Seven new ionic solids built on polyoxometalate (POM) anions and [Co(en)]3+ cations namely, [Co(en)2MoO2(H2O)(Cl)] (DMF), [Co-Mo-P-DMF], [α-PW12O40] [Co(en)]3·6DMF (Co-W-P-DMF), [α-PW12O40] [Co(phen)]3·6DEF (Co-W-P-DEF), [α-PW12O40] [Co(en)]3·5.5DMF (Co-Mo-P-DMF), [α-PMo12O40] [Co(en)]3·6DEF (Co-Mo-P-DEF), [α-SiW12O40] [Co(en)]3·6DMF·3H2O (Co-W-Si-DMF) and [α-SiW12O40] [Co(en)]3·6DEF (Co-W-Si-DEF) have been synthesized from non aqueous (DMF/DEF) media and characterized by single-crystal X-ray diffraction. We attempt to understand if [Co(en)]3+ cations used in these reaction systems play a crucial role in controlling the assembly of these crystals. These ionic solids, after removal of the DMF or DEF molecules, are found to exhibit size selective H2 adsorption properties over N2. The amount of hydrogen adsorption was influenced by POM anion types and their orientations, CoMo-P-DEF has the highest (0.9 wt%) H2 uptake and CoW-P-DEF has the lowest (0.4 wt%) uptake among the series when the adsorbatve pressure approached 1 atm. We believe that the successful synthesis of these seven new ionic solids and the discovery of their selective H2 adsorption properties, as a result of the cooperative behavior between their cationic/anionic component species, will open up new vistas in the search for polyoxometalate based materials with useful absorptive properties.

Keywords: porous, salts, adsorption


Keywords: MOFs, templates, structure-directing agents.

MOFs (Metal Organic Frameworks) are crystalline organic-inorganic polymeric networks which consist of metal ions (isolated or joined in clusters of different dimensionalities) covalently connected by organic ligands to give 1D, 2D or 3D structures. These materials are applied in several fields like gas adsorption, catalysis and controlled drug release [1]. It is well-known that during the self-assembly process, structural directing agents (SDAs) and templates are crucial for obtaining 3D porous structures. This strategy was widely used in zeolites synthesis [2]. However, the use of such agents in the synthesis of MOFs has been less explored, so a distinction between both functions is perhaps subtle in this subject. The primary template effect occurs during the synthesis process when the organic guest molecule is self-included into the host framework by non-covalent interactions acting as a placeholder, thus preventing the interpenetration of the open network. The secondary template effect is a dynamic process that takes place when appropriate guest molecules act as templates and induce reversible structure transformations [3]. In contrast, the SDAs drive the formation of a certain phase but not necessarily are included in the structure. The objective of this work is to study the structural directing or template functions of aromatic molecules (salicylic acid, acetyl salicylic acid, benzene and pyridine) in the formation of MOFs based on the succinate ligand and Ho(III) ion, exploring in turn, the effect of the in situ ligand generation by hydrolysis of the succinyl salicylic acid.

Under different hydrothermal synthesis conditions, two compounds with formulae [Ho2(C4H4O4)2(H2O)]·0.33(C2H3O2) (1) and [Ho2(C4H4O4)2(H2O)] (2), were obtained, both belonging to the triclinic system and P1 space group. In the case of 1, it was found that the aromatic molecules act as templates determining channels that represent a free cell volume of 21.5%. These molecules are hosted with partial occupation of 0.25-0.5 molecules per formula. On the contrary, in compound 2, the auxiliary organic molecules are not included in the framework allowing us to consider them as SDAs due to their presence in the synthesis mixture leading specifically to the formation of this compound, while if they are absent, a third Ho(III)-succinate phase is obtained. It has been found that the role of aromatic molecules varies from SDAs to templates as the corresponding concentration increases.