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Transition from ZIF-L-Co to ZIF-67: A new insight into structural evolution of Zeolitic Imidazolate Framworks (ZIFs) in aqueous system

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A novel Co-containing Zeolitic imidazolate framework with leaf-like morphology (ZIF-L-Co) was synthesized in aqueous media and proved to be the transient phase in the formation of ZIF-67. The phase and morphology of products could be tailored by changing the concentration and molar ratio of reagents. Our study herein provides a new insight into crystal growth of ZIFs.

Zeolitic imidazolate framework (ZIF) materials such as ZIF-8 and ZIF-67 represent an important class metal organic frameworks (MOF) constructed by coordinated bonds between metal ions and organic linker to form a three-dimensional porous structure.[1, 2] Due to high porosity and surface area, tunable pore size, chemical stability and thermal robustness, ZIFs are widely applied in numerous applications such as gas storage,[3, 4] molecular separation,[5, 6] catalysts[7,8] and energy fields.[9, 10]

However, ZIFs with particle-like morphology have been dominant in use so far, it remains a very big challenge to control their morphology. In order to improve structural and morphological control in the synthesis of ZIFs, the formation mechanism of ZIF-8 and ZIF-67 has been investigated.[11-18] It is widely accepted that various structural evolution stages (nucleation, crystallization and growth) involves in the crystallization of ZIFs, and there is likely a metastable phase during crystal growth.[16] Recently, a new two-dimensional leaf-like Zn-containing ZIF (ZIF-L-Zn) was prepared by using zinc salt and 2-methylimidazole (Hmim) in aqueous solution.[19, 20] Interestingly, it was found that ZIF-L-Zn was a metastable phase and would transform to ZIF-8 when immersed into other organic solvents at elevated temperatures.[20]

In this work, we have successfully synthesized a novel Co-containing ZIF with the similar leaf-like morphology (ZIF-L-Co) by mixing Co(NO_3)$_2$ with Hmim in aqueous solution at room temperature. The morphology and phase composition of products can be tailored by simply changing the concentration and molar ratio of reagents. In addition, phase transformation from ZIF-L-Co to ZIF-67 was also observed during crystal growth of ZIF-67. It provides a new understanding on the crystal growth of ZIFs, which is expected to realize the better morphological control of ZIFs or other MOFs.

Fig. 1a shows scanning electron microscopy (SEM) image of the typical leaf-like product synthesized in a mixing cobalt nitrate and Hmim aqueous solution with a Hmim/Co ion molar ratio of 8. The X-ray diffraction (XRD) pattern of ZIF-L-Co (Figure S1) shows an almost repeating curve of the reported ZIF-L-Zn,[19] suggesting the same crystal structure of the as-prepared product as that of ZIF-L-Zn, just like the relation

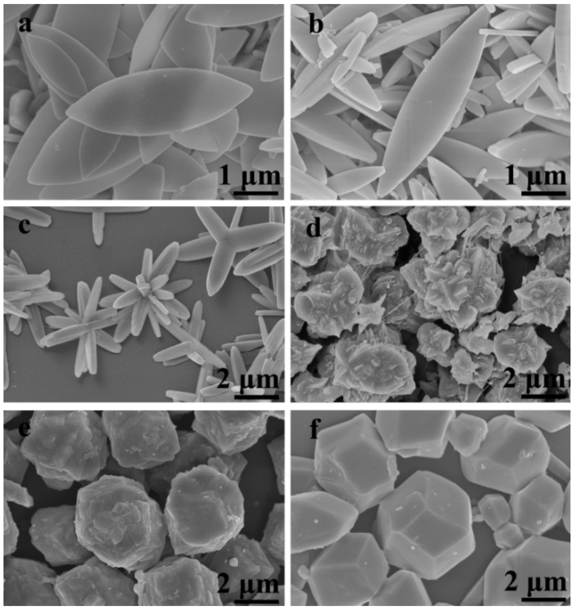

Fig.1 SEM images of products obtained from 400 mM mother solution at different Hmim/Co molar ratio: 8 (a), 16 (b), 24 (c), 32 (d), 40 (e) and 48 (f).

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[†] Electronic Supplementary Information (ESI) available: Synthesis and Characterization, determination of solid transformation, ZIF-L-Co crystallographic information file (CIF), Fig. S1-S8. See DOI: 10.1039/x0xx00000x

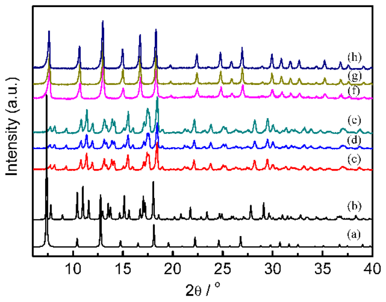

Fig.2 XRD patterns of (a) simulated ZIF-67, (b) simulated ZIF-L-Co and products obtained from 400 mM mother solution at different Hmim/Co molar ratio: 8 (c), 16 (d), 24 (e), 32 (f), 40 (g) and 48 (h).

between ZIF-8 and ZIF 67, they have the identical topological structure, morphology and physiochemical properties except Co takes place of the position of Zn.[1,2] In addition, peaks of the as-prepared ZIF-L-Co sample match well with its corresponding simulated XRD, which is obtained on the base of the reported ZIF-L-Zn by whole pattern fitting and Rietveld refinement. Moreover, according to the elemental analysis result (C: 40.22%; H: 5.62%; N: 24.83%), the sample composition is determined to be $Co(mim)_2(Hmim)_{1/2}(H_2O)_{3/2}$ ($C_{10}H_{16}N_5O_{3/2}Co$), which can be considered as Zn atoms of ZIF-L-Zn replaced by Co atoms in ZIF-L-Co (Figure S2). Furthermore, the TGA results also confirm the composition of ZIF-L-Co (Figure S3).

It is known that the organic linker/metal ion molar ratio was one of the key parameters in the synthesis of ZIF materials. Here we have carried out the experiments at different molar ratio of Hmim/Co (8, 16, 24, 32, 40 and 48), and their corresponding morphologies are shown in Fig. 1 respectively. Increasing the molar ratio from 8 to 24, the leaf-like lamellas narrowed gradually to be rod-like shape, they were bonded to each other presenting a flower-like configuration simultaneously. When the molar ratio rose from 32 to 48, the morphology changed from rough bulgy polyhedron to regular polyhedron with smooth surface. In terms of the XRD results (Fig. 2), it indicated that products at molar ratio of 8 ~ 24 were mainly composed of ZIF-L-Co phase; In contrast, the products at the ratio of 32, 40 and 48 were mainly ZIF -67.These results imply that higher molar ratio leads to the formation of ZIF-67 in comparison to the tendency of ZIF-L-Co formation at lower molar ratio.

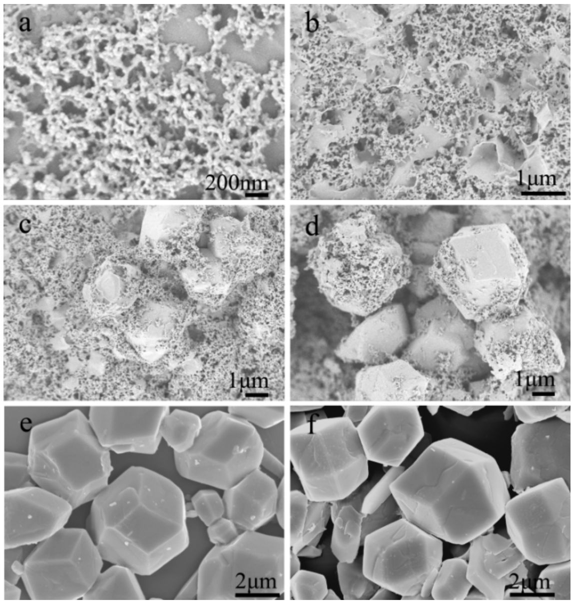

Fig.3 SEM images of products prepared by 400 mM mother solution at Hmim/Co molar ratio of 48 as a function of synthesis time: 5 min (a), 10 min (b), 30 min (c), 60 min (d), 120 min (e) and 720 min (f).

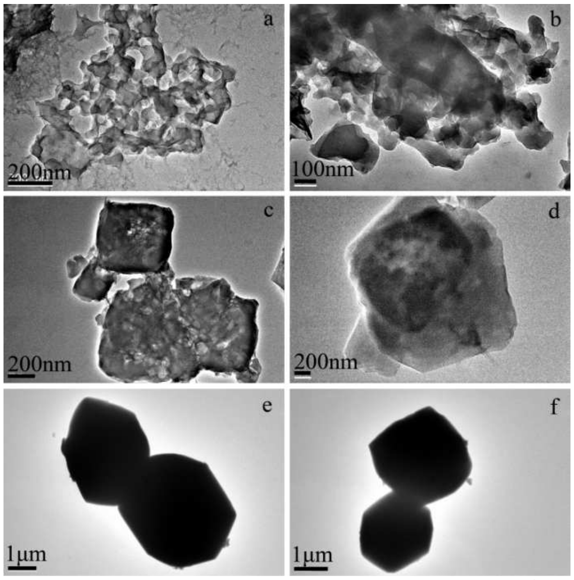

Fig. 4 TEM images of products prepared by 400 mM mother solution at Hmim/Co molar ratio of 48 as a function of synthesis time: 5 min (a), 10 min (b), 30 min (c), 60 min (d), 120 min (e) and 720 min (f).

It has been reported that the 2D layered network structure of ZIF-L-Zn is part of the sodalite (SOD) topology of ZIF-8.[19] Since ZIF-L-Zn and ZIF-L-Co are prepared in aqueous solution instead of other organic solvents in which it gives rise to ZIF-8 and ZIF-67 (Ref.19,20, Figure S4), it is reasonable to assume that the prepared ZIF-L-Co might be a transient phase during the formation of ZIF-67. To verify this assumption, products after 5, 10, 30, 60, 120 and 720 min reaction have been investigated, the molar ratio of Hmim/Co is set as 48 constantly. At 5 min, nanoparticles incorporation with nanoflake morphology can be observed (Fig. 3a). It is noted that these nanoflakes would grow into large pieces in micrometer scale after another 5 min (Fig. 3b); in addition, the large pieces merge into polyhedron after 30 min reaction (Fig. 3c). Subsequently, polyhedron-shaped products grow bigger, the amount of nanoparticles and nanoflakes in products decreased after 60 min reaction (Fig. 3d). When the reaction continuously proceeds with time, the size of polyhedron products increases slightly, the nanoparticles and nanoflakes attached to the polyhedron almost disappear (Fig. 3e and Fig.3f). The transmission electron microscopy (TEM) images in Fig. 4a and b further confirm the mixed morphologies of nanoparticles and nanoflakes in agreement with the above SEM results (Fig. 3a and b). An interesting phenomenon is

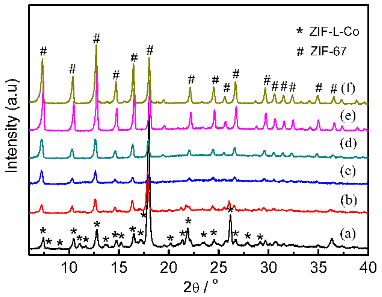

Fig. 5 XRD patterns illustrating the phase transformation from ZIF-L-Co to ZIF-67 corresponding to different reaction time: 5 min (a), 10 min (b), 30 min (c), 60 min (d), 120 min (e) and 720 min (f).

observed that the internal structures of the polyhedron in Fig. 3c and d change from porous into solid gradually. Fig. 5 shows the corresponding XRD patterns at different reaction time. Products at 5 and 10 min have a mixing phase of ZIF-L-Co and ZIF-67, what's more, the intensity of ZIF-L-Co peaks in the 10 min product decreases compared with that of 5 min product. Meanwhile, the peak intensity of ZIF-67 continues increasing with the reaction time from 5 min to 120min. It implies a possibility that ZIF-L-Co is formed firstly at the initial stage (~ 10 min), after that ZIF-67 appears subsequently. As the final crystal gradually increases with the continuous disappearance of intermediate phase during crystallization process, it often follows two formation mechanisms: one is solid transformation of intermediate phase to final product such as zeolite, in which the bonds break and reform inside intermediate phase while liquid phase involving is not needed; the other one is "dissolution-recrystallization" mechanism, solvent is a key media in the process of crystallization. To further determine the possible phase transformation, a series of experiments have been carried out by heating the products at 5 min in vacuum or under water vapor-assisted environments (Figure S5, Figure S6), the results demonstrate that solid transformation plays a dominant role in the process and water media accelerates the transformation. In other words, ZIF-67 is transformed from ZIF-L-Co, which causes the increasing intensity of ZIF-L-Co peaks in XRD results (Fig. 5).

As stated above, the phase transformation process is very fast especially in a high concentration of reagent condition, that's why rare study on this phenomenon has been reported. In our work, we particularly modulate the concentration of mother solutions 400 mM, inspired from the fact that lower concentration of reagents has a lower crystallization rates and a larger particle size.[11, 13, 16, 17, 21,22] The SEM images of products by increasing the concentration of reagents have been presented in Figure S7 when Hmim/Co molar ratio is fixed as 8, the particle size decreases in comparison with that at low concentration, all products are ZIF-L-Co according to XRD results in Figure S8.

In summary, ZIF-L-Co with a leaf-like morphology has been synthesized in aqueous media at room temperature. The Hmim/Co molar ratio plays an important role in the synthesis. Low Hmim/Co molar ratio facilitates the formation of ZIF-L-Co. In addition, the lower concentration results in larger particle size of final products. More importantly, ZIF-L-Co is determined as a transient phase at the initial stage of ZIF-67 crystal growth in aqueous media and the solvent water is a key impact to obtain transient phase ZIF-L-Co, the crystallization process of ZIF-67 follows the solid transformation mechanism. Our study provides a new understanding of ZIF crystal growth which will be highly important for realizing the structural and morphological control in synthesis.

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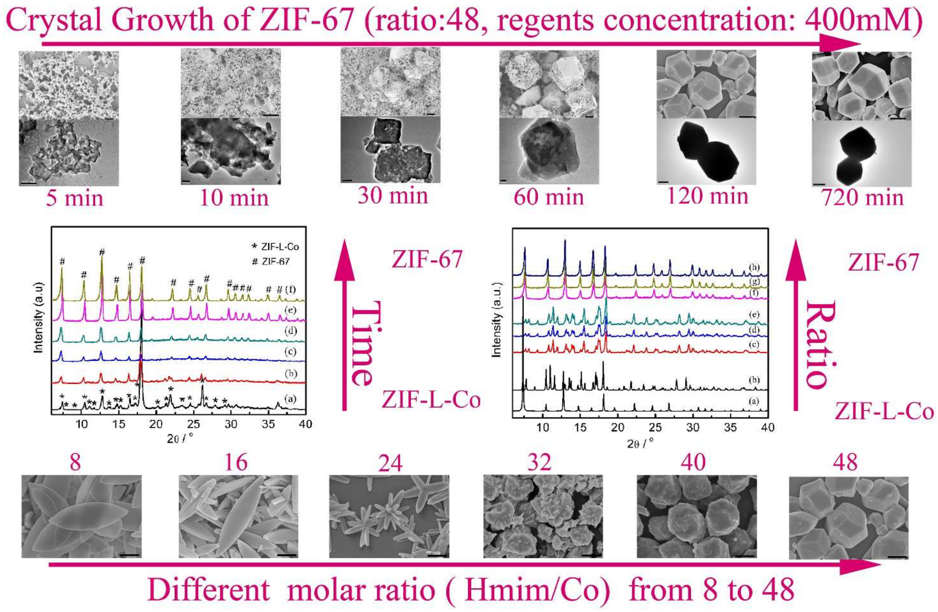

A leaf-like ZIF-L-Co has been synthesized for the first time and the molar ratio of Hmim/Co plays an important role in the synthesis. ZIF-L-Co is a transient phase at the initial stage of ZIF-67 crystal growth, the crystallization process of ZIF-67 from ZIF-L-Co follows a solid transformation mechanism.
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