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Synthesis of metal organic framework materials by performing linker exchanges using solvothermal procedure

Abstract. Metal organic frameworks are crystalline nanoporous material constructed from metal ions and bridging organic linkers. These materials are currently receiving considerable research interest due to their adsorption properties and high surface area, which could be used for gas storage and separation. The research involves two main procedures: 1) synthesis of ZIF-76 with LTA framework and performing linker insertion using SALE technique.

Key words: metal organic frameworks, zeolite-imidazolate frameworks, N,N-diethylformamide, N,N-dimethylacetamide.

Introduction

Metal organic frameworks (MOF) are hybrid porous solids which are derived from inorganic (metal nodes) and organic units (organic linkers) in order to build up one, two and three-dimensional frameworks (Figure 1). Metal and organic components are bonded covalently and feature highly ordered crystalline structures [1].

In the last 20 years, metal-organic frameworks (MOFs) have gained considerable attention from researchers because of their potential useful applications such as carbon dioxide capture, storage of hydrogen fuels, gas separation and catalysis [2]. Moreover, MOFs are gaining importance in thin–film devices, membranes and biomedical imaging [3]. Each year, thousands of metal-organic compounds are prepared and studied by chemists [1]. The scope of this studies ranges from topological analysis to molecular synthesis, from optical and absorptive properties to ferroelectric properties and from applications in biomedicine to gas storage [1]. Porosity and large surface area are the main valuable features of metal-organic frameworks (MOFs). Larger storage spaces can be synthesised with longer organic linkers; however, within the MOFs these can form interpenetrating structures. To avoid such structures, MOF needs to be synthesized with a topology which inhibits interpenetration. The synthesis of metal organic frameworks can be carried out at a low temperature. The solvothermal method is utilised above 100^0C. For many syntheses, water and organic solvents, such as pyridine and alcohols can be used. The main parameters of MOF synthesis are temperature, pH and concentration [1].

Solvent-Assisted Linker Exchange of MOF

The synthesis of MOFs from *de novo* suffers from several vagaries such as low solubility, undesirable topologies and loss of sensitivity [4]. However, a recently discovered synthetic method called Solvent-Assisted Linker Exchange (SALE) circumvents the these problems. SALE is based on a heterogeneous reaction, where parent MOF crystals react with a concentrated solution of linkers. SALE circumvents the problem related with linker solubility ensuring the efficient use of precious linkers and leads to the production of the desired MOF material. The heterogeneous reaction pathway enables alteration of MOF crystals by using multitopic linkers. In addition, SALE solves problems associated with catenation and produces MOFs with longer, mixed linkers.

Zeolite A zeolitic-imidazolate frameworks – ZIF-76

The Zeolitic Imidazolate Frameworks (ZIFs) are the most important subfamily of MOFs due to their large use in water softening, selective separation of nitrogen and oxygen gas mixtures and petroleum cracking [5]. ZIFs are composed from bivalent metal cations, such as Co (II), Cu (II), and imidazolate ligands. The main difference of ZIFs from zeolites is their pore size, which tends to be larger than their inorganic analogs [6].

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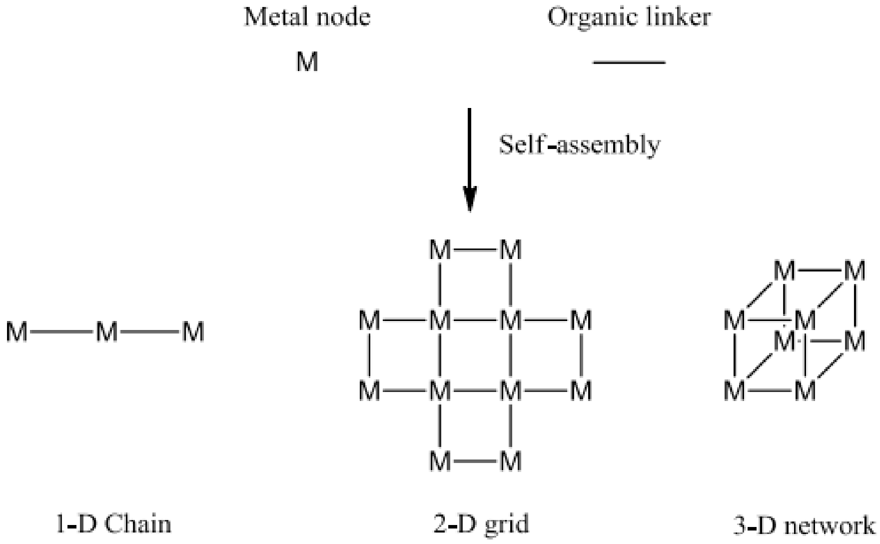

Figure 1 – Different classes of MOF structure[1]

Among the most studied LTA-type ZIFs is $[Zn(Im)_{1.5}(5\text{-}ClbIm)_{0.5})]$ (ZIF-76, Im – Imidazolate, ClbIm – 5-chlorobenzimidazolate) [7]. In ZIF-76, each organic linker connects to two Zn^{2+} centres forming a cubic crystal with a three-dimensional porous framework. Their crystalline properties, such as large pore volume and good stability make them of particular interest for gas adsorption. However, synthesis of ZIF-76 requires an expensive organic linker, 5-chlorobenzimidazolate. To circumvent the problem and retain the LTA framework topology of ZIF, it is important to use relatively inexpensive, structurally related organic linkers such as benzimidazole (bIm). The research is concentrated on synthesising a new LTA-topology $[Zn(Im)_{2-x}(bIm)_x]$ by applying the SALE technique.

Materials and methods

Synthesis

Preparation of ZIF-76 by solvothermal synthesis

The synthesis of ZIF-76 was performed by method described by Yaghi's group. $8.66x10^{-4}$ mol of 5-chlorobenzimidazole (5-ClbIm) and $17.25x10^{-4}$ mol of imidazole (Im) were mixed together in 5 ml of diethylformamide (DEF) and 5 ml of dimethylformamide (DMF). $8.59x10^{-4}$ mol zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ were added to this solution. Following the $Zn(NO_3)_2{\cdot}6H_2O$ $12.96x10^{-4}$ mol of NaOH were added in addition. The synthesis was carried out in 20 ml glass vials, which were heated in an oven at 90 ºC for five days. The solid products separated from solution via vacuum suction and washed with DMF. After separation solid product was immersed in methanol for three days refreshing the methanol every day. Finally, ZIF-76 materials were dried at 50 ºC for an hour.

Solvent-assisted linker exchange (SALE) procedure

The ZIF-76 prepared by solvothermal syntheses were used as a starting material for solvent-assisted linker exchange operation. ZIF-76 (55.15 mg, 0.22 mmol) and bIm (100 mg, 1.47 mmol) were placed to 20 ml glass vials and dissolved in 10 ml of DMF. In other case the mixture of ZIF-76 and bIm were dissolved in 10 ml of 1-proponol and DMA and placed in a Teflon-lined autoclave. The mixtures in DMF, 1-propanol and DMA were heated in an oven at 100ºC for 5 days [8].

Characterization Techniques

The characterization of all the samples was carried out using powder X-ray diffraction (PXRD), elemental analysis, scanning electron microscopy and EDS.

Results and discussion

PXRD pattern of parent and daughter ZIF-76 material

The crystallinity and phase purity of synthesized ZIF-76 was confirmed by PXRD as shown in figure 2 and structure is found to be related to the LTA topology

After the SALE reaction reached completion, the integrity of the parent LTA framework in the new

ZIF-76 was confirmed by PXRD analysis as shown in figure 2. All the products of SALE experiment were phase pure and retained the ZIF-76 PXRD pattern, but with lower intensities and sharpness as the diffraction peak. The work carried out by P. Lu et al. showed that keeping the ZIF-76 in different solvents at 100 ºC does not decompose the structure of the sample but declines the crystalinity [9]. In addition, decrease of intensities and crystallinity could be an indication of possible linker exchange. Obviously the decrease of intensity after linker exchange can be seen at 2θ position between 5.57º and 20º as seen in figure 2.

The PXRD pattern exhibits shifting of peaks to higher angle in all exchanged ZIFs compared to parent material (approximately 0.152º) as shown in figure 2. Shifts could be indication of a reduction in the unit cell parameter compared to starting ZIF-76 material and possible linker exchange. Moreover, systematic shift of peaks at 2θ can be caused by zero or sample displacement error.

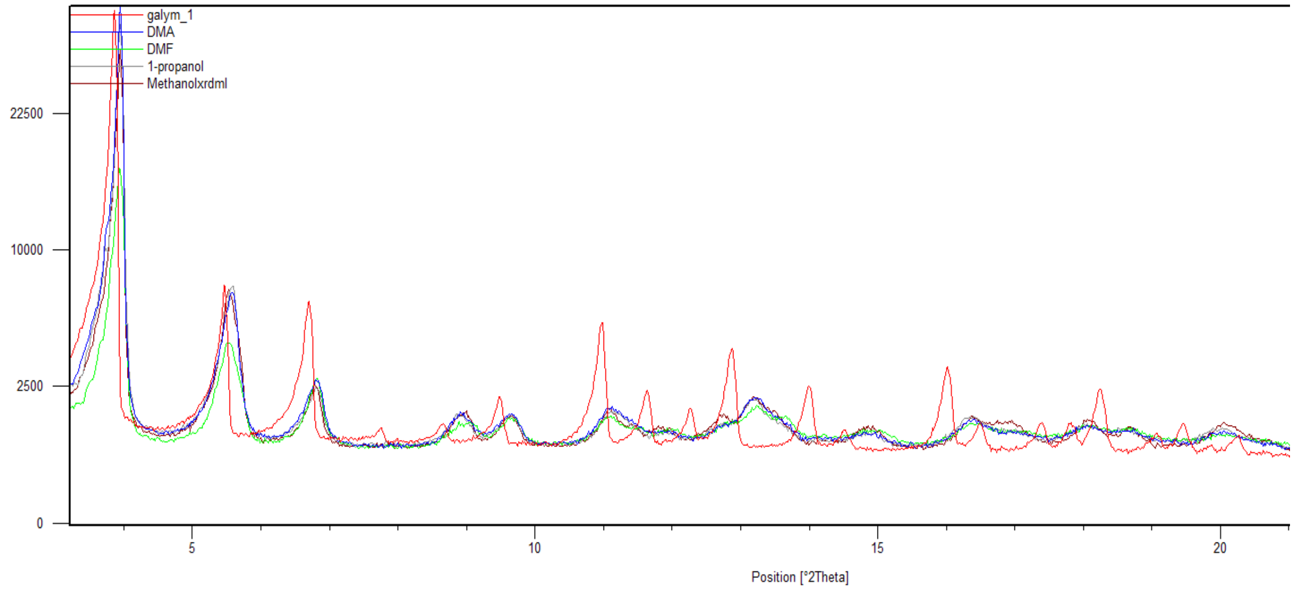

Figure 2 – Comparison of PXRD pattern of parent and exchanged ZIF material

Scanning electron analysis of parent and daughter ZIF-76 material

The size of crystals and morphology of synthesized ZIF-76 material were investigated by Scanning Electron Microscopy. The pure ZIF-76 showed good crystallinity. From the figure 3 it can be seen that ZIF-76 have a cuboctahedron morphology with two destinct facets {100} and {111}. From the SEM it can be observed that {100} face shows square shape while {111} face exhibits triangle shape as expected for cubic symmetry.

The SEM images of all ZIF-76 materials were showed decrease in crystal shape after SALE procedure. The SEM images show that degree of crystal shape from high to low is the ZIFs in methanol, 1-propanol, DMF, DMA . In addition the SEM images of ZIF-76 in methanol and 1-propanol still demonstrates cuboctahedron morphology with two distinct {100} and {111} facets indicating that crystal morphology has been retained.

Elemental analysis and Energy Dispersive Spectroscopy of parent and daughter ZIF-76

To show the evidence of linker exchange elemental analysis (pure ZIF-76, 1-propanol) and EDS (pure ZIF-76, in DMA, DMF, 1-propanol, methanol) were carried out. The main characteristic data of successful of SALE procedure was 0% percentage of chlorine in the product. The pure ZIF-76 contains 5-ClbIm linker. However, the exchange of 5-ClbIm to bIm decreases the percentage of chlorine or in perfect case no chlorine molecules should be detected in composition. Exchanged 5-ClbIm linkers are fully dissolved in solution and removed by vacuum sanction. From the figure 4 it can be seen that intensity of chlorine rapidly decreased indicating exchange of 5-ClbIm to bIm.

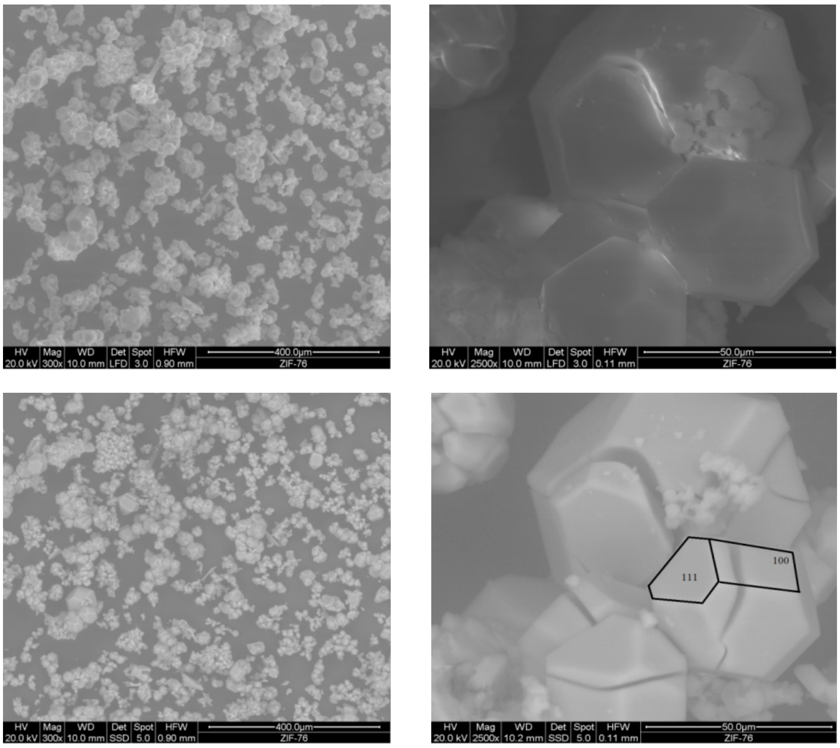

Figure 3 – Scanning electron microscopy images
of secondary and backscattered pure ZIF-76 crystals

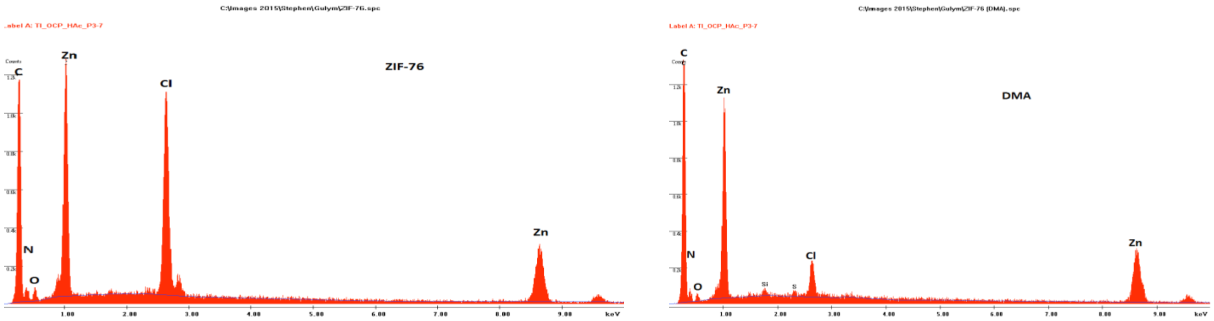

Figure 4 – EDX plot of starting ZIF-76 and after SALE in DMA

Table 1 – The percentage of elements present in ZIF-76 and after the SALE procedure (elemental analysis)

Found	C	H	N	Cl	Zn:Cl ratio
Calculated percentage of elements present from the ZIF-76	42.29	2.48	19.72	23.03	1.85:1
ICP: Reactant ZIF-76	42.28	2.95	20.26	8.86	2.89:1
EDS: Reactant ZIF-76	60.34		6.67	8.50	2.7:1
EDS: Sample 1. DMA	62.80		6.59	1.97	13.5:1
EDS: Sample 2. DMF	68.81		4.29	1.77	12.6:1
EDS: Sample 3. 1-propanol	69.52		5.33	2.59	7.8:1
ICP: Sample 3. 1-propanol	51.75	2.51	18.77	3.31	7.5:1
EDS: Sample 4. Methanol	70.06		4.95	2.80	7.1:1

The elemental analysis of all the samples is given in table 1. The elemental analysis of ZIF-76 after exchange of 5-ClbIm to bIm in propanol gave atomic ratio of Zn to Cl of 7.5:1, which is consistent with EDS (7.8:1). From the EDS it is easy to conclude that the conversion of linker exchange from high to low is DMA, DMF, 1-propanol, methanol. Another noteworthy pattern from the SEM, EDS and elemental analysis is that SALE experiment in DMA and DMF shows good linker exchange but with poor crystal shape. In contrast, SALE experiment in methanol and 1-propanol shows poor linker exchange but with good crystal shape. It indicates that SALE reduces the crystallinity and importance of solvent as a reaction medium.

Conclusion

The new version of ZIF-76 with bIm ligand cannot be achived by direct solvothermal synthesis technique. However, a recently discovered technique known as solvent-assisted linker exchange (SALE) can overcome the above mentioned problem. The findings presented in this project show that successful linker exchange can be achieved in the appropriate solvent. All the data from CHN analysis, Cl analysis, SEM, EDS suggest that the most successful linker exchange was achieved in DMA solvent. The percentage of chlorine in parent ZIF-76 was measured to be about 8%. However, this number falls to approximately 2% in DMA indicating that the majority of 5-ClbIm linker is replaced by bIm ligand. The SEM analysis of parent and all daughter ZIF-76 showed that after SALE, the crystal shape declined. SALE in methanol and 1-propanol demonstrated a good crystal shape compared to ZIF-76 in DMF and DMA. All SALE experiments were carried out with the same reaction time, temperature and ratios. The only variable factor was the reaction medium. From these results it is clear that the solvent size and polarity play an important role in succesful linker exchange. It was observed that the less polar the solvent, the higher the linker conversion. In addition, succesful linker exchange is dependent on the linkers pK_a. The pK_a of 5-ClbIm and bIm is approximately the same and they can replace each other. However, the pK_a of imidazole is about 14.5 indicating that the zinc – nitrogen bond is too strong and stable to be converted by weaker ligands. The adsorption analysis of newly synthesised ZIF-76 in DMA showed that the surface area and pore size significantly decreased. The decline in adsorptivity properities of daughter ZIF-76 can be related to the partial loss of crystallinity as was proven by PXRD analysis. Finally, the accurate selection of ligand and solvent system can improve construction of the porous structures, producing bigger pore sizes.

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