**Supplementary Information** 

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

Jingcheng Zhang,<sup>\*a</sup> Tianci Zhang,<sup>a</sup> Dongbo Yu,<sup>b</sup> Kesong Xiao<sup>a</sup> and Yu Hong<sup>a</sup> <sup>a</sup> Instrumental analysis center, Hefei University of Technology, Hefei, Anhui, 230009,

People's Republic of China

Email : jingcheng1214@163.com (J. Zhang)

<sup>b</sup>School of Chemistry and Material Science, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

### **Experimental Details**

### Synthesis of ZIF-L-Co, ZIF-67 and ZIF-L-Zn

In a typical synthesis condition, firstly appropriate cobalt nitrate hexahydrate  $(Co(NO_3)_2)$ · 6H<sub>2</sub>O) and 2-methylimidazole (Hmim) were dissolved in 100 mL deionized water to obtain 400 mM aqueous mother solution respectively. Then 1 mL as prepared Co(NO<sub>3</sub>)<sub>2</sub>) aqueous solution was mixed with 8, 16, 24, 32, 40 and 48 mL Hmim solution respectively (the molar ratio of Hmim/Co was 8, 16, 24, 32, 40 and 48) and kept stirring for 2 hours at room temperature. The violet product was centrifuged and washed with deionized water for 5 times, and finally dried in a vacuum oven at 50 °C for 12 hours. The time-dependent evolution of ZIF-67 experiment was conducted with the as-prepared 400 mM solution at Hmim/Co molar ratio of 48, the reaction time was assigned to 5, 10, 30, 60, 120 and 720 min respectively. The impact of concentration was investigated by fixing Hmim/Co molar ratio as 8 and concentrating the mother solution for 2, 4 and 8 times. Following the similar procedures except methanol and N,N-Dimethylformamide were used as the solvents instead of water, ZIF-67 was also synthesized at the molar ratio of 8 after stirring for 24 h at room temperature.

In addition, ZIF-L-Zn was synthesized by the method of reference 1. Typically, 0.59 g of Zn(NO3)2·6H2O and 1.30 g of Hmim were dissolved in 40 mL deionized water respectively, and then the two aqueous solutions were mixed and stirred for 4h at room temperature. The product was centrifuged and washed with deionized water for 5 times, and finally dried in a vacuum oven at 50 °C for 12 hours.

# The Conversion of products at 5min reaction (molar ratio of Hmim/Co = 48) in vacuum and under water vapor-assisted heating at 120 °C

The water vapor-assisted heating method was carried out similar to the method reported by Low et al.<sup>2</sup> Simply, about 50 mg of products were placed in a 5 ml of beaker which was elevated by about 4 cm from the bottom of autoclave. 5 ml of water was then transferred into autoclave. The autoclave was heated at 120 °C for several hours. After cooling to room temperature, the solid products were collected by evaporating water in a ventilated fume cupboard. For comparison, the products were also heated at 120 °C in a vacuum drying oven. The resulting materials were collected for characterization after cooling to room temperature in vacuum.

#### Characterization

The crystal phases of all products are determined by a Cu Kα radiation powder X-ray diffractometer (XRD, Rigaku D/MAX 2500 VL). The morphology of products are examined by field-emission scanning electron microscopy (FESEM, Hitachi SU8020)

and high resolution transmission electron microscopy (HRTEM, JEOL JEM 2100). Thermogravimetric analysis (TGA) was performed by using a simultaneous thermal analyzer (STA, STA449F3). Elemental analysis was detected by elemental analyzer (Vario ELcube).

### The Crystallographic Information File (CIF) of ZIF-L-Co

The powder diffraction data of as-synthesized ZIF-L-Co was collected by Cu K $\alpha$  radiation powder X-ray diffractmeter (tube voltage: 40kV, tube current: 150mA, step size: 0.006° 2 $\theta$ , time per step: 2s). Then the CIF of ZIF-L-Co was realized by whole pattern fitting and Rietveld refinement (Software Jade 7.0) based on the reported CIF of ZIF-L-Zn.<sup>1</sup>



**Figure S1** XRD patterns of simulated ZIF-L-Co (a), prepared ZIF-L-Zn (b) and prepared ZIF-L-Co (c). It is obvious to see all the XRD peaks of as-prepared ZIF-L-Zn and ZIF-L-Co locate at the same 2θ positions, revealing the same crystal structure of ZIF-L-Co as that of ZIF-L-Zn.



**Figure S2** (a) The schematic structure of ZIF-L-Co showing the linking Hmim molecules and the Co atoms. C: black; N: light blue; Co:gray. Hydrogen atoms are omitted for clarity; (b) The 2D layer structure of ZIF-L along z, (c) Internal relationship between ZIF-L-Co and ZIF-67 sodalite (SOD) topology. ZIF-67 framework (green color) with a sodalite cage and 2D layer corresponding to ZIF-L-Co highlighted in red.



**Figure S3** TGA curves of as-prepared ZIF-L-Co (Hmim/Co ratio of 8, concentration of 400 mM) under flowing air and nitrogen condition respectively. The first mass loss before 300 °C corresponded to the removal of weakly linked Hmim and guest water molecule, the residue mass at 400 °C was about 28% in the TGA curve under air,

indicating that ZIF-L-Co was converted to Co<sub>3</sub>O<sub>4</sub> totally.



**Figure S4** (a) XRD patterns of products in different solvents at molar ratio of 8 (red curve: DMF, black curve: methanol); SEM images of ZIF-67 in DMF (b) and methanol (c). This result indicated that solvent used in the MOF synthesis played an important role in the coordination interactions between metal ions and organic linkers.



**Figure S5** XRD of resulting materials under different conditions: the starting product after 5 min synthesis at Hmim/Co molar ratio of 48 (a); after vacuum heating at 120 °C

for 3 h (b) and 6 h (c); after water vapor-assisted heating at 120 °C for 1 h (d) and 2 h (e). It could be seen that the original product at 5 min reaction was mainly composed of ZIF-L-Co, which would convert into ZIF-67 after vacuum heating and water vapor-assisted heating, indicating the solid transformation plays a dominant role in the transformation process. In addition, this phase transformation was completed more thoroughly under water vapor-assisted heating than that in vacuum heating, which implies water media may accelerate the transformation.



**Figure S6** SEM images of resulting materials under different conditions based on the starting product (5 min synthesis at Hmim/Co molar ratio of 48): after vacuum heating at 120 °C for 3 h (a) and 6 h (b); after water vapor-assisted heating at 120 °C for 1 h (c) and 2 h (d).



Figure S7 SEM images of products at Hmim/Co molar ratio of 8 obtained by mother solution with different concentration: (a) 400 mM; (b) 800 mM; (c) 1600 mM; (d) 3200 mM.



**Figure S8** XRD results of products prepared at different concentration of reagents at Hmim/Co molar ratio of 8: (a) 400 mM; (b) 800 mM; (c) 1600 mM; (d) 3200 mM.

## References

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