EXAMINING ZEOLITIC IMIDAZOLATE FRAMEWORKS (ZIFs) FOR ETHANOL ADSORPTION

Ciara Byrne
Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
E-mail: ciara.byrne@ki.si

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. Four different ZIF structures have been investigated for heat storage application, with ethanol as the adsorbate. The two main criteria for selecting ZIF structures for selected application are the pore entrance size and the pore/cage but structure stability, hydrophilicity/hydrophobicity and pore accessibility should also be considered. This research shows that ZIF-93 has the highest % ethanol uptake while ZIF-90 had the highest specific surface area and desorption entropy. The % uptake of ethanol is affected by pore/cage entrance and capacity, functional groups of linkers and crystallite size.

Key words: ZIFs, ethanol uptake, DSC.

INTRODUCTION

The increasing demand of heating/cooling is of grave concern due to the ever increasing population. Since energy for heating and cooling represents up to 50% of the world's final energy consumption, there has been an increased interest in finding environmentally friendly methods for the optimization of heat supply/demand. One method that addresses this issue and uses renewable energy is Thermal Energy Storage (TES), which uses the reversible chemical reactions and/or sorption processes of gases in solids or liquids. One major benefit of using this method is that it only shows an insignificant amount of heat loss while reaching a considerably higher energy storage density.

Sorption thermal energy can be examined using traditional adsorbents (*e.g.* zeolites) or innovative adsorbents (*e.g.* metal-organic frameworks) [1,2]. As they have the potential for many application (such as catalysis and gas capture/storage), there has been an increased interest in metal-organic frameworks (MOFs) [3]. 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, with 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].

The ZIFs studied were selected based on their reported pore sizes and pore capacities [8]. ZIF-8, ZIF-90 and ZIF-93 were selected as they have large pore entrances and pore/cage capacities. For comparison purposes ZIF-74, which has a significantly lower reported porosity, was studied [8].

Table 1. Pore entrance size, the pore/cage capacity and topology for the ZIFs examined [8,9].

ZIF	Pore entrance [Å]	Pore capacity [Å]	Topology
ZIF-8	3.5	11.6	SOD
ZIF-74	1.2	2.6	GIS
ZIF-90	3.5	11.2	SOD
ZIF-93	3.6	17.9	RHO

Based on the encouraging result by De Lange et al. (2015), this study will examine four different ZIFs for heat storage and allocation applications, using ethanol as the adsorbate.

EXPERIMENTAL

ZIF-8, ZIF-90 and ZIF-93 were synthesised using optimised methods based on literature. ZIF-74 was synthesised by significantly modifying the method published by Banerjee *et al.* (2008) [10]. The samples used zinc nitrate hexahydrate (ZIF-8 and ZIF-74) or zinc acetate dehydrate (ZIF-90 and ZIF-93) as the zinc-containing precursor. The linkers used were 2-methylimidazole (ZIF-8), Nitroimidazole (ZIF-74), 5,6-dimethylbenzimidazole (ZIF-74), 2-Hydroxyisocaproic acid (ZIF-90) and 4-methyl-5-imidazolecarboxaldehyde (ZIF-93). TG of the as-synthesized sample showed that ZIF-74 did not require activation. The activation of the three other ZIFs was achieved *via* drying in a vacuum over at 150°C overnight (ZIF-8), soaking in methanol for 6-8 hours followed by drying in vacuum oven at 150°C overnight (ZIF-90) and heating in a vacuum oven at 85°C overnight. All ZIFs were characterised using XRD, TG, SEM and Nitrogen physisorption. The % ethanol uptake was examined using an IGA-100 gravimetric analyser (Hiden Isochema Ltd.). The isotherms were collected at two different temperatures (25°C and 30°C) in the relative pressure range from 0 – 0.9. Finally, the ZIFs were analysed with DSC to determine the desorption entropy. The ZIFs were soaked in a desiccator with ethanol for 7 days prior to DSC analysis.

RESULTS AND DISCUSSION

Structural properties were examined using XRD, TG, and nitrogen physisorption, which revealed phase pure products. The crystalline structures of the three ZIFs were confirmed using XRD and comparing to the simulated XRD pattern (Figure 1).

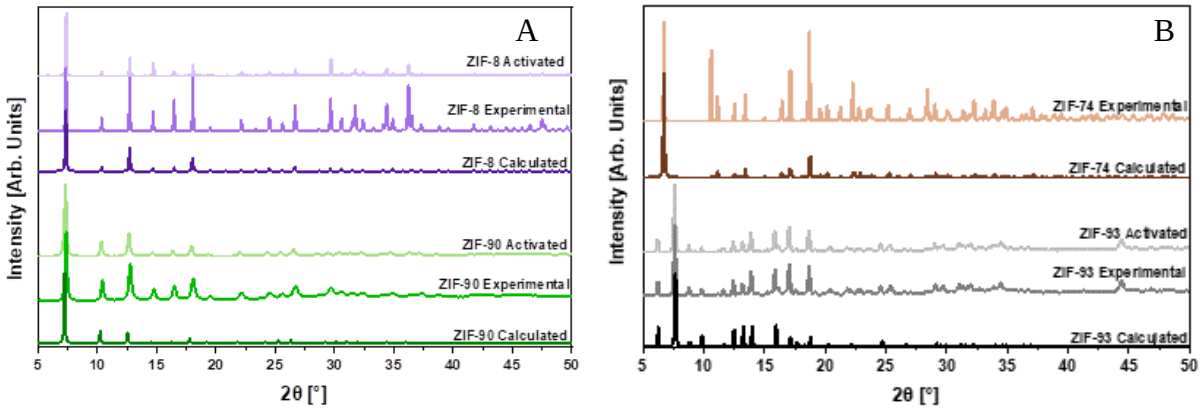

Figure 1. X-ray diffraction patterns of as-synthesized and activated ZIFs. Calculated patterns are also shown. A: ZIF-8 (purple) and ZIF-90 (green). B: ZIF-74 (brown) and ZIF-93 (black/grey).

XRD analysis was repeated after the activation method to ensure that crystalline structure had remained intact (Figure 1). TG analysis was completed prior and after the activation of ZIF

structures to ensure that any solvents present were removed during activation but the remaining structure had not collapsed. SEM was performed on the as-synthesised ZIFs to examine the morphology of the materials and the size of the crystals. As it can be seen in Figure 2, ZIF-8 and ZIF-74 products are made up of large crystals while ZIF-90 and ZIF-93 show significantly smaller crystals.

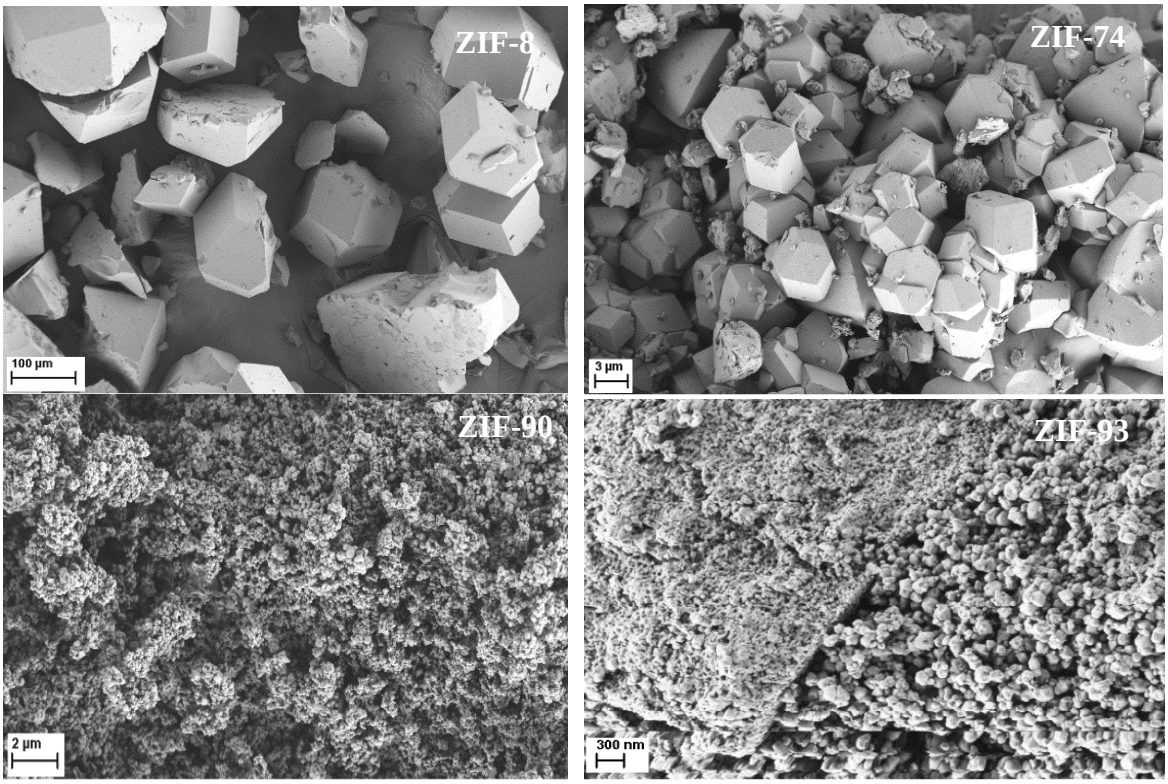

Figure 2. SEM images of as-synthesized ZIF-8, ZIF-74, ZIF-90 and ZIF-93.

Nitrogen physisorption showed that the ZIFs had a specific surface area of up to 1119 m^2/g (Table 2). The ethanol uptake results (Table 2) showed that the capacity up to 37 wt. % ethanol could be reached and that mechanism of sorption of ethanol in selected ZIFs were dominated by diffusion limitations of the molecules through the pores. The structures remained crystalline after the analysis. Based on the all the results for the three ZIFs, the pore capacity and pore size has a direct impact on the surface area and the % ethanol uptake. ZIF-8, ZIF-90 and ZIF-93, which have the larger pore size and pore capacity, showing significantly higher ethanol uptake in comparison to ZIF-74.

Table 2. The specific surface area (S_{BET}), ethanol uptake and DSC analysis for all ZIFs studied.

ZIF	S_{BET} [m^2/g]	Ethanol uptake [%]	DSC [J/g]
ZIF-8	621	19.9	158.4
ZIF-74	6	0.6	58.9
ZIF-90	1119	25.5	260.3
ZIF-93	1058	37.6	206.2

Despite ZIF-8 and ZIF-90 having similar or the same pore entrance, pore/cage capacity and topology, they showed significant differences in the crystal size, specific surface area, % ethanol uptake and DSC results (Figure 2 and Table 2). This difference, at least for ethanol

uptake, is likely due to the hydrophobic linker used for ZIF-8 while ZIF-90 has a slightly hydrophilic linker. DSC analysis (Table 2) showed that the ZIFs had a desorption entropy of up to 260.3 J/g (ZIF-90). DSC analysis showed that there was a 101.9 J/g difference between ZIF-8 and ZIF-90.

CONCLUSION

In this study, the evaluation of four ZIFs as sorbents for sorption based energy storage by using ethanol as sorbate revealed a stable system suitable for potential use in TES. The ZIFs were synthesized using simplified methods. The samples were phase pure and fully activated. ZIF-93 shows the highest % of ethanol uptake while ZIF-90 had the highest specific surface area and desorption entropy. ZIF-74 showed to have the lowest % of ethanol uptake, specific surface area and desorption entropy. Finally, ZIF-90 and ZIF-93 showed that there is not always a direct correlation between % ethanol uptake and desorption entropy.

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