Effect of the surfactant on Metal-Organic Framework Structures Synthesis

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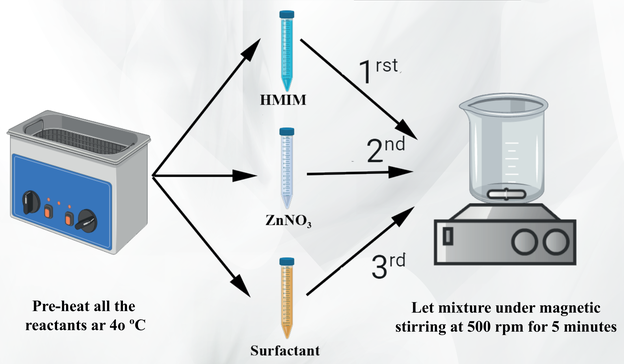
Abstract

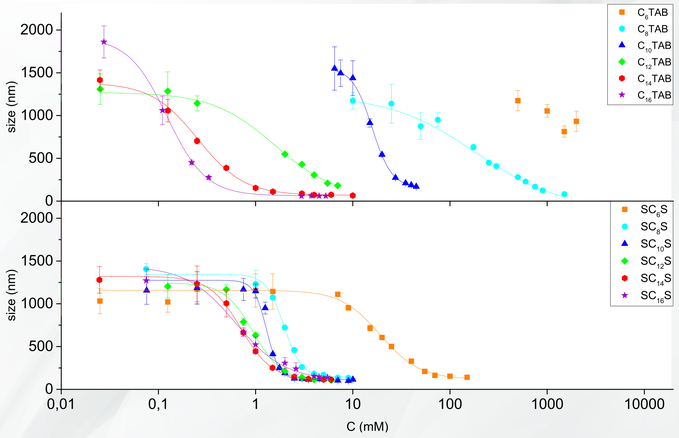
The beginnings of Metal-Organic Frameworks (MOFs) chemistry were established by Yaghi et al. in the 90s[1]. They started a new promising field for which, depending on the nature of the organic functionality and metal−ligand coordination chemistry, diversity of MOFs in terms of their structures and chemical properties is virtually endless. Since the 90s it has been reported different synthetic routes (e.g. hydro-solvothermal synthesis, microwave and ultrasound-assisted synthesis, mechanochemistry, microemulsion synthesis, continuous flow production)[2,3]. Nevertheless, no control on the shape and size of the crystal were achieved in a proper way. The results obtained during this work demonstrates that the surfactant plays an important role in the MOF´s synthesis protocol, in particular, in those with Zeolitic Imidazolate Framework (ZIF-8) structure, by changing the former physico-chemical properties without altering their crystalline structure. Thus, this work is focused on the effect of two surfactants: Sodium Dodecyl Sulfate (SDS) and Hexadecyltrimethylammonium bromide (CTAB). In this sense, for each family of surfactant the influence of the surfactant tail chain length and the nature of their head group were investigated. For these studies, dynamic laser-light scattering (DLS), scanning electron microscopy (SEM) and powder X-Ray Diffraction (PXRD) were performed in order to characterize the physicochemical properties and the morphology of the obtained MOFs.

Methods



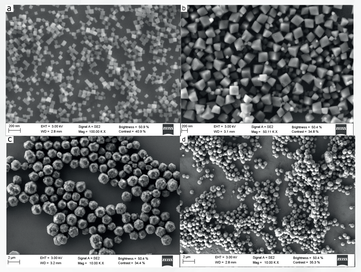
The synthetic protocol was adapted from refs [4] and [5]. The same amount of 2-methylimidazole (HMIM), zinc nitrate hexahydrate and the surfactant are added as shown in the image.

DLS Study

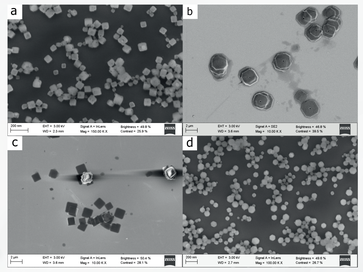


Effect of surfactant's concentration on MOF's size for the different surfactants studied for the CTAB (left) and SDS (right) families

Micrographs

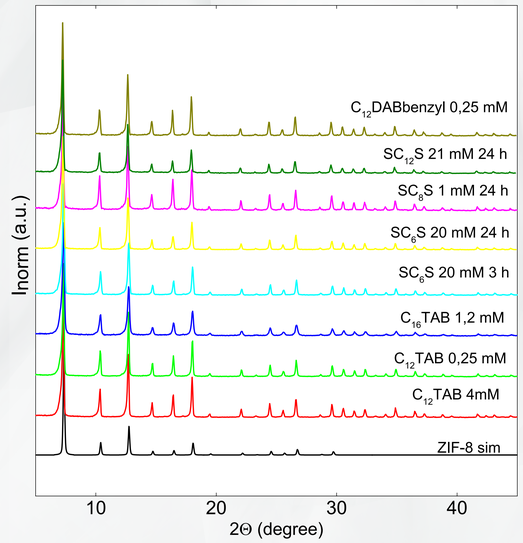


Obtained shapes with the CTAB family. a) C_{16}TAC 4 mM; b) C_{12}TAB 0.25 mM; c) C_{12}TAB 4 mM; d) (C_{12})x2DAB 4 mM

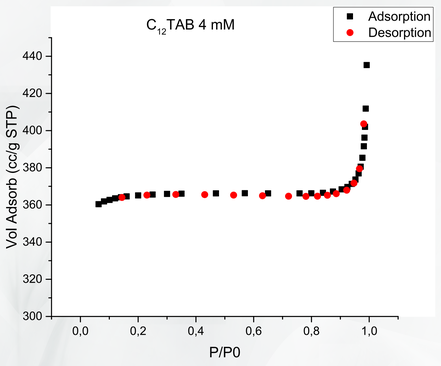


The SDS family synthetised MOFs: a) $SC_{16}S$ 1 mM 24 h; b) $SC_{12}S$ 50 mM 24 h; c) $SC_{12}S$ 21 mM 24 h; d) SC_8S 1 mM 24 h

Powder X-Ray Diffraction



N_2 Physisorption



Bet Surface Area: 1217 ± 31 sq. m/g

Conclusions

1.- Changes in surfactant concentration allow tuning MOF size from c.a. 100 nm to c.a. 1 µm, but also in MOF geometry while keeping the crystalline structure.

2.- Increases or decreases of the hydrophobic tail length allows changing the MOF shape. Remarkably, planar structures were achieved in the SDS family.

3.- Changing the counterion seems not to have any effect on the MOF size, but can alter its shape.

4.- Changes in hydrophilic head volume allow the formation of MOF particles with more resolved and defined shapes.

5.- By increasing the volume of the surfactant hydrophilic head, results in a lower control of MOF size.

References

[1] H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, Nature 402, 276 (1999).
[2] M. Giménez-Marqués, T. Hidalgo, C. Serre, and P. Horcajada, Coord. Chem. Rev. 307, 342 (2016).
[3] N. Stock and S. Biswas, Chem. Rev. 112, 933 (2012).
[4] Y. Pan et al., CrystEngComm 13, 6937 (2011).
[5] Y. Pan et al., Chem Commun (Camb) 47, 2071 (2011).