FACILE SYNTHESIS OF BIMETALLIC ZnCo-ZIFs AND Ag NANOPARTICLES LOADING ON ZnCo-ZIFs (Ag/ZnCo-ZIFs)

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ABSTRACT

A kind of bimetallic Zn/Co zeolitic imidazole frameworks (ZnCo-ZIFs) was successfully synthesized from 2-methylimidazole and two metal salts including zinc nitrate, cobalt (II) nitrate by a solvothermal method at room temperature. Subsequently, Ag nanoparticles (AgNPs) loading on bimetallic frameworks were prepared by a facile impregnation method in acetone solvent. Both ZnCo-ZIFs and Ag/ZnCo-ZIFs were analyzed by several characterization techniques including powder X-ray diffraction (PXRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDX). The results showed that ZnCo-ZIFs crystals had sodalite structure, high thermal stability, and AgNPs were successfully loaded on the ZnCo-ZIFs with content of 18.42%. Ag/ZnCo-ZIFs in this combination may pave a way for preparing a kind of heterogeneous catalyst to remove organic compounds from aqueous solutions.

Keywords
Ag/ZnCo-ZIFs, bimetallic, nanoparticles, zeolitic imidazole frameworks, ZnCo-ZIFs

1 INTRODUCTION

Zeolitic imidazole frameworks (ZIFs) are a subclass of metal organic frameworks (MOFs) that were formed from both inorganic and organic components, namely transition metal ions (M2+ = Zn2+ or Co2+) and organic imidazolate linkers (Im = Imidazole) (Gross et al., 2012). 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 gas storage (Assfour et al., 2011) and separation (Liu and Smit, 2010), adsorption (Du et al., 2017; Zhang et al., 2019) as well as catalysis (Nagarjun and Dhakshinamoorthy, 2019). One of the recently interested ZIFs compounds is ZnCo-ZIFs which are composed of Zn2+, Co3+ cations and 2-methylimidazolate anions with a sodalite-related structure (Han et al., 2019). Notably, syntheses of bimetallic ZnCo-ZIFs frameworks have more outstanding characteristics than monometallic (e.g., ZIF-8, ZIF-67) such as the increase in pore volume and surface area (Kaur et al., 2016).

In science and engineering, nanotechnology is rapidly developed because of their emergent physio-
chemical properties. The intrinsic features of nanoparticles (NPs) depend on the size, shape, surface functional groups and crystalline structure of them (Vreeland et al., 2015). However, NPs have a high surface energy which makes them easy to agglomerate and form larger blocks (Guo and Li, 2004; Lee et al., 2008). That is one of the reasons why the combination of NPs and ZIFs has been more and more attractive to scientists in the world. ZIFs with porous structure can encapsulate NPs (designated NPs@ZIFs) or NPs can attach on the large surface area of ZIFs (designated NPs/ZIFs) and the aggregation can be remarkably relieved, thus preserving the chemical activity and stability of the NPs (Jiang et al., 2011). Moreover, NPs combined with ZIFs can create a new material that integrates both the advantages of each individual component and cannot be obtained from single-component material. In recent years, the materials combined of NPs and ZIFs have considered with different synthesis methods as well as different applications, typically about catalysis (Dhakshinamoorthy and Garcia, 2012). For instance, in 2014, Huang and co-workers demonstrated a facile synthetic strategy to prepare bimetallic alloy nanocrystals were encapsulated in ZIF-8, namely PtPd@ZIF-8 and used for synergistic catalysis of ethylene oxidative degradation. After that, Li et al. (2016) reported to synthesize Pd@ZIF-67 to be used as heterogeneous catalyst for Cr (VI) reduction to Cr (III). The PdNPs could be encapsulated into the uniformly shaped ZIF-67 through the reduction of HCOOH. The as-synthesized Pd@ZIF-67 material had a high catalytic activity and excellent cycle durability which could be reused for 10 times.

Among all the nanomaterials, silver has got more attention because of their optical, electronic and magnetic properties. Silver nanoparticles (AgNPs) seem to be found the most applications in the industry (Li et al., 2012). Indeed, AgNPs have many applications such as antibacterial (El-Rafie et al., 2010), conductivity (Hebeish et al., 2015), optical sensor (Kang et al., 2014), especially catalytic (Joseph and Mathew, 2015). Therefore, herein, a simple and effective method was reported for preparing of ZnCo-ZIFs and Ag/ZnCo-ZIFs which are expected to be a potential heterogeneous catalyst.

2 MATERIALS AND METHODS

2.1 Materials

All reagents and starting materials were purchased from Sigma-Aldrich and Acros, and used as received without further purification.

2.2 Preparation of ZnCo-ZIFs

ZnCo-ZIFs were synthesized at ambient temperature in methanol solvent. The ratio of cobalt nitrate and zinc nitrate was fixed to 3:1 as previously reported (Kaur et al., 2016). Typically, Co(NO₃)₂.6H₂O (0.873 g, 3 mmol), Zn(NO₃)₂.6H₂O (0.297 g, 1 mmol) and 2-MIm (2-MIm=2-methylimidazole; 1.3136 g, 16 mmol) were respectively dissolved in methanol (10 mL). Then, zinc nitrate was slowly added to the cobalt nitrate and magnetic stirring during 15 min to form a homogeneous mixture. Next, this mixture was dropped in 2-MIm solution, resulting in the formation of a purple suspension and they were maintained at room temperature for 24 h. After that, the purple precipitation was obtained by centrifugation, washed with MeOH (3 x 10 mL) for 3 days and dried at 60°C. The molar of two metal salts and ligand was altered by varying the initial concentration of mixture salts and 2-MIm (Zn/Co:2-MIm molar ratio = 1:2, 1:4, 1:6, 1:8, 1:10).

2.3 Preparation of Ag/ZnCo-ZIFs

Before loading Ag nanoparticles, ZnCo-ZIFs was heated at 56°C for 5 h to obtain optimally evacuated sample. Then, Ag/ZnCo-ZIFs catalyst was prepared by a wet impregnation method with AgNO₃ as the metal salt and acetone as the impregnation solvent. The mass ratio of AgNO₃ and ZnCo-ZIFs was fixed to 1:4. Briefly, 62.5 mg of silver nitrate (AgNO₃) was dissolved in 30 mL of acetone, then 250 mg of ZnCo-ZIFs crystals were added into the solution under magnetic stirring for 1 h at 56°C. Subsequently, 0.25 mL of formic acid (HCOOH) was slowly added into the mixture with magnetic stirring, resulting in the dark solid formed. The sample after synthesizing was separated through centrifugation, washing with acetone several times and drying at 60°C for 8 h to obtain the Ag/ZnCo-ZIFs.

3 RESULTS AND DISCUSSION

3.1 Characterization of the ZnCo-ZIFs and Ag/ZnCo-ZIFs

Powder X-ray diffraction (PXRD) patterns of the synthesized ZnCo-ZIFs displayed sharp and prominent peaks analogous to simulation, ZIF-8 and ZIF-67 which confirmed the phase purity of the synthesized. Although five samples were synthesized in different ratios, PXRD results are almost the same (Fig. 1). The clearly peaks indexed to 29 values of 7.3°, 10.4°, 12.7°, 14.8°, 16.5°, 18°, 22.1°, 24.5°, 25.5°, 26.7° and 29.6° corresponding to (011), (002), (112), (022), (013), (222), (114), (233), (224), (134)
and (044), respectively having a good match with previously reported results (Zhou et al., 2017).

Besides, when increasing the ratio of metal salts and 2-MIm in the synthesis, the process yield increased (Fig. 2). The yield of ZnCo-ZIFs-1:8 was about 52%, dramatically increased against the ZnCo-ZIFs-1:2 (10%), ZnCo-ZIFs-1:4 (29%), ZnCo-ZIFs-1:6 (30%), respectively and only lower ZnCo-ZIFs-1:10 was 8% (the yield of ZnCo-ZIFs-1:10 achieved 60%). This proved directly affection of ligand to the formation of bimetallic crystals due to its linking role in the structure of ZIFs. Economically, the ratio of metal salts and ligand selected for the optimal synthesis condition is 1:8.

Fig. 1: PXRD patterns of bimetallic ZnCo-ZIFs samples with different molar ratios of mixture metal salts and 2-MIm

Narrow and strong peaks are obtained from the as-synthesized ZnCo-ZIFs and Ag/ZnCo-ZIFs showed their high crystallinity (Fig. 3). Furthermore, Ag/ZnCo-ZIFs sample appeared the sharp and clear peaks at 2θ values of 38.1°, 44.3°, 64.5°, 77.4° corresponding to (111), (200), (220) and (311), respectively (Fig. 3a). This is entirely consistent with previously reported for the presence of AgNPs (Park et al., 2011). With the participation of silver, PXRD of Ag/ZnCo-ZIFs sample displayed that the structure of ZnCo-ZIFs was only partially maintained with weak intensity. To clarify about presence of silver, EDX and SEM were defined.
EDX analysis was conducted to determine the elemental composition of the nanoparticles. The EDX of ZnCo-ZIFs demonstrated the presence and distribution of C, N, Co and Zn (Fig. 4a). Besides the elements in the original bimetallic frameworks, EDX of Ag/ZnCo-ZIFs had the appearance of Ag, this also demonstrated the successful reduction of formic acid to silver nitrate (Fig. 4b).

Fig. 5 showed the SEM micrographs of representative Ag/ZnCo-ZIFs sample at the different magnification ratios (a), (b), (c) and ZnCo-ZIFs (d), respectively. The results revealed that ZnCo-ZIFs had a polyhedron structure, meanwhile on the surface Ag/ZnCo-ZIFs had appearance of tiny particles that predicted to be silver particles.
Fig. 5: SEM micrographs of Ag/ZnCo-ZIFs at the different magnification ratios (a) x5000, (b) x10000, (c) x30000, (d) ZnCo-ZIFs

For more detailed investigation about properties of materials, Fig. 6 illustrated FT-IR spectra of the molecular structure of Ag/ZnCo-ZIFs, compared to ZnCo-ZIFs and 2-MIm. The FT-IR spectra of linker 2-MIm showed the major absorbance peak was observed at 3400-2200 cm\(^{-1}\) representing the N-H stretching vibration at 1846 cm\(^{-1}\) (Hachula et al., 2010) while it completely disappeared in the FTIR of ZnCo-ZIFs and Ag/ZnCo-ZIFs, indicating that N-H bond of 2-MIm were severed to upon coordination with metal ions. On the spectrum of Ag/ZnCo-ZIFs, peaks appeared in the range of 600-1700 cm\(^{-1}\) which could be indicated to the stretching and bending frequency of the imidazole ring. These peaks almost corresponded to the peaks of 2-MIm as well as ZnCo-ZIFs, they had a little difference but it was insignificant. Indeed, the C=N bond of 2-MIm appeared at 1594 cm\(^{-1}\) while on ZnCo-ZIFs, Ag/ZnCo-ZIFs corresponding 1579 cm\(^{-1}\), 1589 cm\(^{-1}\), respectively. The difference between Ag/ZnCo-ZIFs and ZnCo-ZIFs was only about 0.63%, similar with other links. The decrease in peak intensity might be due to the presence of Ag that covers the surface of ZnCo-ZIFs, which had an impact on energy absorption and emission, reducing the signal strength as well as the movement of the peak.

Fig. 6: FT-IR spectra of 2-MIm, ZnCo-ZIFs, Ag/ZnCo-ZIFs
Furthermore, TGA measurements of ZnCo-ZIFs and Ag/ZnCo-ZIFs were performed from 30°C to 800°C (Fig. 7). For ZnCo-ZIFs, in the published literature, initial weight loss of 2-6% was observed from 135-155°C, from the removal of residual solvent or unreacted 2-MIm (Kaur et al., 2016). In this study, the mass loss occurred mainly at temperatures from 400-720°C, resulting from decomposition of organic linkers. This showed that ZnCo-ZIFs had a stable structure over a wide temperature range. Thermal resistance of ZnCo-ZIFs is considered to be superior to ZIF-67 and ZIF-8 (Kaur et al., 2016). For Ag/ZnCo-ZIFs, initial weight loss of 2.756% at temperature from 30-115°C, this might come from the loss of small molecules or residual acetone solvent. The next weight loss observed from 115-300°C, 300-360°C corresponding to 35.96%, 5.185%, respectively. Up to 460°C, Ag/ZnCo-ZIFs almost completely decomposed and remaining mass were only about 40.18%. Generally, the TGA trace for ZnCo-ZIFs revealed a high decomposition temperature of 530°C while Ag/ZIF-67 were approximately 220°C. This could be explained that in the synthesis process, ZnCo-ZIFs took an hour to disperse in acetone at 60°C, moreover Ag⁺ ions were reduced to Ag₀ by HCOOH. The contact of material with reducing agent under heating stirring conditions, reaction time of more than 90 min might make them lose stability.

**Fig. 7: TGA curves of ZnCo-ZIFs and Ag/ZnCo-ZIFs**

4 CONCLUSIONS

In summary, bimetallic Zn/Co zeolitic imidazole frameworks (ZnCo-ZIFs) were successfully synthesized by facile solvothermal method at ambient temperature with the yield over 52% being obtained. Bimetallic ZnCo-ZIFs were determined to be have similar structure as monometallic ZIF-67 and ZIF-8. Furthermore, this solid was stable in wide temperature range. Besides, Ag NPs were successfully loaded on the surface of ZnCo-ZIFs by using an impregnation-reduction procedure and form to the Ag/ZnCo-ZIFs material. With the unique and individual properties of silver and bimetallic framework as well as this successful combination, Ag/ZnCo-ZIFs are expected to be potential heterogeneous catalyst in removing the persistent organic compounds in the water.

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REFERENCES


