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Zn/Co ZIF family: MW synthesis, characterization and stability upon halogen sorption

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The bimetallic Zn/Co-ZIF MOFs with different Zn:Co ratio were produced by microwave-assisted solvothermal synthesis. The morphological, structural and electronic properties of the obtained materials were probed with different experimental techniques (XRD, TEM, TGA, BET, UV–Vis, IR, Co and Zn K-edge XANES). The result of the overall characterization study evidences that: (i) for all Zn:Co ratio Zn/Co-ZIFs are isostructural to ZIF-8; (ii) Zn and Co occupy the same crystallographic site having the same local environment; (iii) increasing Co content results in the decrease of solvent and iodine amount adsorbed on the surface of the crystals, while the amount adsorbed inside the pores is almost constant. The Zn/Co-ZIF MOFs were tested for iodine and chlorine sorption.

1. Introduction

Metal–organic frameworks (MOFs) are relatively new porous materials that have already found applications in several different areas such as gas: storage, separation, sensors, catalysis [1–20]. MOFs have a modular structure that can be divided into inorganic clusters with metal ions, and organic linkers coordinating them into a 3-dimentional crystal framework [21]. The type of inorganic cluster and linker strongly influences the topology of the framework, the physicochemical properties of the MOF and, consequently, its efficiency in various applications [22–26]. Most MOFs studied over the past decades are based on a single type of metal site and on a single linker [18,19,27–38]. In this work we will not discuss MOFs synthesized with different linkers [39–51] while we will focus on MOFs synthesized with different metals in the secondary building unit (SBU). The presence of two or more different metals in the same structure can lead not only to the summation of properties, but to have a synergistic effect [52–58]. For example, the mixture of Zn and Co metals provides the fluorescent properties to $Co_2Zn_5(OH)_8(DTA)_3{\cdot}H_2O_n$ [56]. The Zn-doped structure of $Cu_{3-x}Zn_x(BTC)_2$ (BTC = benzenetricarboxylate) exhibits improved magnetic properties in comparison to the initial Cu_3BTC_2 compound [54]. The most common strategy for obtaining the mixed MOFs is based on the insertion of a second metal in the primary MOF structure by means of immersion, metal exchange or core–shell methods [59–62]. Direct synthesis of mixed MOF is the most convenient and obvious technique; however, it seems to be still a challenging task since it is difficult to evaluate the mechanism of introduction of the second metal. In some cases, each metal can independently form distinct, mono-metallic, MOF crystals without bounding the SBUs containing the other metal. Alternatively, some examples of post-synthesis functionalization with a second metal of an already formed MOFs are also been reported in the literature [55,57,58]. In this regard, the MOFs allowing to obtain a mixture of metals within a single crystal structure, attracts special attention. Such compounds include, in particular, the MOFs of the ZIF family (ZIF-zeolitic imidazolate frameworks). Their properties, such as high porosity, thermal (>550° in N_2) and chemical stability, make them attractive in several applications such as gas sorption and storage, separation, catalysis [50,63–77]. Among many ZIF structures, ZIF-8 is the most studied structure because of its potential application for gas separation and selective iodine adsorption [68,69,78–81]. This MOF

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consists of the Zn^{2+} ions coordinated tetrahedrally by nitrogen from the imidazole ring of the 2-methylimidazole linker (MIm). More recently, it has been found that Zn^{2+} ions in the ZIF-8 lattice can be partially or completely replaced by the Co^{2+} ions, which have the same charge and are close in size, providing materials with new properties. The endmember specimen with only cobalt has been named ZIF-67. At present, various methods for the production of bimetallic Zn/Co-ZIF-8 are described in the literature [82–86]. Kaur et al. [82] described bimetallic Zn/Co-ZIF-8 and noted an increase in the pore volume and active surface area in comparison with the initial ZIF-8. Also, recently, Wang et al. [87] described the realization of Zn/Co-ZIF-8 membranes for propane/propylene separation founding that the selectivity of the membranes to propylene increases with the increase of the Co^{2+}/Zn^{2+} ratio in the bimetallic ZIF structure. It was demonstrated that doping of ZIF-8 by Co^{2+} enhances the photodegradation of methylene blue dye under visible light irradiation without hydrogen peroxide [77]. ZIF-8 shows better performance for I_2 adsorption than ZIF-67, it means that the reactive metal site plays a role in the I_2 adsorption [88]. Electrodeless quartz crystal microbalance was used for investigating the adsorption kinetics of iodine onto ZIF-8 and ZIF-67 films; the study revealed a high iodine capacity for both materials (2.4 g/g – ZIF-8 and 4.4 g/g – ZIF-67) [89–91].

The last two are relevant points, as one of the most remarkable specific applications of ZIF-8 is iodine adsorption [78]. It should be noted, that for the iodine capping during the past decades, a list of materials was applied. Part of them physically adsorbed iodine gas, like activated carbons and graphene [92–94], polymers [95–98], cements [99,100], zeolites [101,102], hydrotalcites [103] etc. Other materials were functionalized with active species; this is the case e.g. of silver or bismuth particles or ions in the matrix of alumina [104], silica [105] or zeolites [106,107], which can chemically interact with iodine. Also a large list of MOFs was tested for this application [108–121]. All these materials have advantages and disadvantages in this specific application; among others ZIF-8 combines high iodine capacity with high temperature of iodine evacuation.

The iodine adsorption is facilitated by the favorable interactions between I_2 and MIm linker. Later report proved that ZIF-8 framework strongly binds iodine molecules, while I_2 located on the surface of ZIF-8 are restrained by traditional iodine–organic complexes [122]. The strong interaction is driven by the ideal geometry of the ZIF-8 cage, allowing the formation of the two iodine–organic bonds per I_2 molecule. The small pore aperture to the cage combined with strong I_2 – cage binding energy resulted in the retain of iodine up to framework collapse [122]. Comparison of three ZIFs with different linkers (ZIF-4, ZIF-8 and ZIF-69) reported in 2013 proved that ZIF-8 is the best option for sorption and retaining of iodine [123]. Large pore apertures (like in ZIF-69) enhance the iodine uptake but reduce the retaining properties. It was demonstrated that the amortization of the ZIFs using ball-milling or high-pressure significantly increases the temperature at which I_2 is retained [123,124]. Molecular modeling demonstrates that, at low pressure, MOFs with small pore volumes are more qualified for iodine capture; however, at normal pressure, MOFs with high pore volumes are desired [125]. To enhance iodine sorption properties composite materials could be envisaged. A flexible nanocomposite consisting of bacterial cellulose and ZIF-8 nanoparticles was applied for reversible iodine adsorption both from gas phase and I_2/KI solution [126]. High iodine uptake (1.9 g/g from the vapor and 1.3 g/g from the solution) was demonstrated. Composite materials constructed from thin films of ZIF-8 and a glassy Matrimid or a rubbery polyurethane matrix demonstrated higher iodine affinity resulted in better absorptive and retention capabilities than the single phase ZIF-8 material [127]. Specific adsorption of iodine by ZIF-8 could have additional applications such as: (i) electrical detection of the iodine vapor [128]; antimicrobial action [129].

Examples of bromine and chlorine sorption by MOFs, such as the reversible sorption of Cl_2 and Br_2 by cobalt-based MOF [130], are rare in the literature. In 2016 high bromine vapor capacity for ZIF-8 films grown on the surface of quartz was revealed [131].

In the present work, we report a fast microwave (MW) assisted synthesis technique allowing to obtain bimetallic Co^{2+}/Zn^{2+} ZIFs with ZIF-8 structure type. Moreover, comprehensive characterization of the obtained materials is provided. Obtained ZIFs were successfully applied for iodine sorption. Interaction of ZIFs with aggressive chlorine gas was performed too.

2. Experimental details

2.1. Reagents and characterization methods

Reagents $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, triethylamine (TEA) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Ultra-pure water (18 MΩ·cm) was produced by SimplicityUV (Millipore) from distilled water.

Laboratory MW system Mars6 (CEM) was employed for the synthesis. Powder X-ray diffraction (PXRD) of samples were collected using D2 Phaser (Bruker) X-ray diffractometer with Cu Kα radiation. The Fullprof program was used for the Rietveld refinement of the diffraction patterns of the as-prepared samples. Diffuse reflectance (DR) UV–Vis spectra were collected on UV-2600 (Shimadzu) spectrophotometer with 2 nm step by using integrating sphere accessory with $BaSO_4$ blank. The measured %R values were converted into absorbance on instrument's software. Transmission electron microscopy (TEM) was performed on FEI Tecnai G2 Spirit TWIN transmission electron microscope operated at an accelerating voltage of 80 kV. Particle size distribution histogram was build based on graphical analysis of 100 NPs in ImageJ software. The experimental XANES spectra of Co *K*-edge (7709 eV) and Zn *K*-edge (9659 eV) were measured for $Zn_{1-x}Co_xC_8H_{10}N_4$ samples using in-house X-ray spectrometer Rigaku R-XAS Looper. A tungsten cathode and a Ge (311) crystal monochromator were used. X-ray tube voltage was 20 kV and current was 70 mA during Co *K*-edge measurements, while for Zn *K*-edge measurements voltage were reduced down to 11 kV. A gas-filled proportional counter (argon gas at a pressure of 300 mbar) was used to register the intensity of the incident radiation, while a scintillation detector was used to register transmitted radiation.

2.2. Synthesis of bimetallic Zn/Co-ZIF

The bimetallic Zn/Co-ZIFs were synthesized according to the previously reported technique [132]. Briefly, zinc and cobalt nitrates hexahydrates and 2-methilimidazole were dissolved separately in the equal volumes of DMF. Then TEA was added to the linker and both solutions were transferred into the glass vessel, closed hermetically and placed into the MW oven (see Table 1). Then reaction mixture was heated at 140 °C for 15 min. After cooling down to room temperature, a precipitate was collected by centrifugation, washed two times with DMF and once with methanol and dried at 60 °C overnight (photos of obtained powders are provided in the SI – Fig. S1).

2.3. Iodine and chlorine sorption tests

For Iodine adsorption experiments the respective Zn/Co-ZIF sample was pressed into a thin tablet of about 25–50 mg. The tablet was placed in a glass vessel filled with iodine crystals. The glass vessel was tightly closed and heated up to 110 °C. After iodine