Effect of Synthesis Conditions on Formation Pathways of Metal Organic Framework (MOF-5) Crystals

Colin McKinstry[a,b], Edmund J. Cussen[b], Ashleigh J. Fletcher*[a], Siddharth V. Patwardhan[a], Jan Sefcik[a]

[a] Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, G1 1XJ, U.K.

[b] WESTCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, U.K.

In Depth Experimental Procedure for Single and Two Step Process

0.157 g of zinc nitrate Tetrahydrate (Emsure, >98.5%) and 0.0333 g of terephthalic acid (Alfa Aesar, 98+%) (metal ion: linker ratio of 3) were dissolved in 5ml of N,N-diethylformamide (DEF)(Alfa Aesar, 99%) in 23 mm diameter flat bottomed glass vials. For samples using zinc nitrate hexahydrate, the mass used was increased to keep the Zn:acid ratio the same as other experiments. For the two step syntheses, the mother solution was heated to 60 ˚C for 72 hr and data points were carried out in multiples in order to gain the best idea of the solids produced. For single step syntheses, each experimental point was carried out in duplicate. A pre-heated oil-bath was set to experimental target temperature and had reached a stable temperature before addition of vials. An oil-bath was used to reduce any temperature gradients across the samples. For stirred samples, 5 mm PTFE magnetic stirrer bars were used. Vials of solutions were left in an oil-bath for the designated experimental time, varied between 30 min and 6 hr in increments of 30 min or 1 hr. After reaching experimental duration, vials were removed and the solution pipetted onto filter paper to air dry. Disposable pipettes were used in order to minimise any possible cross contamination. When dried, samples were transferred into sample bottles and analysed by XRD immediately, in order to negate any reaction between the MOF-5 compound and moisture in the air, as mentioned by Chen *et al*[1].

Analysis of Two Step Synthesis Route

Initial attempts to monitor the rate of formation of MOF-5 used two temperature regimes to initiate a reaction and then grow crystalline material using a route described in the literature[3]. These reactions were run in multiple parallel batches with, nominally, six reactions being performed simultaneously using identical reaction vessels subjected to the same heat source and stirring rate. A pre-treatment temperature 60 ˚C for up to 72 hr followed by a heating at 75 ˚C or 105 ˚C for 1.5 hr. However, we found that these conditions yielded a mixture of products shown in Figure 1S as compounds (d) and (e). The overall repeatability of the process was analysed by running several repeat runs with identical process conditions to those described by Fischer *et Al*[3]. From our experimental runs we have a success rate of just 5/64 runs, including samples that showed MOF-5 with an alternative phase also being present.

The presence of water of crystallisation in $Zn(NO_3)_2.4H_2O$ is likely to of lead to hydrolysis of DEF. The two step process is far less common than single step syntheses, and the issues with this type of synthesis have been discussed by Feng *et al*.[4] who stated: "*Since DEF is known to hydrolyse to produce formic acid and the electron donor diethylamine (DEA), single crytals of MOF-5 were synthesized from DEF at higher temperature (110 ˚C) than by Kaye et al*[5]*. [80 ˚C*]". Repeating the experiments using $Zn(NO_3)_2.6H_2O$ did not have an effect on the irreproducibility of the reaction. Moreover, inconsistent results were obtained with some large variations in both the composition of the mixture and the crystallinity, as indicated by the width of the Bragg peaks in the powder diffraction pattern.

The effect of stirring upon the synthesis process was monitored by repeating experiments in stirred and unstirred forms. Stirring appears to produce samples with higher crystallinity but did not alter the probability of producing a MOF-5 compound.

The two step process is far less common than single step syntheses and combined with the lack of consistent MOF-5 production that occurs during these experiments suggests that the two step process appears to only be viable with long durations of pre-treatment and an initiation phase >1.5 hr at 105 ˚C. Consequently, the energy and time efficiency is lower than a more conventional, single step process. Though the two step process can produce MOF-5, the system has severe issues with repeatability and for this reason, along with the above, focus was switched to a single step process.

Yield Analysis

The dry yields of solids before solvent extraction were also studied. The yields show further evolution of solids in a clear manner. These masses also show that such a large amount of the systems solids forming mass has formed the Intermediate Phase that this phase must further react to form the final product, MOF-5.

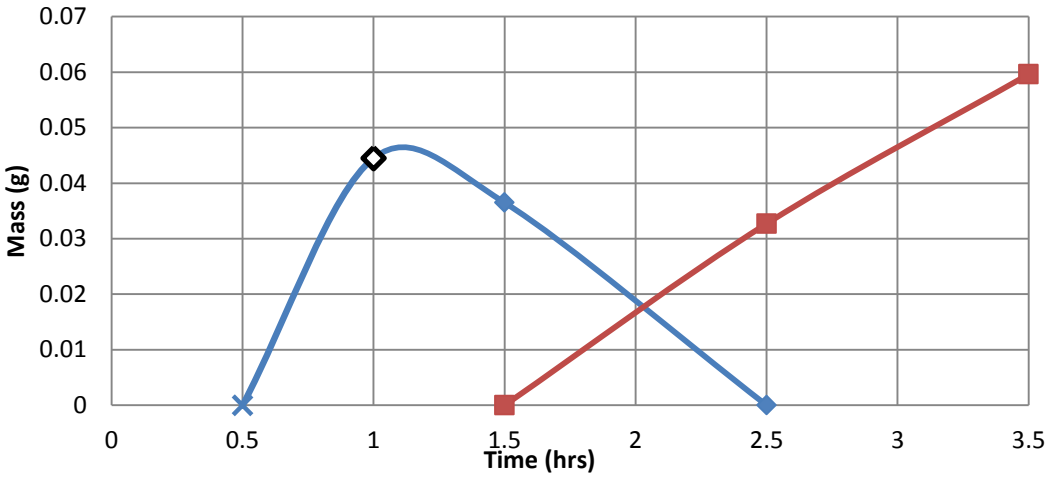

Figure SI1 - Yeild Analysis for solids at 130°C, unstirred. X – No Solids, ◇ - Intermediate Phases, ◆ - Intermediate Phase (IP), ■ - MOF-5.

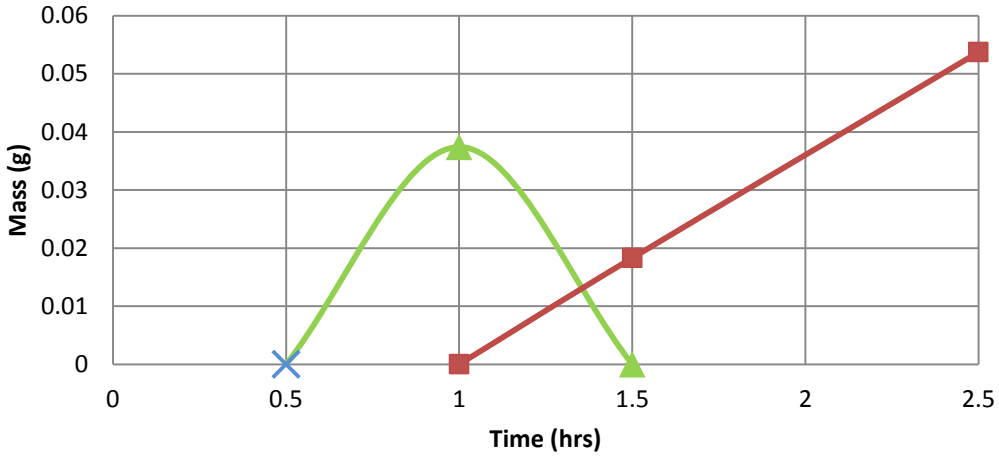

Figure SI2 - Yield Analysis for 140°C, stirred. X – No Solid, ▲ - MOF-5 +Intermediate Phase (IP), ■ - pure MOF-5. The MOF-5 + Intermediate Phase (I) is considered to be completely independent of the pure MOF-5 phase for the purpose of this diagram.

Thermal Stability

The MOF-5 samples produced behave in accordance with the thermal stability for MOF-5. Samples are stable to a temperature of ~ 400˚C at which point breakdown of the structure begins. Post-decomposition weight fractions are in line with expected losses of organics from the system.

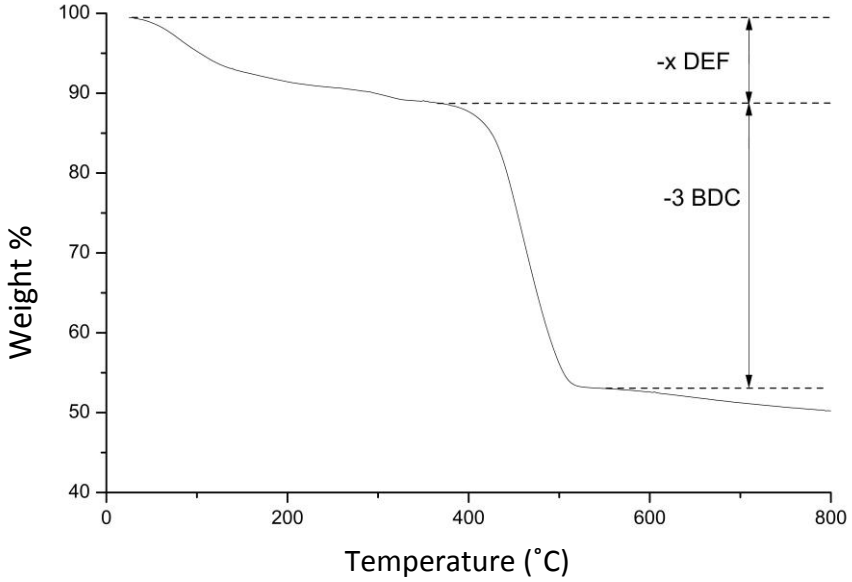

Figure SI3 - Thermal Decomposition of MOF-5

Complete Powder XRD Results

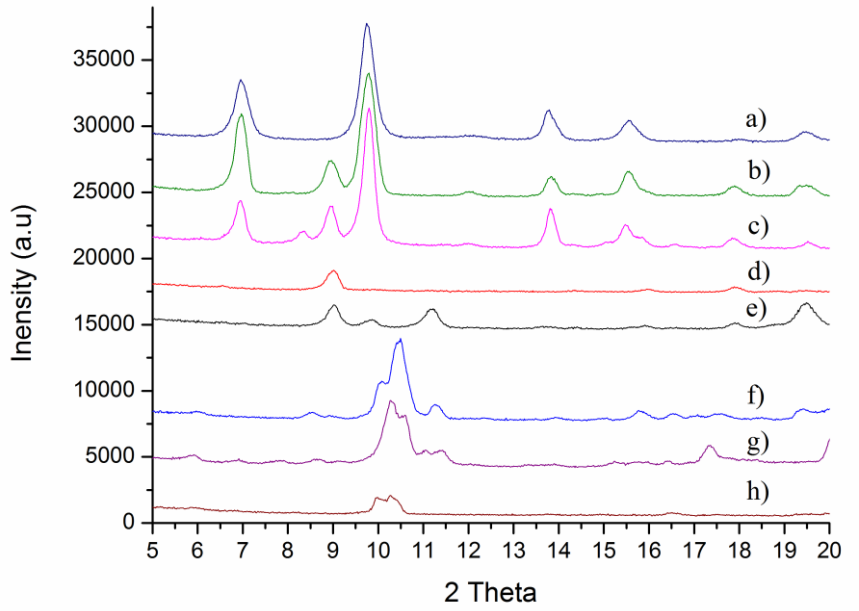

Figure SI4 - Complete Overview of PXRD Results showing a) Pure MOF-5, b) MOF-5 + IP, c) MOF-5 + IP + Intermediate(s), d) pure IP, e) IP + Intermediate(s), f) Intermediate(s), g) Intermediate(s), h) Intermediate(s).

References

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