

ROUTES TOWARDS PREPARATION OF PURE NICKEL ZEOLITIC IMIDAZOLATE FRAMEWORKS

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ABSTRACT

Zeolitic imidazolate frameworks (ZIFs) usually consist of zinc ions coordinated with imidazole linkers, with some other transition metals, such as Cd(II) and Co(II) also showing potential as ZIF-forming cations. Despite the importance of nickel in catalysis, no Ni-based ZIF with permanent porosity has been reported so far. We have found that the presence and arrangement of the carbonyl functional groups on the imidazole linker plays a crucial role in completing the preferred octahedral coordination of nickel, revealing a promising platform for the rational design of Ni-based ZIFs for a variety of catalytic applications. Herein, we report on the synthesis of the first Ni-based ZIFs and demonstrate their high potential as heterogeneous catalysts for Suzuki-Miyaura cross-coupling C-C bond forming reactions.

Key words: MOFs, ZIFs, Nickel-based ZIF, electron diffraction, heterogeneous organocatalyst;

INTRODUCTION

Zeolitic Imidazolate Frameworks (ZIFs) are a subgroup of MOFs, which consist of tetrahedrally coordinated single metal nodes linked together with imidazole and benzimidazole based linkers.^[1] The strong coordination bond between the imidazolate linkers and metal ions together with the preferential formation of rigid cages causes ZIFs to be highly robust permanently porous materials. The similarity to zeolites is attributed to the similar bond angles [Figure 1.3] and topologies of the frameworks.^[2] Imidazoles used in most of the ZIFs are substituted at the 2, 4 or, 4 and 5 positions with the most utilized linker being the 2-substituted 2-methylimidazole.

The most common metal utilised in ZIFs is Zn with Co and Cd following far behind. Almost all ZIFs used in sorption applications tend to be Zn based^[1], while Co based ZIFs are more utilised for catalytic applications^[3]. In comparison to carboxylate MOFs the potential metal precursors in ZIF synthesis are limited. The nature of the frameworks requires the metals to be stable in tetrahedral coordination, which can be problematic. While Cu^[4], Fe^[5], Al^[6], and Mn^[7] ZIFs were prepared, they tend to be very liable to either moisture or air, and as such are not ideal for applications in real systems.

Zinc based ZIF's high stability is also compounded by the framework's high flexibility compared to some of the other transition metal ZIFs^[8]. Variation in the metal nodes of

isoreticular ZIF materials could potentially allow for additional control of framework flexibility, for different separation applications^[9].

Most initial attempts to prepare Ni-based ZIFs were conducted with less expensive linkers such as 2-Methylimidazole and Imidazole, which would result in tetrahedrally coordinated Ni²⁺. With nickel complexes known to prefer octahedral or square planar coordination^[10], and with the latter not leading to 3D frameworks, we decided to look into linkers with functional groups that could form additional coordination bonds, thereby completing the octahedral coordination environment of Ni²⁺. A review of linkers of common ZIFs led us to speculate that the presence of an oxygen containing functional group, such as an aldehyde or ester, could stabilize the framework formation and lead to Ni based ZIFs.^[11]

RESULTS AND DISCUSSION

The high incorporation of Ni into Zn-based mixed-metal ZIF-90^[12] compared to Ni/Zn mixed-metal ZIF-8 led us to hypothesise that potentially the aldehyde group can stabilise the coordination leading to a stable metal node, allowing for higher second metal loading. This was then tested by replacing all the zinc with nickel in the ZIF-90 GVL synthesis procedure.

The initial synthesis attempt with 2-Imidazolecarboxaldehyde (product named NICS-21) was then done with an ageing time of one day, but PXRD analysis showed the sample to have broad peaks with some secondary phase present. The synthesis time was then extended to 3 days to obtain satisfactory crystallinity and phase purity. In the course of optimising the reaction, multiple attempts were made with changes to various parameters. In all cases, higher temperatures led to the formation of nonporous, 2D, leaf-like structure previously reported for Nickel with 2-Methylimidazole^[13]. This is in accordance with the literature reports, that adjustment of reaction parameters can induce structural inter-dimensional (2D/3D) transformations of ZIFs, forming new thermodynamically or kinetically stable phases^[14,15]. Variation in reagent ratios for the attempts to prepare larger crystals resulted in the formation of NICS-21, but there was also always a substantial quantity of impurities, leading us to continue with the initial synthesis conditions.

A product with 4-methyl-5-imidazolecarboxaldehyde (product named NICS-22) was prepared using a modified one-pot solvothermal synthesis at 80°C in a capped round-bottom flask. Due to the elevated temperature, desirable crystallinity and phase purity could be obtained after one day.

The prepared samples were activated to remove solvents and possible remains of reactants from pores, and N₂ isotherms were collected to determine the specific surface area (S_{BET}), micropore volume (V_{micro}), and total pore volume (V_{total}). The results show comparable S_{BET} determined for both samples as for their closest Zn counterparts, namely ZIF-90 and ZIF-93/94. The significantly lower surface area of NICS-22 (663 m²/g) compared to NICS-21 (1230 m²/g) is in accordance with the differences in the measured micropore volumes and the theoretical surface area (CCDC pore analyzer, from ED structures NICS-21 1750 m²/g NICS-22 500 m²/g). Similar trend in reduction of surface area between RHO and SOD topology was observed in the zinc(4-methyl-5-carboxaldehydeimidazolate)₂ isoreticular frameworks ZIF-94(SOD topology as NICS-22) and ZIF-93(RHO topology as NICS-21). The materials were then tested as water and CO₂ sorbents. NICS-21 exhibited a high water uptake (24.5 mmol/g), comparable to that of ZIF-90, while NICS-22 showed the highest CO₂ uptake (2.8 mmol/g) of an as synthesized ZIF.

Due to the small particle size, 3D electron diffraction (3D ED)^[16,17] was used to determine the structures of NICS-21 and NICS-22, as both phases are acquired as nano-sized crystals.

The prepared materials were then successfully used in Suzuki-Miyaura cross-coupling reactions (Figure 1). Where NICS-21 showed the most promise as it allowed for reuse of the catalyst. NICS-22 while showing great promise in the first run, subsequent runs had a drastically reduced conversions, the PXRD of the materials after SM reactions showed retention of framework in the case of NICS-21 and complete amorphisation in the case of NICS-22.

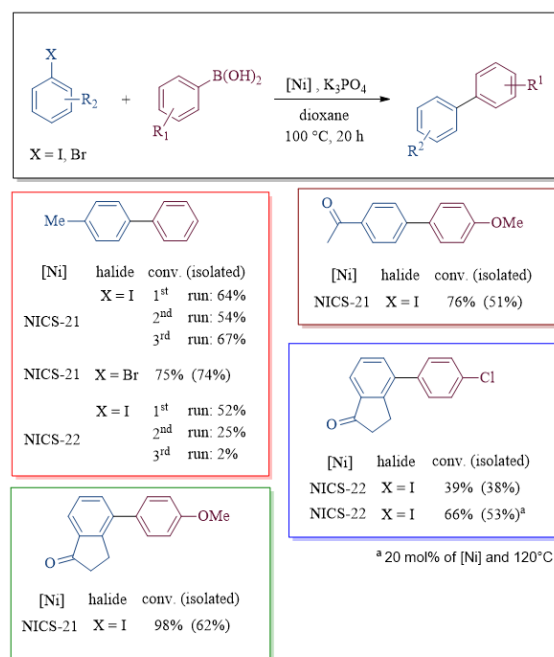


Figure 1: Heterogenous Ni-ZIF catalyzed Suzuki-Miyaura cross-coupling reaction conditions and products obtained from aryl iodide and aryl bromide (blue) coupling with aryl boronic acids (purple) bearing various substituents (H, OMe, Cl) with varying electronic properties. The scope of the heterogenous catalysts with 10 mol% Ni is shown with respect to the aryl halide and 100 °C. The scheme shows the percentage of conversions and isolated materials (yields) in one run and, for one coupling reaction (4-iodotoluene and phenylboronic acid), in three consecutive runs.

CONCLUSION

Herein we report the successful syntheses of the first pure nickel ZIFs with zeolitic RHO (NICS-21) and SOD (NICS-22) topologies. The hypothesis that linkers with additional functional groups that have the ability to coordinate to Ni²⁺ would complete nickel coordination octahedra and stabilise the framework was tested and confirmed. With future work on extending carboxyl-functionalised linkers to other coordinating functional groups that would allow the metal to stabilise in its preferred coordination state, we could possibly further expand the range of potential ZIF forming metal nodes. Both materials under investigation exhibit high thermal stability and permanent porosity, with comparable S_{BET} and CO₂ uptakes to their closest Zn analogues. The prepared materials were then successfully used as heterogenous catalysts in Suzuki-Miyaura coupling reactions, showing promising activity for both materials and, in the case of NICS-21, reusability as well. Moreover, an important advantage of the developed Ni-based ZIFs lies in the ease of their synthesis and the conditions that they require to be catalytically active, i.e. our catalysts allow for the preparation of potentially high-value precursors and intermediates with high yields under mild conditions in selected types of Ni-catalysed transformations. Furthermore, NICS-22's high CO₂ uptake and NICS-21's high water uptake could potentially allow for additional investigation into sorption applications.

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