3).

From the previous plot and from the temperature of starting decomposition (see Table 1) a correlation could be established between stability and crystallite size of CPO-27-Ni obtained by XRD. This correlation demonstrates that the differences in decomposition temperatures determined by TGA are related to a kinetic effect due to different crystallite size.

However, it must be said that the results obtained for the sample with glycerol are not consistent with the rest of the results and the origin of this deviation is unknown, at this stage.

BET surface area measurements were carried out on all the samples of CPO-27-Ni prepared by different water/organic solvent mixtures and after activation at different temperatures, namely

Fig. 5. Morphology of crystals from the different MOFs samples determined by SEM analysis (100 nm). The samples are: (a) CPTHF, (b) CPMEK, (c) CPHEX, (d) CPBUT, (e) CPET94, (f) CPGLY and (g) CPWAT. The images are in 100 nm scale.
150, 200 and 220°C. Full adsorption and desorption isotherms are shown in Fig. 4 after degassing at 200°C apart from when it is differently stated. All samples exhibit microporosity. Table 2 reports the surface area and pore volumes measured for the different samples, after degassing at 150°C and 200°C. The use of different water/organic solvent mixtures for the synthesis of CPO-27-Ni resulted in substantial variations in the surface area of the final product. For some solvents, the surface area was approaching or on the same level than the solvothermally prepared samples[11].

After activating CPGLY and CPWAT at 200°C a BET surface area values of 1025 m²/g and 827 m²/g were measured. Possibly a degassing temperature of 150°C was not high enough to remove the glycerol from the pores of CPO-27-Ni due to the strength of its H-bonds. A surface area of 1370 m²/g was obtained when CPGLY was activated at 220°C. Nevertheless, the activation temperature of 200°C is not always beneficial as we have observed in the case of CPGLY. In Table 2 it is possible to observe that a loss in surface area is observed for CPETBP, CPET94 and CPET67 samples when they are activated at 200°C. Conversely, CPHEX exhibits a similar surface area after activation at 150 and 200°C. The sorption isotherm of sample CPTHF was measured during revision of the manuscript, the aged sample exhibits a low surface area demonstrating that this material ages when stored in ambient conditions. However, re-activation of the aged sample yielded a significantly improved specific surface area and pore volume than the original measurement. The aged material was re-activated by hydrothermal treatment at 110°C for 20 h as a consequence of the observation reported on CPO-27-Co in Ref. [18].

The images of the morphology of each sample obtained by SEM analysis are represented in Fig. 5 and significant differences can be observed between the samples. The samples with larger crystallite size, as CPWAT or CPET94, show the presence of more crystalline hexagonal rods. Meanwhile those with smaller crystallite size show flattened round particles.

The hexagonal rods shown by the more crystalline samples clearly reflect the rhombohedral crystal structure of CPO-27-Ni [5].

3.2. Effect of temperature on the synthesis of CPO-27-Ni under reflux in a mixture of ethylene glycol/water

The values reported in Table 3 show that the temperature has a deep effect on the percentage of nickel and, even more, in the yield. The temperature affects the kinetics of CPO-27-Ni formation.

The difference appreciated in the percentage of nickel could be associated with the nucleation and growth of the crystals. The low temperature at which CPET67 was synthesised (67°C) decreases the supersaturation [19]. The supersaturation is the driving force of the nucleation and is defined as the difference of chemical potential (Δμ) between a molecule in solution and that in the bulk of the crystal. The supersaturation has a logarithmic dependence on the temperature. Then, this lower temperature will reduce the rate of nucleation. Moreover, the growth of the crystals formed also will be affected by the lower temperature, because the building blocks of the framework will not have as much energy to reach the energy barrier of crystal growing [20].

The crystallite size measured for the three samples of ethylene glycol at different temperature are reported in Table 3. At high

<table>
<thead>
<tr>
<th>Code</th>
<th>T experiment (°C)</th>
<th>Yield (%)</th>
<th>Crystallite size (nm)</th>
<th>T start decomposition (°C)</th>
<th>T total decomposition (°C)</th>
<th>Surface area (m²/g) 150°C deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPETBP</td>
<td>110</td>
<td>85</td>
<td>118</td>
<td>260.9</td>
<td>276.8</td>
<td>1082</td>
</tr>
<tr>
<td>CPET94</td>
<td>94</td>
<td>86.2</td>
<td>120</td>
<td>270.1</td>
<td>282.1</td>
<td>1103</td>
</tr>
<tr>
<td>CPET67</td>
<td>67</td>
<td>9.9</td>
<td>98</td>
<td>260.6</td>
<td>277.2</td>
<td>1070</td>
</tr>
</tbody>
</table>

Fig. 6. SEM images (100 nm scale) for the samples of CPO-27-Ni done at different temperatures: (a) CPETBP, (b) CPET67 and (c) CPET94.
temperature (94 and 110 °C), little difference can be observed. Meanwhile, there was a decrease when the temperature was reduced to 67 °C. The reason could be attributed to the less energy available to jump the energy barrier between the building units and the growing crystal [20].

In terms of structure, no difference was detected in the XRD spectrum, as it is shown in Fig. 1. All the samples matched accurately with the pattern.

The thermogravimetric analysis (Supporting Information) showed that stability is not affected by synthesis temperatures and confirmed our hypothesis that stability relates to crystallite size, due to a kinetic effect.

The SEM images (Fig. 6) obtained for each sample revealed some changes in the morphology of the particles. The sample obtained at 67 °C shows flattened irregular particles, like those observed in the images of CPHEX. The one at 94 °C, on the other hand, has large, also irregular, particles, some with clear hexagonal shape. Finally, the sample made at 110 °C has lost the hexagonal-shaped particles but still maintain large sizes, however, more irregular.

These results match with the crystallite size obtained by XRD for each sample and suggest the existence of an optimum temperature on which CPO-27-Ni shows the best properties, perhaps related to the change of the solvent mixture properties with the temperature. There is a clear temperature effect on the crystal morphology.

4. Conclusions

CPO-27-Ni was synthesized successfully by a reflux method yielding a material with properties as good as or better than the material prepared by the more routinely used solvothermal synthesis. The use of the reflux method represents a more attractive synthesis route for large scale production. Moreover, the effect of the solvent and the effect of temperature in the synthesis of CPO-27-Ni have been studied. The nature of the solvent was found to influence the particle size and morphology of the final MOF product. In a general basis, those solvents with higher polarity and ability to form H-bond gave rise to an improved crystal growth. This ability for H-bond formation is directly proportional to the thermal treatment required for the pore evacuation. In particular, an optimum surface area and solvent removal temperature was achieved when the organic solvent employed was ethylene glycol. In addition, modification of the solvent resulted in significant changes on the morphology of the final material. More polar solvents which have a better ability to form H-bonds provided larger and better defined crystals. Specifically, when water was used as unique solvent, SEM analysis displayed well defined hexagonal rods. Thus, we have demonstrated that the use of polar solvents which are able to form H-bonds can emulate the solvothermal conditions in terms of crystal growth. We could speculate that the plausible presence of H-bond between the ligand and the solvent molecules could be the reason for a preferential direction of crystal growth. Finally, neither the structure nor the stability suffers relevant changes due to solvent modification. A temperature effect was shown where the temperature appears to affect crystal morphology but not crystallite size. Therefore it is possible to conclude that only solvent has an influence on crystallite size.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.10.018.

References
