Terephthalic acid as a linker in preparation of a new Ni-doped, Zn-based MOF

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Abstract

Metal organic frameworks (MOF) contain inorganic and organic network that can easily functionalized to get tuneable properties. MOFs as highly porous crystalline materials constructed by coordination bonds between metal ions/cluster and organic ligands, have developed very fast due to not only their intriguing structures but also the potential application, such as gas separation, storage and sensing. They have great potential as adsorbent/catalysts due to their extremely large surface area, well-ordered porous structures, and diverse means available for functionalization. MOF-5 consists of four $[Zn_4O]^{6+}$ clusters in octahedral subunit that are connected to each other by terephthalate or benzene-1,4-dicarboxylate (BDC) groups, to form a porous cubic framework. in the work, we have synthesis Ni-doped MOF-5 by solvothermal method according to the literature. The Ni-MOF-5 was formed with cubic structure but changing the reaction conditions resulted to novel hexagonal structure. The characterization was performed by FTIR, XRD and SEM methods.

Introduction

In the past two decades, porous metal-organic frameworks (MOFs) have attracted considerable scientific interest on account of their extremely high surface area and specific microporous volume, this materials have potential applications in gas adsorption and storage/separation, drug delivery and heterogeneous catalysis [1].

An important material within this group is $Zn_4O(BDC)_3$ (MOF-5; BDC=1,4-benzenedicarboxylate), a three-dimensional (3D) cubic porous framework, crystalline solid comprised of 1,4-benzenedicarboxylate (BDC) as a linear and with BET surface area from 260 m^2/g to 4400 m^2/g [2]. However, MOF-5 is moisture sensitive even under atmospheric conditions, because the relative weak metal oxygen coordination allows for attack by water molecules, resulting in phase transformation and structure collapse. Recently, researchers have found that doping other metal ions into the MOF-5 exhibit enhanced or unique performance, such as increasing the hydrostability of MOF-5 by doping Ni(II) ions. Control over the shape and size of particles is an important theme because the particle shape and size dictate chemical and physical properties of the particles [3].

Herein we demonstrate solvothermal synthesis of Ni(II)-doped MOF-5 and Effect of reaction time on the formation of Ni(II)-doped MOF-5 particles was investigated and it was found that the reaction solvent is important for the generation of particles and changing of their size and shape.

Experimental

Materials: Zinc(II) nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$], Nickel(II) nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$], N,N-dimethylformamide (DMF), terephthalic acid (H_2BDC) are all purchased from Merck

Synthesis of Ni(II)-doped MOF-5: Ni(II)-doped MOF-5 was prepared by modified procedures reported previously [ ]. $Zn(NO_3)_2 \cdot 6H_2O$ (4.6 mg, 0.015 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (4.3 mg, 0.015 mmol) and H_2BDC (2.5 mg, 0.015 mmol) were dissolved in 25mL DMF at room temperature. The mixture was transferred into a 50 mL Teflon-lined autoclave, which was sealed and maintained at 100 °C for 7 h (sample 1, cubic structure) and 17 h (sample 2, hexagonal structure). The reaction vessel was then removed from the oven and allowed to cool. The particles were isolated by centrifugation and washed several times with CH_2Cl_2 and DMF and then dried in a vacuum at 60 °C for 12 h.

Results and Discussion

The FTIR spectra of MOF-5 (blue: sample1, red: sample 2) are shown in Fig. 1. The peaks at 1589 and 1510 cm^{-1} correspond to the asymmetric stretching vibration of –COO. The peak at 1381 cm^{-1} assigned to the symmetric stretching vibration of –COO. The peaks at 1141, 1102 and 1016 cm^{-1} correspond to the in-plane bending vibration of C–H. The peaks at 825, 723 and 668 cm^{-1} are attributed to the out-of-plane bending vibration of C–H. The FTIR spectroscopy results, confirm the generation of the MOF-5.

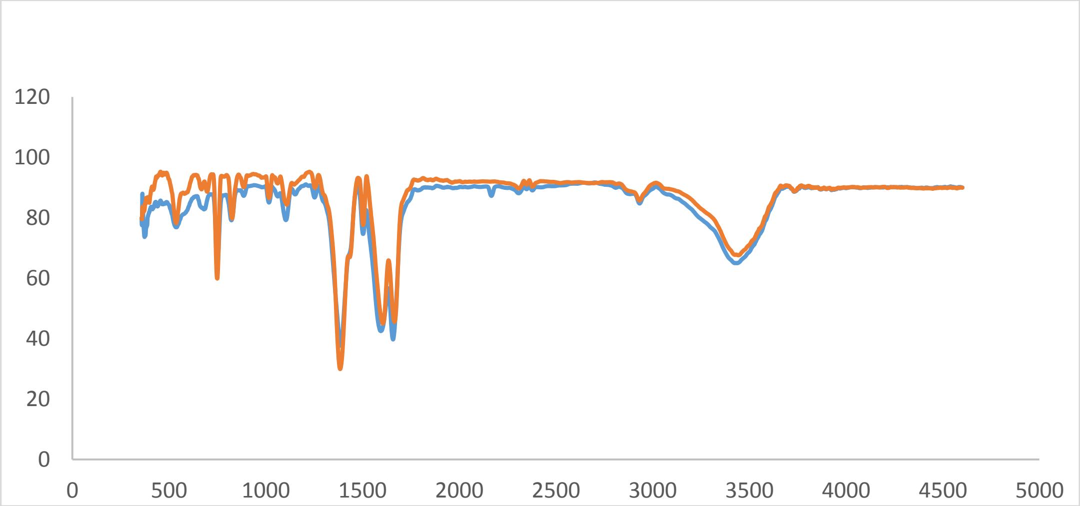

Fig. 1: FTIR spectroscopy (blue:sample1, red: sample 2)

PXRD patterns of synthesized sample 1 and sample 2 illustrated in Fig. 2, are in good agreement with the simulated patterns from the single crystal data.

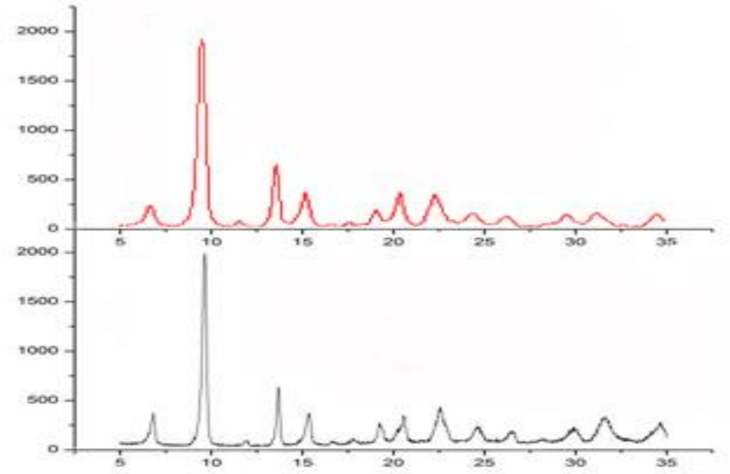

Figure 2: Comparison of PXRD patterns (black: sample1, red: sample2)

The SEM images of Ni(II)-doped MOF-5 crystals synthesized under different reaction times are shown in Fig. 3. sample 1 was made of single-phase cubic structured particles (7h in 100°C) and sample 2 was hexagonal column structured (17 h in 100°C).

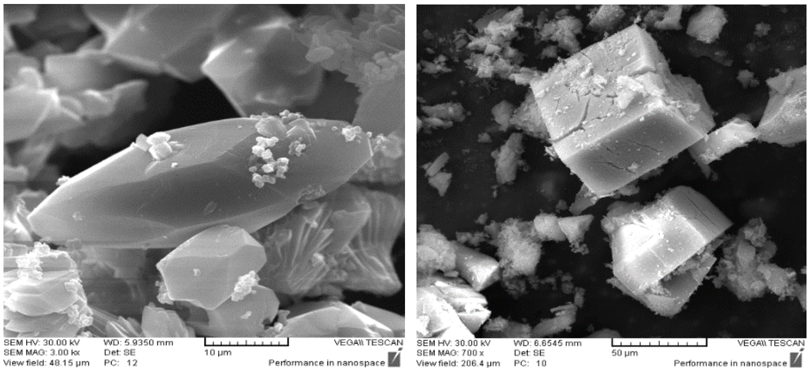

Figure 3: SEM images (left: sample 2, right: sample 1)

Conclusion:

In summary, the present study explored an effective strategy for morphology of Ni(II)-doped MOF-5 crystals by changing the reaction conditions such as reaction time. In this project we succeeded to synthesize the Ni-doped MOF-5 with hexagonal morphology and particle size of 10 µm.

References:

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