Synthesis of ZIF67 with recycling of 2-methylimidazole solution and impact on particle size

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Introduction

ZIF-67 is one of the most used forms of ZIFs, due to its excellent textural and morphological properties, such as high surface area (S_{BET} > 1700 m^2/g) with pore diameters of approximately 0.34 nm[1] and the possibility of controlling particle sizes.[2] Different strategies have been adopted to manipulate crystal size and morphology, such as precursor type, reactant concentration, temperature and synthesis time. These parameters influence both the particle size and morphology of ZIF-67 crystals.[1,3,4] Some authors have already reported the possibility of reusing the initial 2-methylimidazole solution to synthesize more ZIF67 batches in a sequence. This work investigates the reuse of 2-methylimidazole solution to increase the yield of ZIF67 crystals through successive synthesis batches. The physicochemical properties of ZIF67 synthesized with and without reuse of 2-methylimidazole solution were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Materials and Methods

Synthesis of ZIF67 was carried out based on results previously reported in the literature.[1,2,4] $Co(NO_3)_2 \cdot 6H_2O$ (≥98%, Vetec) and 2-methylimidazole (≥99%, Sigma Aldrich) were dissolved in methanol (≥99.8%, Neon) and the system was kept under agitation at room temperature (20±3 °C) for 6 h. The reaction product was separated by centrifugation, the remaining 2-methylimidazole solution was reserved and the precipitate was washed three times with methanol before drying at 60 °C for 24 h. For consecutive syntheses, the same procedure was followed with the exception that the remaining 2-methylimidazole solution from the previous synthesis was used, and the reaction periods were 24 h (1st recycling) and 48 h (2nd recycling). The yields of ZIF67 were calculated based on the initial amount of Co in each reaction.

Results and Discussion

The yield of ZIF67 in the first synthesis was 100%, and the particles presented a dodecahedral morphology with an average diameter of 232 nm. In the 1st and 2nd recycling syntheses, the yields were approximately 77% and 85%, with average diameters of 521 and 1043 nm, respectively. Rietveld refinement (**Fig. 1**) was performed based on XRD patterns using Thompson-Cox-Hastings pseudo-Voigt model in the FullProf software.[5] The material presented an expected loss of crystallinity after recycling. This is because the obtained densities, i.e., 0.15 g cm^{-3} in the 1st recycling and 0.43 g cm^{-3} in the 2nd recycling, were smaller than the density of the initial synthesis (0.49 g cm^{-3}), resulting in higher reflection intensities per sample weight.[6]

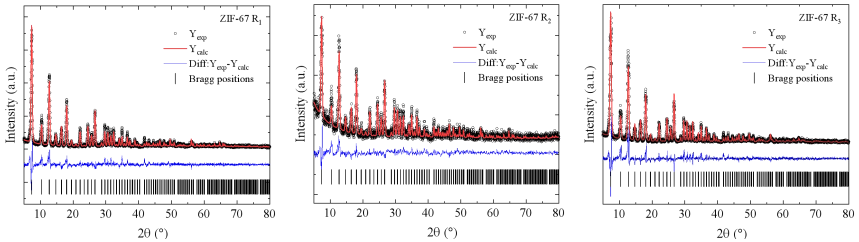

Fig. 1. Rietveld refinements for ZIF67 samples. The observed XRD was collected at room temperature at a wavelength of 1.54056 Å

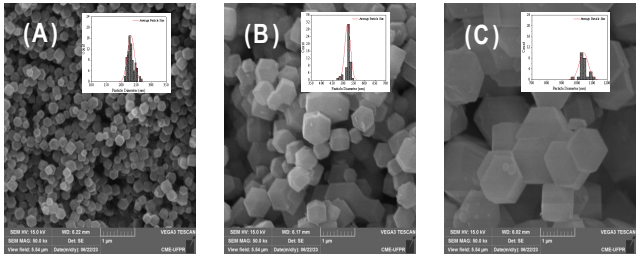

Fig. 2. Scanning electron micrographs (SEM) of (A) initial synthesis, (B) 1st recycling, and (C) 2nd recycling

Fig. 2 shows that the rhombic dodecahedral morphology of ZIF67 particles was maintained after the recycling procedures. The results indicate that the reuse of 2-methylimidazole solution is feasible and corroborates the previously published results.[2,4]

Significance

In summary, the yield of ZIF67 can be increased by reusing the supernatant solution as a source of imidazole. The 2-methylimidazole:Co ratio used in recycling procedures influences the crystallinity, but properties such as thermal stability, morphology and chemical structure remain unchanged.

References

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