

COPPER'S STORY IN ZIF-62: SURFACE OR STRUCTURE?

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ABSTRACT

Metal-organic frameworks (MOFs) have emerged as versatile materials with applications in gas adsorption, separation, and more. Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, have drawn attention for their exceptional molecular sieving properties and potential to exist in liquid states, leading to ZIF glasses.

Among them, ZIF-62 stands out for its unique stability range. However, achieving precise control over its composition, especially regarding the incorporation of dopants like copper, poses challenges. Conventional liquid-phase synthesis methods for ZIFs have drawbacks such as solvent use and scalability limitations. Mechanochemistry offers a promising solvent-free alternative, enabling precise control over composition and large-scale production.

In this study, we employed acetate-assisted mechanosynthesis to produce copper-doped ZIF-62 and its amorphous counterpart. Our investigation focused on understanding how the presence of copper influences glass formation. Through a combination of techniques, including solid-state NMR, FTIR, Raman spectroscopy, and others, we aimed to unravel the enigma of copper incorporation in ZIF-62. Our findings indicate that, while copper is present in the material, it may not have integrated into the framework and is instead localized on the surface or within pores. This study underscores the importance of comprehensive analysis and provides insights for future research on optimizing metal incorporation in MOFs.

Key words: Zeolitic imidazolate frameworks, ZIF-62, Copper doping, Mechanochemistry, Glass formation

INTRODUCTION

Metal-organic frameworks (MOFs) represent a class of hybrid materials where inorganic nodes or clusters are linked together by organic ligands.[1] The primary focus within the MOF community currently revolves around the realm of crystalline structures.[2] Researchers are primarily engaged in exploring materials with high internal surface areas for applications in gas adsorption and separation.[3] Zeolitic imidazolate frameworks (ZIFs), a family of MOFs, have gained notable recognition as exceptional molecular sieves due to their flexible frameworks, which allow for the simultaneous achievement of high gas adsorption capacity and selective separation.[4,5] Furthermore, recent investigations into the ZIF family have revealed the intriguing possibility of a stable liquid state, provided that the structure's melting temperature (T_m) is lower than its thermal decomposition temperature (T_d). These liquid states can be rapidly cooled, resulting in the formation of ZIF glasses. These glassy materials exhibit a topological resemblance to silicate glasses but feature tetrahedral metal nodes interconnected by imidazolate linkers. Their unique property is their intrinsic porosity, which is both permanent and reversible without the need for post-synthetic treatments. This feature distinguishes them from other common forms of melt-quenched glass, such as metallic, organic, and inorganic glass. As a result, they have drawn a lot of attention and are now recognized as a new class of porous glass materials that are remarkably diverse and tunable. [6-8]

ZIF-62 is a hybrid material with a mixture of linkers, namely, imidazole (Im) and benzimidazole (bIm). Notably, ZIF-62 exhibits an extended region of stability between its melting and decomposition phases. However, achieving precise control over the ligand ratio in ZIF-62 can pose a challenge, often resulting in significant disparities between the intended reaction composition and the actual ligand incorporation in the final framework. Accurate control of this ratio is imperative, as it significantly impacts various critical properties such as melting temperature, glass transition temperature, refractive indices, and mechanical characteristics of the resulting glasses. [9] Conventional methods for producing ZIFs rely on liquid-phase coordination reactions, which have drawbacks such as excessive solvent usage, lengthy reaction times, and limited scalability. In contrast, mechanochemistry offers a promising solvent-free alternative. [10]

EXPERIMENTAL

For the mechanochemical synthesis, all reagents were combined in a 10 ml stainless steel grinding jar along with two 10 mm stainless steel grinding balls. The sealed jar underwent shaking at 30 Hz for 30 minutes using a Retsch MM400 mixer mill. Subsequently, the resulting powder was extracted, isolated *via* centrifugation, washed with ethanol, and dried overnight at 60 °C. In the glass fabrication process, approximately 15 mg of the synthesized samples were pressed into pellets using a stainless-steel mold and hydraulic press. These pelletized samples were then subjected to heating in an argon-purged muffle furnace, gradually reaching 350 °C at a rate of 10 °C/min, then held at 350°C for 10 minutes, followed by natural cooling to room temperature.

Materials characterization encompassed several methodologies. X-ray diffraction data were obtained utilizing a PANalytical X'Pert PRO high-resolution diffractometer employing CuK α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) within the 2θ range from 5 to 50°. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were conducted using a TA Instruments Q5000 and Q2000 MDSC, respectively. Measurements were executed under controlled conditions with a continuous air stream (25 ml/min air, 10 ml/min Ar) with samples undergoing heating from 25 °C to 750 °C at a ramp rate of 10 °C/min for TG, and heating at the same rate to 450 °C for DSC. Subsequent to cooling to room temperature at 10 °C/min, the second upscan was performed employing identical parameters. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) was employed to analyze crystal morphology and size utilizing a Zeiss Supra 35 VP microscope, operated at an electron high tension voltage of 1.00 kV with an aperture size of 30.00 μm . Liquid-state nuclear magnetic resonance (NMR) spectroscopy, specifically proton NMR, was performed on an AVANCE NEO Bruker 400 MHz spectrometer at room temperature. Approximately 1.5 mg of each sample was digested in a mixture of DCl (35%)/D₂O. Additional analyses, including Solid-State Nuclear Magnetic Resonance (ssNMR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Diffuse Reflectance Ultraviolet–Visible Spectroscopy (DR UV-VIS), Fourier Transform Infrared Spectroscopy (FTIR), and Raman Spectroscopy, were conducted.

RESULTS AND DISCUSSION

We aimed to improve the solvothermal synthesis of ZIF-62 by adopting a mechanosynthetic approach, offering precise control over metal/ligand ratios while reducing solvent usage. By utilizing ZnO as a metal source and only small amounts of zinc acetate, we completed the synthesis in just 30 minutes, avoiding acidic by-products detrimental to ZIF formation. Introducing Cu(OAc)₂·2H₂O during synthesis aimed to integrate Cu²⁺ into the ZIF-62 structure.

XRD patterns confirmed successful synthesis, with minor differences indicating retained ZIF-62 structural features. Consistent linker ratios in both pure and copper-doped ZIF-62 samples were crucial for understanding their thermal properties.

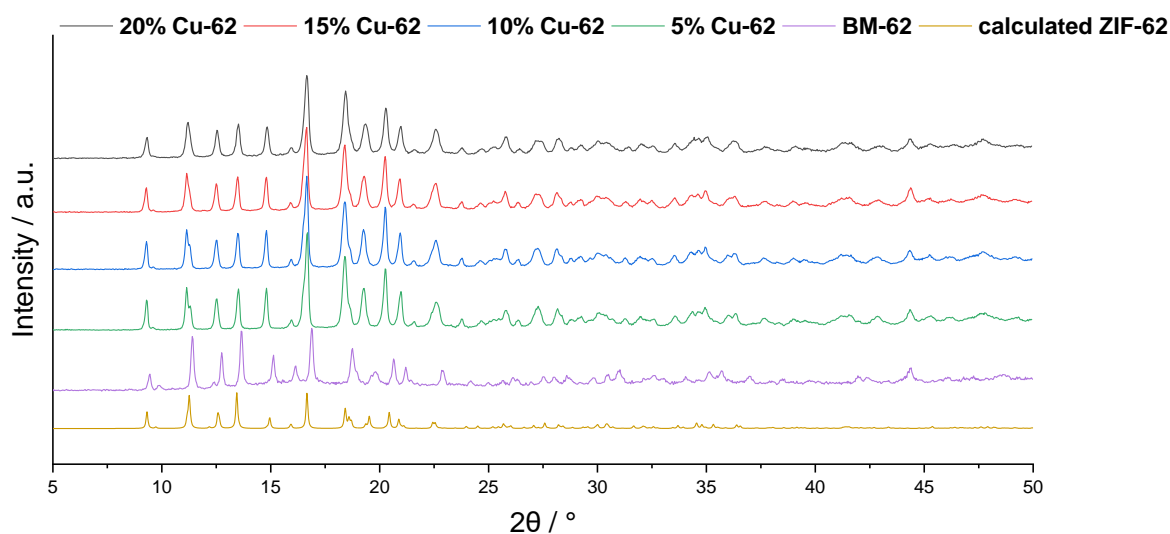


Figure 1. X-ray diffraction patterns of calculated, ball-milled pure and copper doped ZIF-62

Thermogravimetric and calorimetric analysis revealed notable differences in the thermal behavior of mechanochemically produced pure and copper-doped ZIF-62 as well as solvothermally produced ones, which could be attributed to various factors including particle size. SEM imaging supported the observation of smaller particle sizes in the mechanochemically produced ZIF-62 samples, potentially influencing their melting behavior. Additionally, EDX analysis showed a uniform distribution of Cu throughout the material, indicating successful incorporation of the metal. DRUV-vis spectra demonstrated clear absorption peaks that are in line with copper content, providing strong evidence of Cu(II) presence in ZIF-62.

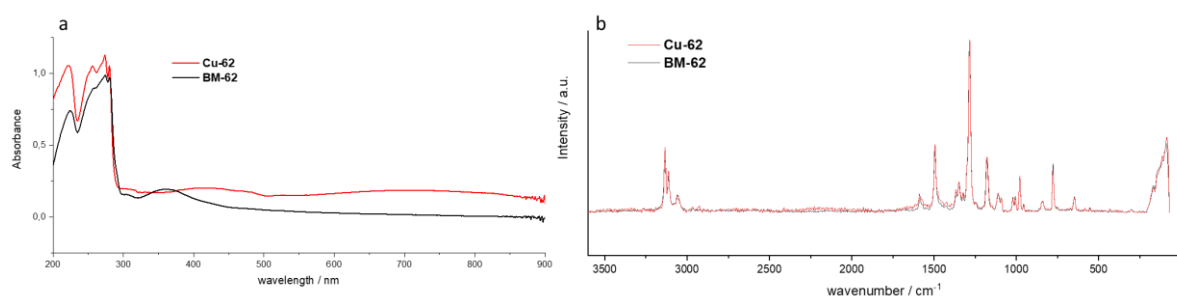


Figure 2. DR UV-Vis spectra ball-milled pure and copper doped ZIF-62 (a) Raman spectra of pure and copper-doped ZIF-62 (b)

NMR spectra provided additional evidence suggesting the presence of copper in the structure, although no significant signal shifts were detected, indicating a subtle structural change. On the other hand, FTIR spectra did not reveal conclusive evidence of copper integration, as they exhibited similar features for both samples, suggesting no significant alterations in the chemical environment associated with the introduction of copper. Raman spectra confirmed the

formation of ZIF-62, but the absence of a discernible Cu-N bond in the spectra suggested the possibility that copper might not be fully integrated into the framework.

CONCLUSION

In summary, we successfully employed acetate-assisted mechanosynthesis to produce copper-doped ZIF-62 and its amorphous counterpart. Our investigation shed light on the influence of copper incorporation on glass formation and properties. While copper was present in the material, it didn't appear to be incorporated into the structure; it might have only been present in the pores or surface of the substance. This study underscores the importance of comprehensive analysis in elucidating metal incorporation mechanisms in MOFs and provides insights for future research on optimizing metal doping strategies for desired properties in MOF glasses.

To delve deeper, future studies will employ advanced techniques such as Extended X-ray Absorption Fine Structure (EXAFS), X-ray Absorption Near Edge Structure (XANES), and X-ray Photoelectron Spectroscopy (XPS). These methods will offer detailed insights into the local coordination environment, oxidation state, and surface chemistry of copper within the ZIF-62 framework, elucidating its role and potential applications.

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