The Influence of Working Fluids on the Heat Storage Performance of ZIF-93

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ABSTRACT

Zeolitic imidazolate frameworks (ZIFs) are comprised of transition metal ions (Zn) and imidazolate linkers. Due to their properties (large surface areas, suitable pore size distribution and structure stability), ZIFs have great potential for adsorptive separation and storage applications. ZIF-93, with a RHO topology, was studied to determine the impact of various synthesis methods and the use of working fluids (water and ethanol) had on the heat storage performance. The ZIF-93 samples were prepared by conventional solvothermal synthesis as well as greener mechanochemical approaches. The research shows that ZIF-93, exhibits a high energy storage potential with water as a working fluid, due to high water uptake capacity, high sorption enthalpies and high hydrothermal stability.

Key words: ZIF-93; sorption studies; green synthesis; desorption enthalpy

INTRODUCTION

The increasing demand for heating and cooling energy is of great importance due to the constantly growing population. As energy for heating and cooling accounts for up to 50% of the world's final energy consumption, interest in environmentally friendly methods of optimising heat supply and demand has increased. One method that addresses this problem and utilises renewable energy is thermal energy storage (TES), which uses reversible chemical reactions and/or sorption processes of gases in solids or liquids. A major advantage of this method is that it only has an insignificant heat loss and at the same time achieves a much higher energy storage density.

Sorption-based thermal energy storage can be examined using traditional adsorbents (*e.g.* zeolites) or innovative adsorbents (*e.g.* metal-organic frameworks (MOFs)).[1,2] One of the subgroups of MOFs is Zeolitic imidazolate frameworks (ZIFs), which are comprised of transition metal ions (Zn, Co, etc.) and imidazolate linkers.[3] ZIFs are structured similarly to zeolites, where the metal ion replacing the Si/Al and the imidazolate linker replacing the O atoms. ZIFs are considered to be highly stable. Due to their properties, including ordered porous structures and possibility to shape them in glass-like monoliths, ZIFs also have been proposed as supports for adsorptive separation applications.[4] In spite of a great potential, the reports on the optimization of ZIF for heat storage and allocations applications are scarce and majority focusing on water as working fluid. On the other hand, using ethanol instead of water is reportedly advantageous, which can be seen in a study by De Lange *et al.* (2015).[5] The use of ethanol as an adsorbate has seldom been explored for this purpose but may prove to be beneficial for applications at lower temperatures when compared to water.[6,7] Furthermore, their large-scale application is limited by the absence of low-cost mass production, as well as the lack of sustainable synthesis routes, that would lower the environmental impact of the ZIF preparation.[8] Most of the stable ZIFs are synthesized via solvothermal synthesis, which requires higher temperatures and can take up to 72 h or more. Large amounts of *N*,*N*-dimethylformamide (DMF) are often used as well, as it is decomposed during the synthesis in

a way to stimulate the ZIF formation. As DMF is known to be toxic and carcinogenic, a great effort has been made to implement greener solvents to the ZIF synthesis process and lower its impact on the environment.[9] Additionally, the search for a DMF replacement has gained greater interest as a result of the EU heavily restricting or in some cases completely banning the use of DMF as of last year (2023).

ZIF-93 was studied as it has a large pore entrance and pore/cage capacity (3.6 Å and 17.9 Å, respectively). [10–12] ZIF-93 has a RHO topology. DMF was successfully replaced with methanol in the synthesis of ZIF-93.[13] However to the best of our knowledge, ZIF-93 have not been successfully synthesized *via* mechanochemical synthesis, which is also considered a green synthesis approach, since we can exclude solvents from the synthesis or use a minimum amount (µL). Therefore, this presentation will discuss the green synthesis of ZIF-93 and the impact that this has on the structural and sorption properties. Furthermore, the impact of different working fluids, i.e. water and ethanol, on TES performance will be evaluated.

EXPERIMENTAL

ZIF-93 was synthesised using three different methods: as per literature (1-ZIF93-ST), using an optimised precipitation method (2-ZIF93-P) and *via* ball milling (3-ZIF93-BM), see Figure 1. ZIF-93 was synthesized using zinc acetate dihydrate as the zinc precursor, 4-methyl-5-imidazolecarboxaldehyde as the linker and methanol, water or ɣ-valerolactone (GVL) as the solvent depending on the synthesis method (see Figure 1). 2-ZIF93 used ammonia in small quantities to act as a catalyst. The samples that required activation were heated in a vacuum over at 150°C overnight. The structural properties of the ZIF samples were determined using PXRD, TGA and N2 physisorption. The water and ethanol uptake (mmol) were examined using a dynamic vacuum sorption analyzer (Surface Measurement Systems). The isotherms were collected at 25°C in the relative pressure range from 0 – 0.9. Finally, the ZIFs were analysed with DSC to determine the desorption enthalpy. The ZIFs were placed in a desiccator with water-saturated solution of NaCl (rh = 75%) or ethanol for 1-5 days prior to DSC analysis.

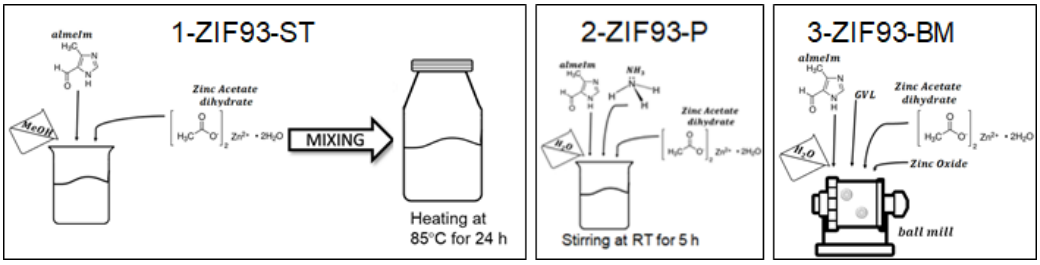

Figure 1. Synthesis methods for the 3 ZIF-93 samples examined.

RESULTS AND DISCUSSION

Figure 2 (a) shows the PXRD for all 3 samples synthesised and the calculated ZIF-93 patterns. The formation of ZIF-93 in the synthesised samples was confirmed by comparing them with the calculated patterns (see Figure 2 (a)). As there were no additional peaks in any of the samples, they were shown to be phase pure. PXRD was performed after activation to show the structure remained intact after the process.

TGA was primarily used to determine if the ZIF samples required activation, though the temperature at which the structure collapsed was also of interest. All samples needed activation. As an example, Figure 2 (b) shows the TGA for 3-ZIF93 before and after activation. The 3-ZIF93 sample, shows a large peak below 100°C (solid red line Figure 2 (b)) and an approx. mass loss of 10% (solid black line Figure 2 (b)). This mass loss can be attributed to the removal of water/GVL from the sample. After the sample has been activated (3-ZIF93-ACT), a small

peak (dotted read line Figure 2 (b)) is still present and there is a mass loss of approx. 2% (dotted black line Figure 2 (b)). Any peaks or mass loss before 100°C in activated samples are generally assigned to vapours/solvent that is on the surface of the sample.

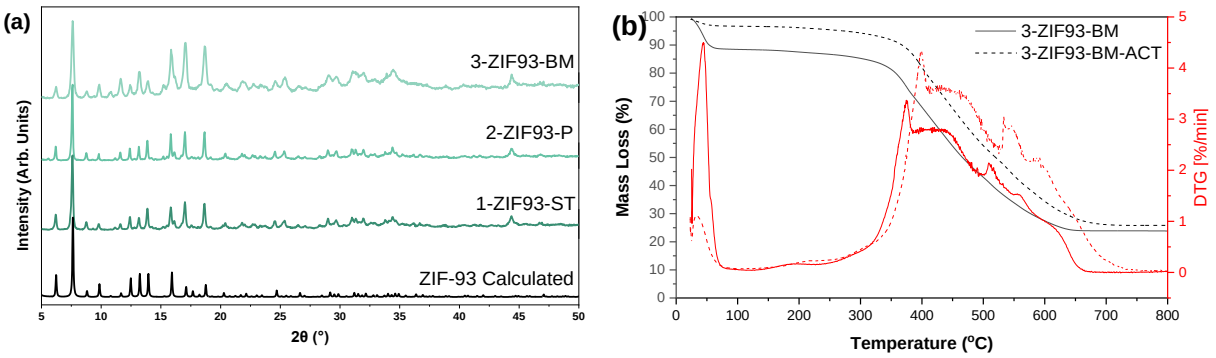

Figure 2. (a) PXRD of the as-synthesized ZIF-93 samples with the calculated pattern and (b) TGA of as-synthesized and activated 3-ZIF93.

Nitrogen physisorption was completed to determine the specific surface area. This ranged from 587-1239 m^2/g for ZIF-93 (see Figure 3). All of these are outside the range of previously published results, with 1-ZIF93-ST and 2-ZIF93-P showing an improvement and 3-ZIF93-BM showing a reduction compared to previous studies (604 m^2/g – 864 m^2/g) ZIF-93.[12–16]

Figure 3 also shows the water uptake for all samples. The ZIF-93 samples showed a water uptake ranging from 13.3-15.3 mmol/g (23.9-27.5%) and an ethanol uptake of 4.6-5.2 mmol/g (21.3-24.0%). The modified precipitation method showed the highest sorbate uptakes and largest specific surface area. It is worth noting that despite 3-ZIF93-BM having a significantly smaller specific surface area compared to the other two samples, there is not a big difference in the water or ethanol uptake.

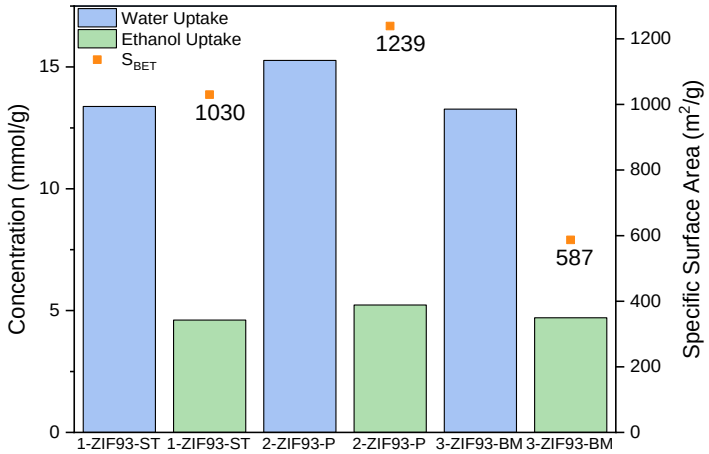

Figure 3. Water and ethanol uptake at 0.8 P/P_0 obtained at 25°C with the specific surface area (S_{BET}) for all samples

Finally, DSC was used to determine the heat storage potential of all samples. The best performing ZIF-93 sample showed a desorption enthalpy that reached 503 J/g. This is slightly lower than the currently best preforming ZIF (ZIF-90) by ~40 J/g, but has been proven to be more hydrothermally stable that ZIF-90.[17] This was confirmed by XRD measurements of ZIF-93 samples after sorption studies.

CONCLUSION

In this study, ZIF-93 were synthesised using solvothermal, precipitation and mechanochemical methods. Our study showed the successful preparation of ZIF-93 samples at room temperature, by using water as a solvent or by following the mechanochemical route. The thermal energy storage potential was assessed by using DCS based desorption enthalpy measurements, which revealed ZIF-93 to have good heat storage potential over a longer period of time, also when prepared by greener mechanochemical approaches. The specific surface area did not have a limiting factor on the uptake results. Finally, ZIF-93 and water as a working fluid proved to be the optimum adsorbate-adsorbent pairing.

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