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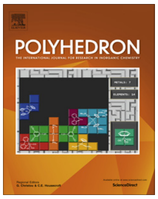

Zn/Co ZIF family: MW synthesis, characterization and stability upon halogen sorption

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ABSTRACT

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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