Bimetallic CuCo-Zeolitic imidazole frameworks (CuCo-ZIFs): Synthesis and characterization

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ABSTRACT

A kind of bimetallic Cu/Co zeolitic imidazole frameworks (CuCo-ZIFs) has been successfully synthesized in ethanol solvent by ultrasound method. The morphology, structural features and physicochemical properties of CuCo-ZIFs were analyzed by several techniques including powder X-ray diffraction, thermo-gravimetric analysis, Fourier-transform infrared spectroscopy, scanning electron microscope, and nitrogen physisorption measurements. The results showed that CuCo-ZIFs nanocrystals demonstrated a ZIF-67-like polyhedral morphology with high thermal stability. The Brunauer-Emmett-Teller surface areas of CuCo-ZIFs were achieved approximately 1172 m²/g, while its Langmuir surfaces areas were achieved approximately 1907 m²/g.

Keywords

Bimetallic, CuCo-ZIFs, ultrasound, zeolitic imidazole frameworks

1. INTRODUCTION

As a subclass of metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) are a new type of porous crystals with extended three-dimensional structures constructed from tetrahedrally coordinated metal centers (typically Zn and Co) bridged by imidazolate derivatives (Im –) (Yao & Wang, 2014). Specifically, the transition metal ion centers (M = Zn and Co) are attached to nitrogen atoms at the 1,3-positions of the imidazolate bridging ligand (Im = C3N2H3) to form an angle of 145° at the M–Im–M center similar to the Si–O–Si angle in silicas and zeolites (Tan et al., 2010). The unique properties of ZIFs such as high surface areas, excellent thermal and chemical stability help them to have been widely used for several potential applications including sensing (Lu & Hupp, 2010), separation (Song et al., 2012), gas storage (Mu et al., 2012), catalysis (Dey and Banerjee, 2013; Zhang et al., 2014) and adsorption (Li et al., 2016).

In recent years, bimetallic zeolitic imidazolate frameworks are being popularly studied. One of them must be mentioned is ZnCo-ZIFs which is composed of Zn²⁺, Co²⁺ cations and 2-methylimidazole anions with a sodalite-related structure (Han et al., 2019). According to a study on the adsorption capacity of ZnCo-ZIFs to CO₂, CH₄, N₂ gases, it showed that ZnCo-ZIFs achieved higher efficiency than ZIF-8 and ZIF-67 due to the large specific surface areas and high porosity (Zhou et al., 2017). Similarly, bimetallic CuCo-ZIFs materials with a combination of both Cu²⁺ and Co²⁺ ions in the structural framework had more outstanding characteristics than monometallic ZIFs. In 2012, Yang et al. successfully studied and applied Cu-doped ZIF-67 materials (denoted: Cu/ZIF-67) in the field of gas...
adsorption and photocatalytic degradation of organic dyes (Yang et al., 2012). According to this study, Cu/ZIF-67 was synthesized under solvothermal conditions by mixing Cu(COO\textsubscript{2})\textsubscript{2}, Co(COO\textsubscript{2})\textsubscript{2} and 2-methylimidazole in mixed ethyleneurea hemihydrate (e-urea) and ethanol solvent at 140°C for 7 days. However, it had low efficiency because of limited experimental conditions, complicated synthesis processes, and time-consuming. To overcome those drawbacks, Khan and Jhung (2015) reported that the use of high intensity ultrasonic waves was a versatile synthetic method for nanostructured materials. The ultrasonic waves could not only lead to homogeneous crystal formation but also speed up the reaction and decrease the synthesis time (Kim and Kim 2008; Suslick, 1990). Therefore, in this work, CuCo-ZIFs were prepared by an ultrasound method in ethanol solvent at ambient temperature. Compared with organic solvents such as N,N-Dimethylformamide (DMF), methanol, acetone,... ethanol was considered a green solvent because it was biodegradable and less toxic. Besides, the synthesis process was carried out under mild conditions and shortened reaction times while the sample still had high crystallinity. The physicochemical properties of CuCo-ZIFs were then characterized by several techniques. This material has a great potential for applications in the catalytic fields.

2. EXPERIMENT

2.1. Materials

2-methylimidazole (C\textsubscript{4}H\textsubscript{6}N\textsubscript{2} 99%) was purchased from Sigma-Aldrich. Cobalt (II) nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O ≥ 99% purity), copper (II) nitrate trihydrate (Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O ≥ 99% purity), ethanol (C\textsubscript{2}H\textsubscript{5}OH ≥ 99.5% purity) were purchased from Xilong chemical Co., Ltd. China. All the reagents were used without further purification.

2.2. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα (λ = 1.5406 Å) radiation source on a D8 Advance - Brucker powder diffractometer. Energy-dispersive X-ray spectroscopy (EDX) was used to analyze elemental composition of CuCo-ZIFs. The morphological features were examined by scanning electron microscope (SEM, Hitach S-4800). The specific surface areas of the samples were calculated using Brunauer-Emmett-Teller (BET) method. Fourier-transform infrared spectroscopy (FT-IR) were obtained on a Bruker TENSOR27 instrument, with samples being dispersed on potassium bromide pallets. Thermo-gravimetric analysis (TGA) was performed on a thermobalance TA instrument TGA-Q500 with the heating rate of 10°C/min in the air atmosphere.

2.3. Synthesis of CuCo-ZIFs

CuCo-ZIFs were synthesized at ambient temperature in ethanol solvent. CuCo-ZIFs was synthesized according to the previous report with the molar ratio of Co\textsuperscript{2+} and Cu\textsuperscript{2+} is 1:1 (Ma et al., 2015). The molar ratio of metal salts and 2-MIm was fixed to 1:4 (Ma et al., 2015). Briefly, Co(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O (0.582 g, 2 mmol) and Cu(NO\textsubscript{3})\textsubscript{2}.3H\textsubscript{2}O (0.483 g, 2 mmol) were separately dissolved in 10 mL ethanol. Another solution was prepared by dissolving 2-MIm (1.3136 g, 16 mmol) in 20 mL ethanol. Then, copper nitrate solution was slowly added to the cobalt nitrate solution. The mixture was stirred for 15 min to form a homogeneous mixture. After that, this mixture was dropped in 2-MIm solution under magnetic stirring, a purple suspension was formed. Subsequently, the mixture salts and 2-MIm were subjected to ultrasound for 15 min and maintained at ambient temperature for 24 h. The purple precipitation was then obtained by centrifugation (6,000 rpm, 15 min). The purple solid was washed by ethanol (3 x 10 mL) for 4 days. Finally, the sample was dried at 60°C to obtain the CuCo-ZIFs crystals. The molar of Co\textsuperscript{2+} and Cu\textsuperscript{2+} were altered by varying the initial concentration of two metal salts (Co\textsuperscript{2+}:Cu\textsuperscript{2+} molar ratio = 1:4, 1:8, 1:12, 1:16).

3. RESULTS AND DISCUSSION

3.1. Characterization of the CuCo-ZIFs

Powder X-ray diffraction (PXRD) patterns of the synthesized CuCo-ZIFs displayed sharp and clear peaks. Although five samples were synthesized in different ratios, PXRD results are almost the same (Figure 1). At the Co\textsuperscript{2+}:Cu\textsuperscript{2+} molar ratios such as 1:1, 1:4, 1:8, 1:12, 1:16, the clearly peaks indexed to 20 values of 7.4°, 10.4°, 12.8°, 14.8°, 16.5°, 18.1°, 24.5°, 25.6°, 26.7°, 29.7°, 30.8° and 31.5° corresponding to (011), (002), (112), (022), (013), (222), (114), (233), (134), (044), (244) and (235), respectively having a good match with previously published results (Chen et al., 2020; Ma et al., 2015; Yang et al., 2012). Although those materials were synthesized in ethanol solvent with different molar ratios, they could completely create a crystal structure of CuCo-ZIFs.
However, the efficiency of the synthesis tended to decrease with increasing molar ratio of cobalt nitrate and copper nitrate (Table 1). Out of all the five ratios of CuCo-ZIFs synthesis, the ratio 1:1 had the highest efficiency (15.9%) while the remaining ratios (1:4, 1:8, 1:12 and 1:16) decreased slowly, as 13.2, 11.9, 10.9 and 9.3%, respectively. This proved that the molar ratio of cobalt nitrate and copper nitrate influenced the formation of bimetallic crystals. Therefore, the molar ratio 1:1 was chosen to be the optimal condition for the next study.

Additionally, the element component was analyzed by energy-dispersive X-ray spectroscopy (EDX) (Figure 2). The EDX of CuCo-ZIFs demonstrated the full presence of elements in the compound including C, N, Co and Cu.

To examine morphology of CuCo-ZIFs, a scanning electron microscope (SEM) was used. In detail, SEM micrographs of representative CuCo-ZIFs sample at the different magnification ratios were shown in Figure 3. The results demonstrated that the synthesized CuCo-ZIFs had relatively uniform cubic particles. This was consistent with the previous result of Gholinejad et al. (2020).
Moreover, the Brunauer-Emmett-Teller surface areas of CuCo-ZIFs were achieved approximately 1172 m$^2$/g, while its Langmuir surfaces areas were achieved approximately 1907 m$^2$/g. Besides, according to the Dubinin-Astakhov method (DA), the pore size distribution of CuCo-ZIFs was determined to be 9.6 Å (Figure 4). It could be concluded that the obtained material had high surface areas. Compared to the previous report, the BET and Langmuir surface areas of Cu/ZIF-67 are 1324.1 m$^2$/g and 1935.5 m$^2$/g (Yang et al., 2012), which were a little higher than those of CuCo-ZIFs. However, the bimetallic CuCo-ZIFs material in this study were synthesised in a facile method include shortening time, saving energy and restricting environmental pollution.

Figure 4. The pore size distributions of CuCo-ZIFs was analyzed by DA method

Figure 5 shows N$_2$ adsorption isotherms of the CuCo-ZIFs sample. The result showed that the adsorbed amount increased suddenly at a high relative pressure and this phenomenon was similar to the work of Yang et al. (2012). It might be due to physisorbed liquid nitrogen on the crystal surfaces of the nanoparticles.
CuCo-ZIFs were then measured by FT-IR to determine the presence of characteristic functional groups in the sample, and compared with FT-IR spectra of ZIF-67 and 2-MIm. Figure 6 showed that the spectrum of CuCo-ZIFs had many similarities with ZIF-67 but there were differences with 2-MIm. In the 600-1500 cm\(^{-1}\) region, the spectral shape of all three samples showed similar, although different peak intensity, because of imidazole ring oscillation. One vibration stretched N-H at 1842.17 cm\(^{-1}\) in 2-MIm and it disappeared for ZIF-67 and CuCo-ZIFs. This demonstrated the reduction of N-H groups in 2-MIm when combined with metal ions (Zhou et al., 2017). Besides, the position 1595.36 cm\(^{-1}\) of 2-MIm was the oscillation of C=N bond corresponding to ZIF-67 and CuCo-ZIFs were 1585.18 cm\(^{-1}\) and 1582.40 cm\(^{-1}\), respectively. The peak at 2924.3 cm\(^{-1}\) appeared in CuCo-ZIFs and ZIF-67 could be attributed to the stretching mode of C-H of the aliphatic chain and aromatic ring in 2-MIm. Notably, the position 421.36 cm\(^{-1}\) and 423.97 cm\(^{-1}\) correspondings to ZIF-67 and CuCo-ZIFs were the oscillation position of the metal-N bond. It means that the CuCo-ZIFs material completely achieved the desired crystal structure (Gholinejad et al., 2020).

Figure 5. \(\text{N}_2\) adsorption/desorption isotherms of CuCo-ZIFs

Figure 6. FT-IR spectra of 2-MIm, ZIF-67 and CuCo-ZIFs
Thermal stability was one of the important criteria for solid materials. Hence, thermo-gravimetric analysis (TGA) was performed for CuCo-ZIFs in the temperature range from 30°C to 800°C (Figure 7). The results showed that CuCo-ZIFs had a stable structure over a wide temperature range. Specifically, the weight of the material decreased slightly by about 4% to 5% when the temperature was between 30°C and 510°C. It was due to the evaporation of small-sized impurities, residual ethanol solvents or unreacted 2-MIm (Kaur et al., 2016). A pronounced weight loss of about 46% was observed from 510°C to 800°C, this was the process of decomposition of CuCo-ZIFs to form metal oxides with a residual mass of only about 48.9%. Besides, the sample still tended to lose weight when the temperature exceeded 800°C as it continued to decompose until the structure was completely broken down. Generally, the TGA curve showed that the thermal stability of CuCo-ZIFs was up to 510°C and be considered superior to ZIF-67 (Chen et al., 2014).

![Figure 7. TGA curve of CuCo-ZIFs](image)

4. CONCLUSIONS

In summary, CuCo-ZIFs has been successfully prepared in ethanol solvent by ultrasound method. It is a simple synthesis, low energy consumption and using environmentally friendly solvent compared to previous studies. Meanwhile, the material still has high crystal strength and polymorphic morphology, which is consistent with other studies. On one hand, the thermal stability of CuCo-ZIFs was higher than ZIF-67. Furthermore, this material has a high surface area which is an outstanding advantage when it is used as a catalyst. Thus, this study provides more new features in the study of catalytic materials belonging to the MOF group.

ACKNOWLEDGMENTS

This study is funded in part by the Can Tho University Improvement Project VN14-P6, supported by a Japanese ODA loan.

REFERENCES


