# GREEN SYNTHESIS OF ZIF-90 AND ITS MIXED METAL ANALOGUES

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## ABSTRACT

In this study, a new green solvent-based synthesis of Zeolitic Imidazolate Framework - 90 (ZIF-90) is investigated. Two biobased aprotic dipolar solvents Cyrene™ and γ-valerolactone (GVL) successfully replaced DMF in the synthesis of ZIF-90 at room temperature with a comparable product yield. After thermal treatment, PXRD showed that the Cyrene™-based product exhibited reduced porosity while the GVL-based products preserved its crystallinity and porosity after thermal burst activation. The primary particles of 30 nm to 60 nm in all products further form agglomerates of different sizes and interparticle mesoporosity, depending on the type and molar ratios of solvents used. The optimal solvent ratio was then used to synthesize mixed-metal ZIF-90 with Mg, Cu, Co, and Ni. The synthesized ZIFs were characterised using PXRD, TGA, $N_2$ physisorption and SEM-EDX. For all mixed-metal samples, a decrease in the specific surface area was observed. Finally, preliminary adsorption tests were completed on the optimal solvent ratio ZIF-90 and its mixed metal analogues.

Key words: mixed-metal ZIF, ZIF-90, green synthesis, GVL.

## INTRODUCTION

Zeolitic imidazolate frameworks (ZIFs) are a subgroup of metal-organic frameworks (MOFs), which have shown promising results as functional materials for different applications, mainly in adsorption and catalysis. Of the wide array of known ZIFs, the largest portion of articles is on ZIF-8, ZIF-67, and ZIF-90. While ZIF-8 and ZIF-67 synthesis already use more environmentally friendly solvents, ZIF-90 synthesis still mainly relies on DMF.

A water based ZIF-90 synthesis has already been reported [1]. However, due to the lower surface area and large particle size of the products, it has yet to be widely used. Another approach towards greener synthesis was reported [2] using the mixed solvent system of DMF/MeOH, where the amount of DMF was halved compared to the typical ZIF-90 synthesis. Overview of biobased DMF alternatives that have already been used in MOF chemistry narrowed down the list of possible alternatives to dihydrolevoglucosenone with commercial name Cyrene™, and gamma-valerolactone (GVL).

After successful substitution of DMF, we investigated the impact of mixed metal(MM) systems on the various ZIF-90 properties, as MM ZIF-67 with Co/Zn was shown to exhibit increased stability [3].

## EXPERIMENTAL

The green synthesis method was adapted from *Brown*[2], where a volumetric substitution of DMF was done with both pure and Methanol diluted green solvents, as described for single-metal ZIF-90 [4].

In a 100 mL beaker, 1.93 g (19 mmol) of 2H-imidazole carbaldehyde (HICA) was added to 50 mL linker solvent (Table 1). The mixture was stirred at room temperature until either fully suspended or fully dissolved in the solvent. A separate solution of 1.46 g (6.5 mmol) of $Zn(AcO)_2{\cdot}2H_2O$ in 50 mL of metal precursor solvent (Table1) was prepared in a 150 mL beaker. The HICA suspension was then slowly poured into the zinc solution and was stirred for 1 h.

The product was isolated by centrifuging at 9000 rpm for 35 min, washed with MeOH, and centrifuged again. The precipitate was left to air-dry overnight at room temperature in the centrifuge bottle.

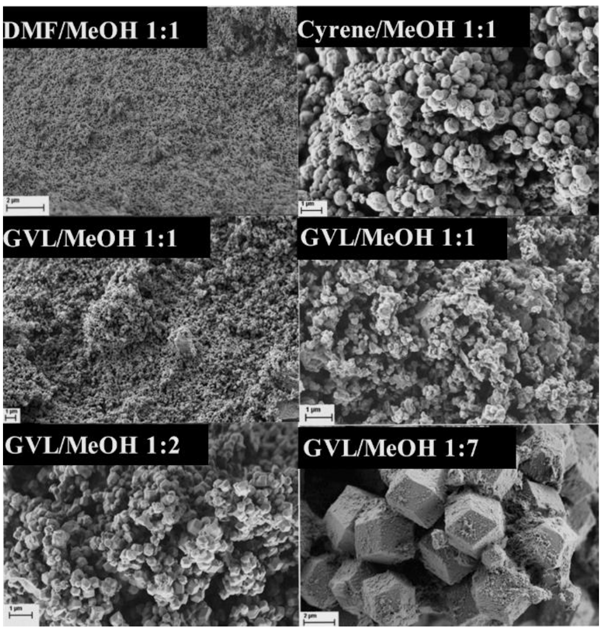
The MM ZIF-90 were prepared using the same method as ZIF-90-GM, with 20 mol. % of $Zn(AcO)_2 \cdot 2H_2O$ substituted with Mg, Co, Cu and Ni acetates hydrates. Unlike the pure ZIF-90-GM, which was activated by heating at 200 °C for 1.5 h, the MM samples were activated by soaking in methanol and then heated at 150 °C overnight. The as-synthesised green ZIF-90's were characterized using PXRD, TGA, SEM and $N_2$ physisorption.

Table 1. Solvent composition for the synthesised zeolitic imidazolate frameworks (ZIF)-90 samples.

| Product | Linker Solvent | Metal Precursor Solvent |
|---|---|---|
| ZIF-90-C | Cyrene™ (481 mmol) | MeOH (1250 mmol) |
| ZIF-90-G | GVL (525 mmol) | MeOH (1250 mmol) |
| ZIF-90-2G | GVL (263 mmol) + MeOH (625 mmol) | GVL (263 mmol) + MeOH (625 mmol) |
| ZIF-90-GM | GVL (263 mmol) + MeOH (625 mmol) | MeOH (1250 mmol) |
| ZIF-90-G2M | GVL (179 mmol) + MeOH (825 mmol) | MeOH (1250 mmol) |

**RESULTS AND DISCUSSION**

The as-synthesised green ZIF-90's were characterised using PXRD, TGA, SEM and $N_2$ physisorption. Using the Scherrer equation, the particulate size of the prepared ZIFs were calculated to be in the range of 30 – 60 nm. SEM imaging showed that larger agglomerates formed in the case of ZIF-90-D, ZIF-90-GM, and ZIF-90-G2M with the latter's SEM (Figure 1) also showing a large amount of impurities.



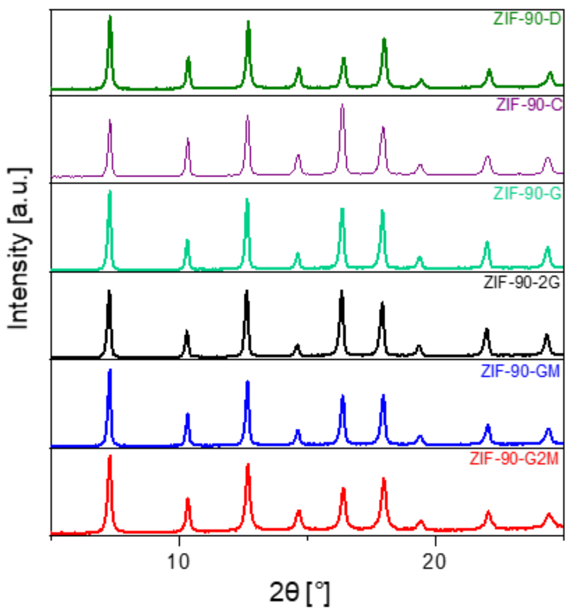




Figure 1. Left - SEM images of ZIF-90 prepared with different solvent ratios; Right - XRD patterns of synthesized ZIF-90.

As a result of its higher specific surface area and higher thermal stability, the ZIF-90-GM procedure was selected for the synthesis of the MM samples.

All as synthesized ZIF-90 PXRD showed similar crystallinity of MM samples if compared to a single-metal analogue. The calculated particle sizes ranged from 40 to 70 nm. Dopant metal ion concentration in MM ZIFs was detected using SEM-EDX on palletized samples. All dopant ions except Mg were detected in significant amounts. The determined dopant concentration showed that from the initial 20% in the metal precursor mixture around 9.7 – 11.4 % remained.

The activated MM samples were also analysed using SEM-EDX for metal ion ratio in the product with no significant change observed. The activated samples were then analysed using $N_2$ physisorption to determine surface area and porosity followed by preliminary gas sorption tests with $CO_2$, $CH_4$, and $N_2$ at room temperature.

Table 2. Gas sorption test results for ZIF-90-GM and MM ZIF-90-GM samples.

| Product | Dopant amount (%) * | $S_{BET}$ ($m^2/g$) | $CO_2$ uptake at 1 bar (mmol/g) | Selectivity** $CO_2/N_2$ | Selectivity** $CO_2/CH_4$ |
|---|---|---|---|---|---|
| ZIF-90-GM | N/A | 1044 | 2.03 | 17.8 | 6.8 |
| ZIF-90-GM-Mg | 2.6 | 1003 | 1.92 | 14.6 | 5.8 |
| ZIF-90-GM-Ni | 11.3 | 959 | 1.92 | 17.9 | 6.0 |
| ZIF-90-GM-Co | 11.4 | 949 | 1.37 | 6.4 | 3.8 |
| ZIF-90-GM-Cu | 9.7 | 967 | 1.18 | 21.7 | 6.1 |

*Percent of dopant metal determined from M/M+Zn ratio, ** calculated from individual isotherms at 1 bar

While metal incorporation had less of an impact on specific surface area, it did have a detrimental effect on $CO_2$ uptake in the case of Cu and Co MM ZIF-90 (Table 2). With Co doped showing extreme decrease in selectivity for both $CO_2/N_2$ and $CO_2/CH_4$, while the Cu showed a significant increase in $CO_2/N_2$ selectivity compared to ZIF-90-GM. While the Ni doped sample showed almost no change in uptake or selectivity, the opposite effect was observed in the Mg MM ZIF, which despite the very small amount of Mg in the sample showed a large decrease in selectivity for $N_2$. The pure ZIF-90-GM and Ni modified sample showed similar selectivity as observed in literature [5], with a slightly higher uptake.

## CONCLUSION

This study showed that we have successfully implemented the use of a green biobased solvent to synthesise ZIF-90 nanoparticles, with a comparably high surface area. The synthesis was then used to prepare different mixed metal ZIF-90. The ZIFs were characterised, and preliminary adsorption tests were carried out, in all cases the MM showed reduced surface area, which consequently led to slightly reduced $CO_2$ uptake in Ni and Mg MM ZIF. Most metals did have a significant impact on $CO_2/N_2$ selectivity, with the Co presence having a significant impact on selectivity for both gasses tested.

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