



Effect of water addition on the formation of copper/zinc terephthalate MOFs

Nikita Bogachev, Andrey Mereshchenko, Mikhail Rebogov and Mikhail Skripkin

Saint-Petersburg State University, 7/9 Universitetskaya mb., St. Petersburg, 199034, Russia Presenting author e-mail: skripkin1965@yandex.ru

The synthesis and study of metal-organic frameworks (MOFs) is one of the most extensively developed fields of modern coordination chemistry. Effect of pH, synthesis duration, temperature etc. on the formation and properties of MOFs is under consideration. Meanwhile far less attention is paid to a very important factor namely to the effect of solvent composition on the composition and structure of crystallizing compounds. To reveal this effect the study of solid phase formation in the systems $Cu(NO_3)_2-1,4$ -BDC-amide- H_2O and $Zn(NO_3)_2-1,4$ -BDC-amide- H_2O (amide- N_i)-dimethylformamide, DMF or N_i N-dimethylacetamide, DMA) was undertaken in the temperature range 90–180°C. As a result, the crystallization fields of distinct MOFs were determined. In copperterephthalate systems with low water content $Cu_2(BDC)_2(amide)_2$ MOFs are formed at temperature up to 130°C, upon heating they gradually transform to $Cu(BDC)(NHMe_2)_2$. In water-rich solutions formation of copper basic terephthalate ($CuOH)_2(BDC)$ takes place.

In the zinc-terephthalate systems higher variety of compounds formed have been found that can be explained by high lability of complexes forming by ions with d^{10} configuration. Dimethylamide formed under acid-promoted hydrolysis of amide can both coordinate to zinc ion and serve as counterion in protonated $NH_2Me_2^{\frac{1}{2}}$ form.

The special attention will be paid to anomal basicity of water in DMF – H_2O systems effect that effect on both composition of MOFs and the conditions of their crystallization.

Acknowledgements: Authors acknowledge Saint-Petersburg University Research Park (Centre for X-Ray Diffraction Studies) for their assistance in experimental work.

Thern

Water interpretation As regards this phenor contribution azeotropy and additive) for body refere molecular aspecies in the species in the spe