

Systematic Design of Defect Engineered Zr-MOFs and their Applications in Liquid- Phase
Esterification Reactions

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Degree Work to Opt for the Degree of Doctor in Chemical Engineering

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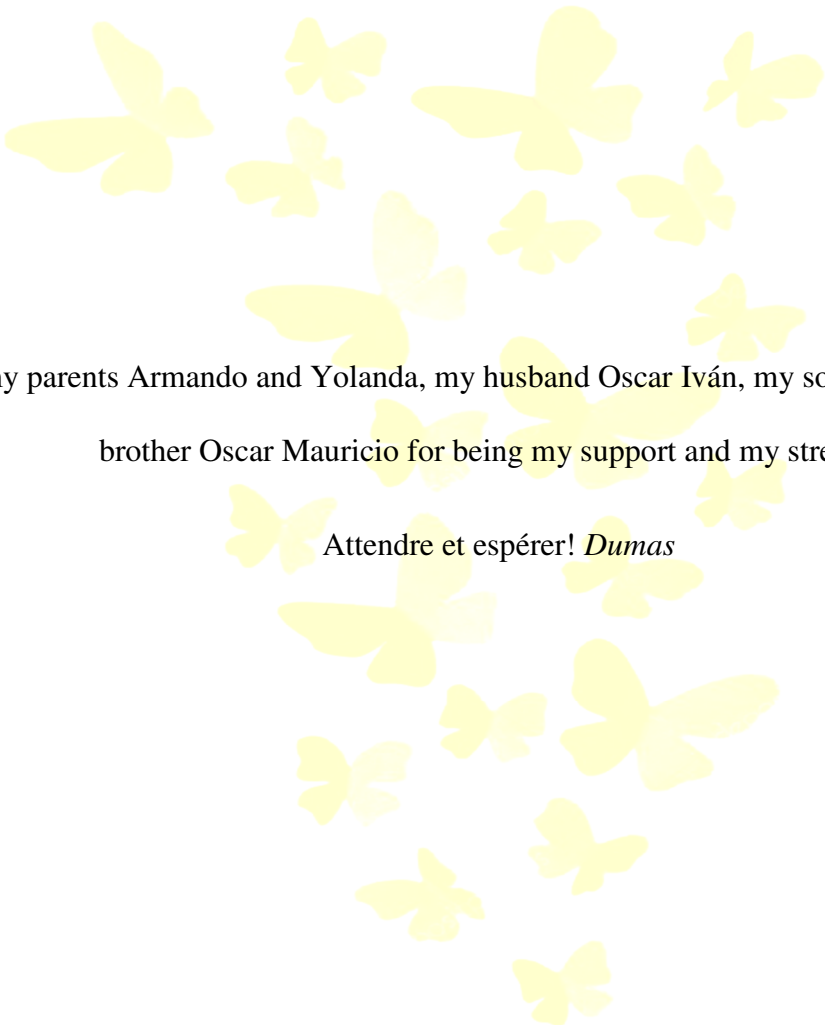
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2020

Dedication



To my parents Armando and Yolanda, my husband Oscar Iván, my son Nicolás, and my brother Oscar Mauricio for being my support and my strength.

Attendre et espérer! Dumas

Acknowledgments

I want to especially thank my advisors, Dr. Gustavo Ramirez, for the opportunity and support on my work in his Group and Dr. Victor Baldovino, for always encouraging me to go further during my studies and research all these years at Universidad Industrial de Santander, UIS. Thanks to Dr. Álvaro Ramirez to see in me a future on research. Thanks also to Dr. Perla Balbuena for becoming part of her Group during my internship at Texas A&M University, her guidance, and unconditional support. I much appreciate the opportunity provided by Dr. Raphaël Schneider and Dr. Halima Alem to work at the LRGP of the ENSIC during my internship at the Université de Lorraine.

Special thanks to my long life friends and my initial labmates but now inseparable friends from GIP and CICAT groups at UIS. We grew up always supporting each other through all these years. I also want to thanks to my co-workers at the Balbuena's Group and my labmates at the LRGP for their warm welcome.

This research was possible thanks to Vicerrectoría de Investigación y Extensión (VIE) at Universidad Industrial de Santander (UIS) through the agreement of cooperation (code 9457) between UIS University and Fundación para la Promoción de la Investigación y la Tecnología, FPIT, and the agreement of cooperation (code 9462) between UIS University and COLCIENCIAS – ECOS Nord. Thanks also to COLCIENCIAS for my Ph.D. fellowship through the *Programa Doctorados Nacionales* (National Doctorates Program).

The Supercomputer resources from the Texas A&M University High-Performance Computer Center, the Texas Advanced Computing Center (TACC), the SC3-UIS High

Performance and Scientific Computing Centre, the Laboratorio Central de Rayos X – UIS, the Laboratorio Central de Microscopia – UIS, and the Laboratorio de Ciencia de Superficies-UIS are gratefully acknowledged.

Last but not least, I want to express my sincere gratitude to my beloved family for their permanent and unconditional encouragement and support. None of this would have been possible without you.

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Resumen

TÍTULO: Diseño sistemático de MOFs de zirconio a través de ingeniería de defectos y su aplicación en reacciones de esterificación en fase líquida *

AUTOR: Carolina Ardila Suárez **

PALABRAS CLAVE: MOFs, ingeniería de defectos, catálisis heterogénea, química superficial.

DESCRIPCION: La MOF-808 es un material prometedor de la familia de MOFs a base zirconio, debido a su alta área superficial. Sin embargo, el carácter microporoso de este material es una desventaja para aplicaciones prácticas debido a limitaciones de transporte causadas por el acceso restringido de moléculas dentro de la estructura.

En este trabajo se desarrolló tanto el diseño sistemático de la MOF-808 como su subsecuente modificación con el fin de obtener materiales ácidos, ordenados e interconectados con porosidad multimodal y su evaluación en la esterificación del glicerol con ácido acético en fase líquida. Se realizaron simultáneamente cálculos teóricos y mediciones experimentales con el fin de correlacionar la acidez del material con su actividad catalítica. Además, la adición de surfactantes y moduladores permite la síntesis de materiales micro/macroporosos ordenados y cristalinos. La adición de CTAB no parece alterar la composición química superficial ni las propiedades ácidas de las MOFs en comparación con los materiales sintetizados sin surfactante. Asimismo, las mediciones catalíticas reflejan que la porosidad interconectada de los materiales sintetizados con surfactantes favorece la difusión y accesibilidad de las moléculas, lo que conlleva a un mejoramiento del comportamiento del catalizador en la reacción de esterificación de glicerol en fase líquida.

En cuanto a la sulfatación de las MOFs, esta modificación postsintética no afecta la interconectividad de los materiales y sí aumenta el número y fuerza de los sitios ácidos de los catalizadores y por consiguiente su actividad catalítica. Finalmente, la caracterización superficial refleja que los grupos sulfatados se encuentran unidos y bien distribuidos sobre la superficie del catalizador.

*Tesis Doctoral

** Facultad de Ingenierías Físicoquímicas. Escuela de Ingeniería Química. Director: Dr. Gustavo Emilio Ramírez Caballero. Codirector: Dr. Víctor Gabriel Baldovino Medrano.

Abstract

TITLE: Systematic Design of Defect Engineered Zr-MOFs and their Applications in Liquid-Phase Esterification Reactions *

AUTHOR: Carolina Ardila Suárez **

KEYWORDS: MOFS, defect engineering, heterogeneous catalysis, surface chemistry.

DESCRIPTION: The MOF-808 is a promising material of the Zr-based MOFs family due to its high surface area and large pore size distributions. However, this material's microporous character is a disadvantage for practical applications due to accessibility and transport limitations caused by the restricted access of molecules into its structure. In this contribution, the systematic design of MOF-808 and its subsequent modifications were performed to synthesize acidic, ordered, and interconnected materials with multi-modal porosity and its evaluation in the liquid-phase glycerol esterification with acetic acid.

In this work, a systematic design of the MOF-808 and its subsequent modification was performed for the obtainment of acidic, ordered, and interconnected materials with multi-modal porosity and their evaluation in the glycerol esterification with acetic acid in the liquid phase.

Theoretical calculations and experimental tests were employed to correlate the materials' acidity with their catalytic activity. Furthermore, the surfactant and modulator's addition allows the synthesis of ordered and crystalline micro/macroporous materials. The CTAB addition seems not to affect the chemical composition at the surface neither the surface properties of MOFs compared to the materials synthesized with no surfactant. Furthermore, the catalytic tests reflected that the interconnected porosity of synthesized materials favored the diffusion and accessibility of bulk molecules, leading to improved catalyst performance during the glycerol esterification in liquid-phase. Related to the MOFs sulfation, this post-synthetic modification does not affect the materials' connectivity and does affect the number and strength of the catalysts acidic sites and, consequently, their catalytic activity. Finally, the surface characterization reflected that the sulfated groups are attached and well distributed on the catalyst surface.

* Ph.D. thesis

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Introduction

Metal-organic frameworks (MOFs) are porous crystalline materials in which a metallic center is connected to organic ligands through coordination bonds. Their versatility, high surface areas, and the possibility of a precise design of their structure and distribution of their active sites make them potential candidates for applications such as gas adsorption/separation, and heterogeneous catalysis.

Defect engineering of MOFs emerges as an approach for tailoring their properties. The intentional removal of part of the organic ligands or the metal clusters would lead to the control of the pore structure and changes in the electronic, physicochemical, and surface properties of synthesized materials. The versatility of MOFs also allows the engineering of their pore structure through template-assisted routes and the addition of active target sites during synthesis or through post-synthetic methodologies.

Zirconium-based MOFs are known for their high thermal and chemical stability. Therefore, the strength of the coordination bonds of the *Zr6O8* cluster comes from the strong acid-base interactions between Zr (IV) and oxygen atoms. Among them, MOF-808 arises as an attractive option since compared to the well-known UiO-66 material, it exhibits higher surface area and larger pore volume but maintaining the inherent thermal, chemical, and mechanical stability of the Zr-based MOFs. However, the microporous character of MOFs, including MOF-808, is a drawback for practical applications, owing to accessibility, diffusion, and mass transport limitations caused by the restricted access of molecules into the

internal porous structure. Motivated by the possibility of bringing MOF-808 closer to practical applications, this Dissertation work is focused on the study of the effect of the engineering of the pore structure during the synthesis of MOF-808. This aiming the obtainment of materials with pore spanning different length scales ranging from micro to macropores and through post-synthetic modification process on the textural, physicochemical, surface and acidic properties of the materials. And finally, evaluated how the fine-tuning of their structure influences their activity in a catalytic application, namely the liquid-phase esterification of glycerol with acetic acid.

Catalysis and adsorption processes are surface phenomena, which is why this Dissertation deepened the study of the surface chemistry of MOF-808. The quantification of elements was carried out; also, chemical species were proposed and quantified on the surface of the synthesized and modified materials. The proposed chemical species were correlated with their stoichiometric molar ratios, and according to our results, it can be suggested that at the surface, the materials synthesized herein differ from the bulk chemical structure reported in the literature.

Throughout this Dissertation, we performed the synthesis of multi-modal MOF-808 materials using the defect-engineering strategy. We started with materials with different pore scales, however, with drawbacks related to pore blocking and cavitation, and we continued developing MOFs with ordered and interconnected pores of different scales, forming a pore network that improves accessibility and transport of the reactant species. Thus, the achieved of ordered and interconnected microporous-mesoporous/macroporous MOFs lead us to the possibility of exploiting the features of the crystalline microporous structure and the improved mass transport assured by the non-microporous structure. Furthermore, the textural properties of materials were thoroughly studied. Due to the multi-modal porous network of

the synthesized materials, we discussed the applicability of the BET method for their surface area measurement, and we proposed and applied the χ theory and compared them.

We performed a post-synthetic modification process for the addition of acid sites to the synthesized materials and also analyzed the effect of this modification on the textural, surface, and acidic properties on the different materials synthesized in this work. The acidic properties were studied through experimental and theoretical approaches and correlated them with the catalyst performance of the reaction of interest.

This work is focused on the performance of a fundamental study in materials science of Zr-based MOFs, aiming to control Zr-MOFs properties as well as correlate the engineered defects and the formation of ordered and interconnected structures with the inclusion of active acid sites during their synthesis and after post-synthetic modifications and final catalytic activity in the selected reaction, the esterification of glycerol with acetic acid.

Accordingly, this Dissertation is organized into seven Sections. The first one, the LITERATURE SEARCH section, is devoted to establishing the antecedents and main points of theoretical and experimental research works that support the results and conclusions obtained in this work. Afterward, CHAPTER 1 is dedicated to the rigorous assessment of the intrinsic effect of the use of different metallic precursors on the final properties of a Zr-MOF. The thermal stability, structure, and surface chemistry state of the materials is understood as key properties since they play a significant role in their performance as catalysts and adsorbents.

CHAPTER 2 delves into the activation process of MOF-808 and the study of its acid sites through DFT calculations along with AIMD molecular dynamics and classical reactive molecular dynamics (with the reactive force field ReaxFF). The adsorption calculations of a probe molecule allow to elucidate the acidic nature of MOF-808 active sites and quantify

their acidic strength. CHAPTER 3 encompasses the analysis of the effect of modifying the concentration of the modulator, on key physicochemical properties of MOF-808 with the further assessment of the effect of performing a post-synthetic process for the addition of more acid sites. The focus of the work was on the analysis of the evolution of the thermal stability, crystallinity, porosity, molecular structure, and surface chemistry of the synthesized materials. Theoretical calculations were employed to get additional molecular level insight into the observed effects. CHAPTER 4 discusses the synthesis of the MOF-808 with an ordered and interconnected porous network composed by the micropores of its crystallites and the external mesopores or macropores and what are the consequences on the physicochemical properties of the synthesized MOFs after implementing strategies towards such a goal. CHAPTER 5 is devoted to studying the effect of the post synthetically sulfation of MOF-808 with ordered and interconnected pore structure on its textural and surface properties as well as the strength of acid sites. Furthermore, the materials are evaluated and compared on the liquid-phase esterification reaction of glycerol with acetic acid by analyzing their activity, selectivity, and reusability. The general conclusions are summarized in the final section of the document.

Literature Search¹

Metal-Organic Frameworks (MOFs) are porous crystalline materials. They have many potential applications in catalysis (Cirujano, Corma, & Llabrés i Xamena, 2015b; Chughtai, Ahmad, Younus, Laypkov, & Verpoort, 2015), host-guest separation (X. Zhang et al., 2015), sensors (Cao, Guo, & Wang, 2017), drug delivery (H. Zheng et al., 2016), and gas storage (DeSantis et al., 2017). The solvothermal synthesis of MOFs is performed by mixing a dilution of a metal salt and an organic ligand, which are linked through coordination bonds (Dey, Kundu, Biswal, Mallick, & Banerjee, 2014). Usually, a modulator agent which acts as a regulator of crystallization kinetics and crystal morphology is also added during the synthesis (Schaate et al., 2011).

MOFs, in contrast to inorganic materials such as zeolites and mesoporous silica, are metal-organic structures building from inorganic clusters coordinated to organic ligands to form 3D

¹ Parts of this chapter are adapted from:

Ardila-Suárez, C., Rodríguez-Pereira, J., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). An analysis of the effect of zirconium precursors of MOF-808 on its thermal stability, and structural and surface properties. *CrystEngComm*, 21(9), 1407-1415, doi: 10.1039/C8CE01722K.

Ardila-Suarez, C., Perez-Beltran, S., Ramirez-Caballero, G. E., & Balbuena, P. B. (2018). Enhanced acidity of defective MOF-808: effects of the activation process and missing linker defects. *Catalysis Science & Technology*, 8(3), 847-857. doi: 10.1039/C7CY02462B.

Ardila-Suárez, C., Díaz-Lasprilla, A. M., Díaz-Vaca, L. A., Balbuena, P. B., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). Synthesis, characterization, and post-synthetic modification of a micro/mesoporous zirconium-tricarboxylate metal-organic framework: towards the addition of acid active sites. *CrystEngComm*, 21(19), 3014-3030, doi: 10.1039/C9CE00218A.

Ardila-Suárez, C., Daniel R. Molina V, Halima Alem, Baldovino-Medrano, V.G., & Ramírez-Caballero, G. E. "Synthesis of Ordered Microporous/Macroporous MOF-808 through Modulator-Induced Defect-Formation, and Surfactant Self-Assembly Strategies." *Physical Chemistry Chemical Physics (PCCP)*, 22 (2020): 12591-12604. doi: <https://doi.org/10.1039/D0CP00287A>, **all with permission from The Royal Society of Chemistry.**

coordination frameworks. The vast amount of transition metals and the large variety of organic ligands that can be employed the MOFs synthesis lead to the formation of thousands of possible frameworks with different structures, composition and properties (J. Liang, Liang, Zou, & Zhao, 2017). Concerning heterogeneous catalysis applications, MOFs exhibit several features that commend them as potential candidates, such as (i) high surface areas that allows high density of active sites (L. Chen et al., 2016; Miner & Dincă, 2016) (ii) the possibility of the addition of catalytic active groups during synthesis or through post-synthetic processes (Yin, Wan, Yang, Kurmoo, & Zeng, 2019) (iii) the possibility of tuning their pore structure (Huang et al., 2018), among others (D. Yang & Gates, 2019).

Zirconium-based MOFs

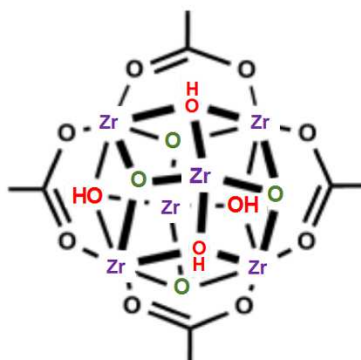
The coordination bonds from the MOFs frameworks lead, however, to their low stability due to their reversible nature. Since this is a drawback for practical applications, the efforts are devoted to the engineering of MOFs with improved stability. The metal-organic ligand bond interactions are affected by the oxidation state and charge density of the metal ions (Bai et al., 2016). The high charge density and bond polarization of Zr (IV) allow a strong affinity between them and oxygen atoms from the carboxylate ligands in the Zr-based MOFs (M. Zhang et al., 2014).

Zirconium-based MOFs exhibit diverse structures, excellent stability, and interesting textural properties, hence being promising families of MOFs for catalyst applications (Bai et al., 2016). The strength of the Zr-O coordination bonds in Zr clusters is caused by hard acid hard base interactions between Zr (IV) atoms and oxygens (Planas et al., 2014). This feature is responsible for their thermal and chemical stability (Matthew J. Cliffe et al., 2014). The

Zr_6O_8 is the most common cluster in Zr-MOFs. It is constituted by six central zirconium atoms, which form the vertices of an octahedron capped alternatively by four μ_3 -O and four μ_3 -OH species. In the cluster, each Zr (IV) atom is octa-coordinated by oxygen in a squared antiprismatic geometry. One the face of the square- antiprism is formed by oxygens from the oxo and hydroxo groups; the other consists of four oxygens provided by carboxylate groups (Figure 1) (Artner, Czakler, & Schubert, 2015; Guillerme et al., 2010). Therefore, the zirconium cluster exhibits a high connectivity and its stability makes it a promissory platform for catalysis particularly, after post-synthetic addition of active sites (Bosch, Zhang, & Zhou, 2014).

Figure 1

Schematic representation of the Zr_6O_8 core of the $Zr_6O_4(OH)_4(OOCR)_{12}$ framework (Michael J. Katz et al., 2015).



The most well-known zirconium-based MOFs are the UiO (Zr) (UiO= University of Oslo) family. The UiO – 66 MOF was firstly reported by Cavka *et al.* (Cavka et al., 2008). They coordinated the zirconium cluster with terephthalic acid (BDC) (organic ligand). The UiO-66 structure can be expanded (by an isorecticular expansion), increasing the organic ligand length without changing the synthesis conditions (solvothermal synthesis, 120 °C and 24 h

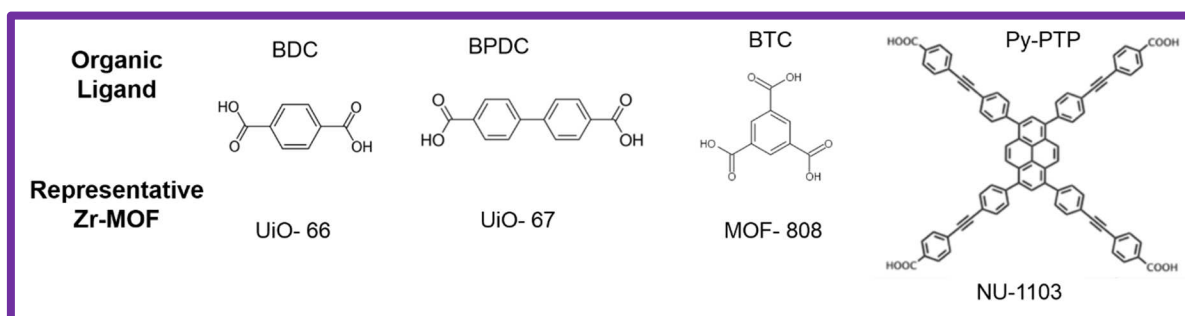
in DMF solvent) (Cavka et al., 2008). The parent UiO-67 and UiO – 68 MOFs have been synthesized with 4,4' biphenyl-dicarboxylate (BPDC) and terphenyl dicarboxylate (TPDC) as organic linkers. An increase to three benzene rings in the ligand increases the surface area from 3000 to 4170 m²/g. UiO-66 and UiO- 67 demonstrated stability at temperatures up to 540 °C. This thermal stability is more considerable than the reported for MOFs such as CuBTC, which exhibits paddle-wheel type nodes and the MIL-100, which contains a trimeric SBU that decomposed at around 300 and 400 °C, respectively (Healy et al., 2020). On the other hand, Rahmawati *et al.* (Rahmawati, Ediati, & Prasetyoko, 2014) studied the effect of temperature and reaction times on properties of the UiO-66 synthesized by the solvothermal method. The authors found that raising the temperature from 120 °C to 140 °C decreases the synthesis time from 24 to 6 h. Remarkably, materials exhibited similar crystallinity and topology as a standard UiO-66.

Wang *et al.* (T. C. Wang et al., 2015) also reported the isorecticular expansion of other Zr-MOFs, the NU (Northwestern University) family, using tetratopic ligands. The synthesized MOFs with $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(L_{1-4})_3$ structure known as NU 1101- 1104, where $L_1 = 4',4'',4''',4''''-(\text{pyrene-1,3,6,8-tetrayl})\text{tetrakis}(2',5'\text{-dimethyl-[1,1'-biphenyl]-4-carboxylic acid})$ (Py-XP), $L_2 = \text{meso-tetrakis-(4-carboxybiphenyl)porphyrin}$ (Por-PP), $L_3 = 4,4',4'',4''''-(\text{pyrene-1,3,6,8-tetrayl})\text{tetrakis}(\text{benzene-4,1-diyl})\text{tetrakis}(\text{ethyne-2,1-diyl})\text{tetrabenzoic acid}$ (Py-PTP) and $L_4 = \text{meso-tetrakis-(4-((phenyl)ethynyl)benzoic acid)porphyrin}$ (PorPTP) showed surface areas of 4422, 4712, 5646, and 5290 m²/g, respectively. Furthermore, the NU- 1103 exhibits a BET surface area of 6650 m²/g, the highest reported until now for a Zr-MOF.

Zr-based MOFs using tricarboxylate ligands are less common than dicarboxylate and tetracarboxylic organic ligands (Figure 2). Wang *et al.* (R. Wang et al., 2014) synthesized a Zr-MOF using the 5'-(4-carboxyphenyl)[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid as the ligand. The obtained MOF exhibited low gas uptake as well as low thermal stability. Although the significant amount of benzene – 1,3, 5 – tricarboxylic acid based MOFs that have been reported until relatively recently, Furukawa *et al.* (H. Furukawa et al., 2014) reported the synthesis of the zirconium tricarboxylate MOF, known as MOF-808.

Figure 2

Carboxylate ligands used in representative Zr-based MOFs synthesis (Cavka et al., 2008; H. Furukawa et al., 2014; T. C. Wang et al., 2015).



The Zirconium tricarboxylate MOF-808

Furukawa *et al.* (H. Furukawa et al., 2014) synthesized the MOF from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ using dimethylformamide (DMF) as the solvent and formic acid as a modulator at 100 °C. The authors assessed the structure of MOF-808 by XRD and N_2 and Ar physisorption. According to their results, the synthesized MOF-808 had a surface area larger than 2000 m^2/g estimated by the Brunauer-Emmet-Teller (BET) method, a pore volume of 0.84 cm^3/g , an average pore diameter of 1.8 nm, and a structure with a 6,3-connected three-dimensional

framework of **spn** topology. Considering the latter, the authors described the synthesized MOF-808 as constituted by tetrahedral cages formed by a tetrahedron with inorganic secondary building units (SBUs) at the vertices and the 1,3,5-benzene tricarboxylic acid (BTC) linkers at the faces. Liang et al. (W. Liang et al., 2014) also aimed to synthesize MOF-808 with DMF and formic acid but using ZrCl_4 as the metal precursor. In general, they found that the crystallinity of the material differed according to the synthesis conditions despite using the same metal precursor. The surface area of the material by the BET method was $1606 \text{ m}^2/\text{g}$.

The structure mentioned above of MOF-808 leads this material to be a highly active catalyst caused by its intrinsic lower connectivity compared to other Zr-based MOFs i.e., UiO-66, 6 and 8 organic ligands per Zr_6 , respectively. The zirconium nodes of MOF-808 are then more exposed, bearing additional $-\text{OH}/-\text{H}_2\text{O}$ groups (Dissegna, Epp, Heinz, Kieslich, & Fischer, 2018). Its pore structure and low-connected structure are likely responsible for the remarkable performance of MOF-808 in applications such as biosensing (H.-Q. Zheng et al., 2018), selective uptake of phenolic compounds (Jia et al., 2019), and indeed, catalysis (P. Liu et al., 2019; Ly et al., 2018; Mautschke, Drache, Senkovska, Kaskel, & Llabrés i Xamena, 2018).

Defect Engineering in Zr-based MOFs

Defect engineering in MOFs is related to the controlled adjustment of their porous structure through the intentional addition of defects that allow the tuning of the physical and chemical properties of synthesized materials (Fang, Bueken, De Vos, & Fischer, 2015). Accordingly, there are two proposed types of defects: missing cluster defects and missing linker defects. Related to the missing cluster defects, Goodwin and co-workers (Matthew J

Cliffe et al., 2014) demonstrated that the use of formic acid as a modulator in the UiO-66 MOF leads to a material in which these missing clusters are formed in nanoregions of the *reo* topology in which the clusters exhibit reduced linker connectivity compared to the parent UiO-66.

The missing linker defects inclusion, on the other hand, occurred when monocarboxylic acids (known as modulators) replaces the organic linker molecules and compensate them, allowing the zirconium cluster to retain their well-known arrangement. The thermal activation of the synthesized materials will lead to the dehydroxylation of the zirconium cluster but to the removal of the free and coordinated modulators (Vandichel et al., 2015a; Frederik Vermoortele et al., 2013). It is important to highlight that during mild conditions in which thermal activation occurs, the metal oxo clusters of MOFs could undergo local structural transitions. These transitions do not perturb the long-range lattice symmetry leading to modifications in the electronic state of the MOFs that could be relevant in their final applications and must be thoroughly studied (Platero-Prats et al., 2016).

Schaate *et al.* (Schaate et al., 2011) on the other hand, studied the inclusion of missing linker defects through the addition of benzoic and acetic acids as modulators for zirconium-based MOFs. The authors found that these acids might control the nucleation rate of the materials. Furthermore, with varying the relative concentration of the modulators, it was possible to adjust the crystallite and particle sizes of UiO-66. Wu *et al.* (Wu et al., 2013) found that with the addition of acetic acid as the modulator for UiO-66, ligand vacancies and mesopores could be obtained. There was an increase of 150% and 60% in both pore volume and surface area, respectively. Recently, Shearer *et al.* (Shearer et al., 2016) studied the defect chemistry of UiO-66 MOF using monocarboxylic acid as modulators (formic, acetic,

difluoroacetic and trifluoroacetic acids). The authors found that the porosity of the MOFs systematically increases as the acidity of the modulator increases. Also, they concluded that the monocarboxylate terminated defects increases as the acidity of the modulator increases. Liang *et al.* (W. Liang et al., 2014) found that zirconium-tricarboxylate MOFs synthesized from $ZrCl_4$ exhibited tunable porosity as a function of the chain length of the monodentate ligand used as the modulator (formic, acetic and propionic acid). According to that, there is an increase in surface area and pore volume of final MOF with the decrease in chain length of the modulator used during its synthesis.

Defect Engineering allows the control of the defect structure, which leads to heterogeneity within the MOFs, and hence it permits tailoring the material properties. Accordingly, it is possible to design complex MOF structures from stable Zr-MOFs for target applications such as catalysis (Fang, Bueken, De Vos, & Fischer, 2015; H. Furukawa, Muller, & Yaghi, 2015).

Sholl *et al.* (Sholl & Lively, 2015) pointed out that efforts must be made to understand defects in MOFs structures, to control their catalytic properties. The design and understanding of the nature and concentration of defects in metal-organic frameworks is still a challenge. In the case of defects in zirconium-based MOFs and their relationship with their acidic properties is an attractive field that needs to be more developed.

Gutov *et al.* (Gutov, Hevia, Escudero-Adán, & Shafir, 2015) studied the formation of the missing linker defects in the UiO-67 MOF. Authors were able to find particle sizes varying from 20 to 50 nm. They obtained spherical nanoparticles (formic or acetic acid used as modulators) or single crystals using benzoic acid modulation. The MOF with the highest surface area was obtained using formic acid as the modulator (2600 m²/g). Katz *et al.* (Michael J Katz et al., 2013) presented a reproducible and scalable method for UiO-66 MOF

synthesis. The method uses HCl as the modulator. HCl induced the dissociation of linkers from metal nodes, hence creating defects within the material's framework.

Hu *et al.* (Z. Hu et al., 2016) studied the effect of the modulator (formic, acetic or trifluoroacetic acid) on crystallinity, morphology, porosity, defects, stability, and gas separation performance of Zr/Hf MOFs. They found mathematical models that established the molar ratio (modulator to ligand) as a function of its acidity to correlate it with their performance. Authors determined that for the same modulator, either acetic or formic acid, it is needed more amount of modulator with decreasing ligand acidity. Likewise, for the same ligand, it is required to use larger quantities of the modulator with lower acidity to assist the crystallization processes avoiding the fast precipitation of amorphous materials.

Canivet *et al.* (Canivet, Vandichel, & Farrusseng, 2016) affirmed that the intentional addition of defects (to catalytic sites inclusion) by the removal of organic ligands from the ideal structure allows the creation of defects and generates surface for Lewis or Brønsted sites. According to Vandichel *et al.* (Vandichel et al., 2015b), an ideal UiO-66 metallic node is completely coordinated with the organic linkers, and thus zirconium atoms are inaccessible for catalytic activity. However, with the inclusion of defects through the use of modulators, it is possible to create unsaturated metallic sites with Lewis acidity. Vermoortele *et al.* (F. Vermoortele et al., 2013) used trifluoroacetic (TFA) and hydrochloric acids as modulators for UiO-66 synthesis simultaneously. The resulting material was highly crystalline and with partial substitution of ligands by trifluoroacetate. As a consequence, the more significant number of open sites led to an increment in the catalytic activity of the materials for Lewis acid-catalyzed reactions. Cirujano *et al.* (Cirujano, Corma, & Llabrés i Xamena, 2015a) reported a correlation between the concentration of missing linker defects and the catalytic

activity of UiO-66 (Zr) MOF in the esterification of levulinic acid with different alcohols; the creation of defects led to the formation of open zirconium sites with Lewis acidity.

Unlike the largely studied MOFs Lewis sites, only recent studies reported the inclusion of Bronsted acid sites, which has been only achievable on highly chemically stable MOFs like zirconium-based frameworks. (Juncong Jiang & Omar M. Yaghi, 2015). For this type of materials, the authors concluded that the addition of linker defects allows the introduction of additional Bronsted sites stronger than the weak $\mu_3 - OH$ sites, which are already present in the defect free structure. Liu *et al.* (Y. Liu, Klet, Hupp, & Farha, 2016) studied the effect of zirconium-based MOFs defects on their activity during epoxide ring-opening reaction with an alcohol, finding out a direct relationship between the catalytic performance and the defective structure. For all tested materials, MOF-808 reported significant-high catalytic activity, which is consistent with its inherent defect structure. To our knowledge, the MOF-808 has reported the best catalytic activity between all tested zirconium MOFs, which is consistent with its inherent defect structure (Y. Liu et al., 2016). In this regard, we believe a comprehensive understanding through molecular modeling of the activation process is needed to describe the resulting defective structure, which would allow elucidating the correlation between the missing linker defects and the MOF catalytic activity.

Vandichel *et al.* (Vandichel et al., 2015a) studied the synthesis and activation treatment of UiO-66 MOF through periodic DFT-D calculations. They reported a competing dynamics between the thermal TFA removal and a dehydroxylation process. In a subsequent work (Vandichel et al., 2016), several techniques like periodic density functional theory (DFT), ab initio molecular dynamics (AIMD) method, and the nudged elastic band method, were used for studying the correlation between the number of missing linker defects and the final

defective structures of UiO-66, and the mechanistic pathways for the dehydration of zirconium nodes. It was reported the organic linker defects produce distortions of the zirconium oxo cluster and the rearrangement of the Zr-O coordination. In another work, Ling and Slater performed AIMD calculations to investigate the proton mobility in UiO-66 zirconium-based MOF (Ling & Slater, 2016). They concluded that there is a relation between the dynamic behavior of defective structures and the rapid proton transfer involving hydroxide ions and physisorbed water molecules, which could be the reason for the defect sites to show enhanced acidity. The authors also pointed out, however, that further work is needed to determine the effect of missing linker defects on zirconium-based MOFs, including their reactivity.

Ordered and Interconnected Zr-based MOFs

Interconnected MOFs with multi-modal pore size distributions emerge as interesting materials for applications such as catalysis, in which mesopores or macropores are relevant for molecular diffusion and mass transfer (Gueudré, Milina, Mitchell, & Pérez-Ramírez, 2014; Parlett, Wilson, & Lee, 2013). Additionally, large pores can also benefit the accessibility to the microporous in which active sites are attached (T.-Y. Ma et al., 2012; Y. Yang et al., 2014). Most remarkably, these materials enhance the valuable features of microporous and mesoporous/macroporous components (Guan, LeBlanc, Xie, & Yue, 2018). Different approaches to the generation of larger pores have been studied. These include post-processing (Y. Kim et al., 2015; Park, Wang, Sun, Chen, & Zhou, 2012), the employment of mixed ligands (Férey et al., 2004; Llewellyn et al., 2008), and ligand extension (Hiroyasu Furukawa, Cordova, O’Keeffe, & Yaghi, 2013; Koh, Wong-Foy, & Matzger, 2008).

However, these methods have drawbacks, such as the generation of mesopores with uncontrollable sizes, frameworks interpenetration, and instability.

As mentioned previously, the modulator-induced defect-formation strategy is a versatile strategy for the controllable synthesis of MOFs with tunable pore sizes and pore volumes. Furthermore, another approach for the synthesis of MOFs with interconnected pore structures is the employment of structure-directing agents (Seoane et al., 2015). Indeed, surfactants have been extensively used in the template-directed synthesis of mesoporous silicas (Che et al., 2003; Richer & Mercier, 2001), mesostructured metal oxides (Lyu et al., 2004), among other materials (Mirhadi, Hassanzadeh Nemati, Tavangarian, & Daliri Joupri, 2018; Ungureanu et al., 2015; H. Zhang et al., 2015). Thus, the surfactant molecules first self-assembled into micelles to then serve as templates for the formation of mesopores or macropores for the formation of the hierarchically structured materials (Duan et al., 2018; Duan et al., 2017). Among others (Jothi et al., 2016; Tian et al., 2015), the cetyltrimethylammonium bromide (CTAB) is a cationic surfactant widely used as a soft template in, e.g., the well-known ZSM-5 zeolite (Y. Zhang et al., 2014; Y. Zhu et al., 2011).

In the case of MOFs, Seoane et al. (Seoane et al., 2015), studied the effect of CTAB addition in Al trimesates. The final materials are disordered mesoporous materials with tunable mesopore size distributions from 3 to 33 nm. On the other hand, Hu et al. (S. Hu et al., 2017), synthesized H-CuBTC, and H-ZIF-8 materials. The porosity of final materials was controlled by varying the molar concentration of the template. The authors also found that the increase in the porosity improved the adsorption capacity of RhB and enhanced the diffusion of pollutants during their photodegradation.

Furthermore, Yan et al. (Yan, Hu, & Komarneni, 2014), synthesized mesoporous CuBTC MOF/silica composites with the help of the CTAB surfactant. The surface area of the composites significantly decreased compared to the blank MOF. However, they obtained materials with narrow mesopores with an average size of ca. 7.5 nm.

Related to the surfactant-templated synthesis of Zr-MOFs, Li et al. (K. Li, Lin, Li, Zhuang, & Gu, 2018) studied the incorporation of amphoteric surfactants, i.e., CAPB or OAPB on the mesoUiO-66-NH₂ synthesis. They found that the dimensions of mesopores are tailored by changing the alkyl chain length of the employed surfactant. Furthermore, Zhang et al. (Zhang et al., 2019) employed the non-ionic block copolymer P123 as a templating surfactant for the synthesis of UiO-66 MOF. The authors found that the microporous/mesoporous material exhibited two mesopore size distributions with average sizes of ca. 4 and 20 nm, respectively. They suggest that the first PSD could be related to missing-linker defects and the latter one due to the incorporation and self-assembly of P123.

Use of Zirconium-based MOFs as Heterogeneous Acid Catalysts

Zirconium based MOFs have been used as catalysts for Lewis catalyzed reactions such as the CO₂ cycloaddition of styrene oxide (J. Kim, Kim, Jang, Seo, & Ahn, 2013), the cyclization of citronellal to isopulegol, the Meerwein- Ponndorf- Verley (MPV) reduction (F. Vermoortele et al., 2013) and the acetalization of benzaldehydes (Arrozi, Wijaya, Patah, & Permana, 2015). On the other hand, referred to Brønsted catalyzed reactions, they are just beginning to be explored, taking advantage of the chemical stability of these MOFs.

Piscopo *et al.* (Piscopo, Polyzoidis, Schwarzer, & Loebbecke, 2015) studied the stability of MOF UiO-66 in different aqueous acid solutions, intending to analyze possible future post-

synthetic modifications through the addition of Brønsted sites. Authors showed that viable to use of UiO-66 under strongly acidic conditions, but its use limited to electrophilic non-cationic species. Furthermore, Klet *et al.* (Klet, Liu, Wang, Hupp, & Farha, 2016a) found that the potentiometric acid-base titration is a useful technique for the determination of Brønsted active sites in Zr-MOFs and the quantification of defect sites resulting from a deficit of organic ligands.

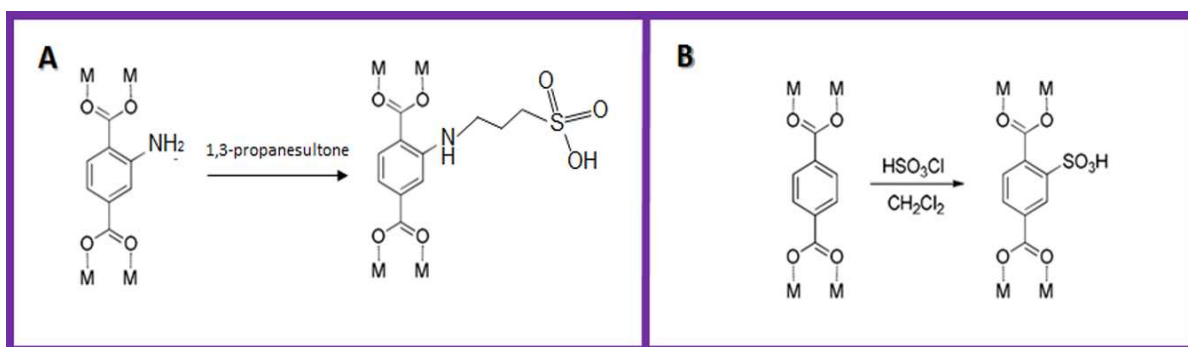
Brønsted acid functional groups also have been covalently bonded to the organic linkers in zirconium-based MOFs. Luan *et al.* (Luan, Zheng, Qi, Yu, & Wang, 2014) developed a UiO-66- NH₂- derived active Brønsted acid catalyst through the post-synthetic addition of 1,3- propane sultone (See Figure 3A). The catalytic activity, high reactivity and selectivity of final MOF were evaluated in the acetalization reaction of benzaldehyde. The catalyst zirconium-based MOF did not suffer from leaching and can be recycled over six times without activity or selectivity loss. However, despite the significant results of this work, it is important to note out that 1,3-propane sultone is a highly toxic reagent.

Besides MIL series MOFs, Chen *et al.* (J. Chen et al., 2014a) added sulfonic acid functionalities to the UiO-66 (Zr) through post-synthetic modifications using chlorosulfonic acid (See Figure 3B). In the evaluation as the catalyst in the transformation of fructose to hydroxymethylfurfural (HMF), the UiO-66 (Zr) – SO₃H leads to a fructose conversion > 99%, the same as MIL-101 (Cr) - SO₃H and MIL-53 (Al) - SO₃H MOFs. Nevertheless, the selectivity to HMF using UiO-66 (Zr) – SO₃H is 86 %. This result is in the middle of the MIL series catalysts. Thus, MIL-101 (Cr) - SO₃H allows a fructose selectivity of 91 %, whereas MIL-53 (Al) - SO₃H lets a fructose conversion of 80%. Piscopo *et al.* (Piscopo et al., 2015) also performed the post-synthetic treatment of UiO – 66 (Zr) using chlorosulfonic

acid. However, in this case, the authors found that the zirconium-based MOF collapsed after the sulfonation process.

Figure 3

Brønsted acid functional groups bonded to the organic linkers in zirconium-based MOFs.
 (A) Through post-synthetic addition of 1,3- propane sultone in UiO-66- NH₂ (Luan *et al.*, 2014) and (B) Through post-synthetic modifications using chlorosulfonic acid in UiO-66 (J. Chen *et al.*, 2014).

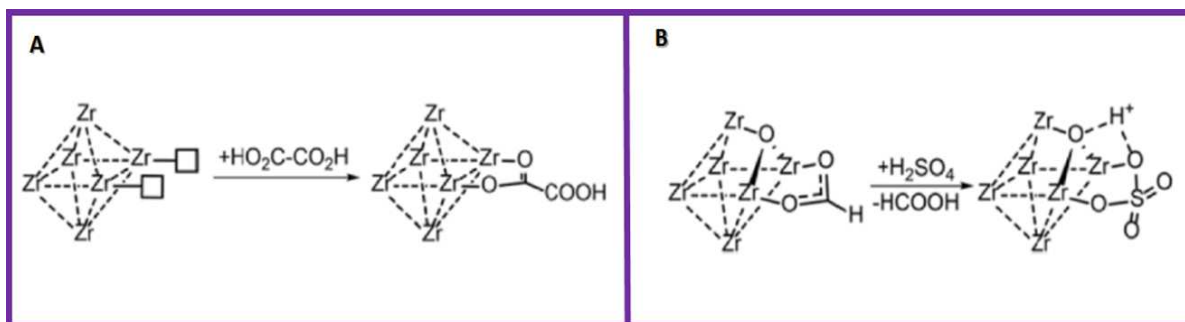


Brønsted active sites have also been grafted to the metal node in zirconium-based MOFs. DeCoste *et al.* (DeCoste, Demasky, Katz, Farha, & Hupp, 2015) synthesized UiO-66 MOF with a defect caused by the use of HCl as the modulator. These defects were further modified with oxalic acid. The authors found that one carboxylate group from the oxalic acid is bounded to the SBUs on vacant sites. As a consequence, the other free carboxylic acid of oxalic acid created Brønsted acid sites within the MOF (See, Figure 4A). Jiang *et al.* (J. Jiang *et al.*, 2014) reported the synthesis of sulfated tricarboxylate zirconium-MOFs with super acidity (Figure 4B). Post-synthetic modifications with sulfuric acid were done via solvent exchange and subsequent activation. The authors highlighted that it is not possible to obtain crystalline materials if activation is performed without a prior solvent exchange process. The acidity of resulting the MOF was evaluated through the citronellal cyclization to isopulegol and through the alpha-pinene isomerization to camphene. The observed selectivity in these

reactions suggested the presence of strong acid sites ligated to the metallic node in the prepared zirconium-based MOFs.

Figure 4

The ligated Brønsted Acid Groups in zirconium-based MOFs. (A) An oxalic acid group bound to missing linker defects (DeCoste et al., 2015) and (B) Sulfation of zirconium node (Juncong Jiang et al., 2014).



Experimental and Theoretical Approaches to characterize acid sites in MOFs

The study of the chemical activity of the active acid sites for understanding their performance as catalysts can be conducted through experimental and theoretical approaches by determining their characteristic infrared bands and using selected adsorbates binding as a function of the acid sites strength.

Lewis and Brønsted acidity can be observed by infrared spectroscopy studies of adsorbed strong bases such as pyridine. However, this probe molecule is not recommended for MOF-based acids since their characteristic IR absorption bands overlap with the IR absorption bands of the carboxylate groups and other functional groups of MOFs structures. Carbon monoxide is a small molecule with almost no steric hindrance that is a soft, weak Lewis base, useful to probe either Lewis and Brønsted acid sites (J. Jiang & O. M. Yaghi, 2015). If the later is presented, there are H-bonded CO molecules. The strength of the acid sites is related

to both $\nu(OH)$ and $\nu(CO)$ shifts. Volkringer *et al.* (Volkringer et al., 2012) investigated the acid sites in the MIL100 (Al) MOF through the IR spectroscopy, using adsorbed CO and acetonitrile as spectroscopic probe molecules. The authors found an agreement between observed results obtained from CO adsorption and ^{27}Al NMR experiments, which validates the quantitative experimental results obtained by IR spectroscopy. Furthermore, the acidity of solids has also been studied through the adsorption of ammonia molecules, which react with the Brønsted sites to form surface ammonium ions (Z. Wang et al., 2016).

Liu *et al.* (D. Liu & Zhong, 2010) used DFT for studying the adsorption behavior of CO on Lewis acid sites of Cu-based MOFs. The interaction between the probe molecule and the MOF cluster studied by calculating the adsorption energy of CO and also by vibrational frequency of adsorbed CO. Authors remarked that CO is a good option for the measurement of the acid sites due to its sensibility to the electronic properties of the active sites. Concerning the study of Brønsted active sites, the analysis of the O-H stretching frequency is used for quantifying the acidity strength of surface groups in MOFs (J. Jiang & O. M. Yaghi, 2015). It is possible to complement the experimental O-H stretching IR bands measurements with computationally calculated frequencies of the Brønsted active surface groups, an advantageous methodology for Brønsted site study in zeolites (Hernandez-Tamargo, Roldan, & de Leeuw, 2016). The well-implemented Bader charge analysis for the atoms charge through the electronic distribution density for determining the acid character of a specific surface group can also be implied for MOFs theoretical studies (Tang, Sanville, & Henkelman, 2009).

MOF 808 as Heterogeneous Catalyst

Since first reported in 2014 (Hiroyasu Furukawa et al., 2014), MOF-808 has been proved as an efficient acid catalyst due to its coordinatively unsaturated units and Brønsted acid sites along with its large apertures compared to other Zr-based MOFs (Klet, Liu, Wang, Hupp, & Farha, 2016b; Rojas-Buzo, García-García, & Corma, 2019). Considering the remarkable linker defective structure of MOF -808, Plessers et al. (Plessers, Fu, Tan, De Vos, & Roeffaers, 2016) synthesized a defective MOF-808 by synthesizing it with an excess of Zr precursor compared to the trimesic acid ligand leading to the modulator deficiency and the increase of unsaturated Zr sites. The resulting material was highly active in the Meerwein–Ponndorf–Verley reduction of trans-cinnamaldehyde with a conversion > 99% and selectivity to trans-cinnamyl alcohol > 99%. Also, the resulting material activity increased 20-fold compared to the results obtained using the UiO-66 catalyst after 2 h reaction at 120 °C. Moreover, Mautschke et al. (Mautschke et al., 2018) synthesized the MOF-808 by mixing the trimesic acid with small amounts of dicarboxylate ligands such as isophthalate (IP), and pyridine-3,5-dicarboxylate (Pydc) among others, in order to further increase the acid sites available in MOF-808. The authors found that the yield of cyclohexanol obtained from the Meerwein-Ponndorf-Verley reduction of cyclohexanone was 12 %, 69%, 91%, and 93 % using UiO-66, pristine MOF-808, MOF-808-IP, and MOF-Pydc, respectively. They attributed the increase in MOF activity in the higher concentration of coordinatively unsaturated Zr sites in the defective materials.

Regarding Brønsted acidity of MOF-808, Klet et al. (Klet et al., 2016b) performed potentiometric acid-base titration for the determination of the Brønsted acidities of the protons embedded in the zirconium clusters. The authors found three types of protons on

MOF-808 viz. μ_3 -OH, M-OH₂, and M-OH that are common for Zr-based MOFs. They also found a fourth type of proton. However, they did not find an assignation to it, which suggests a more complex topology of MOF-808 compared to other MOFs.

The catalytic activity of Brønsted acid sites of MOF-808 has been studied in different reactions. Zheng et al. (H.-Q. Zheng et al., 2018) studied the MOF-808 on the oxidation of the 3,3',5,5' – tetramethylbenzidine using H₂O₂ as oxidant. They found that the material exhibits catalytic activity over a pH range from 3-10, and also, it is possible to employ it as a biosensor for H₂O₂, ascorbic acid, and glucose. In another example, Moon et al. (Moon, Liu, Hupp, & Farha, 2015) studied the catalytic activity of MOF-808 on the hydrolysis of the nerve-agent simulant dimethyl 4-nitrophenyl phosphate, DMNP. They found that the TOF of MOF-808 is higher compared to other Zr-based MOFs and postulated that this result could be related to the number of water molecules ligated to the zirconium node that face its larger pores compared to other MOFs. Moreover, the MOF-808 structure exhibited a more significant number of missing linker defects compared to Zr-Uio-66, Hf-Uio-66, Zr-NU-1000, and Hf-NU-1000 materials and as reported by Liu et al. (Y. Liu et al., 2016). The number of missing linker defects is correlated to the catalytic activity of these materials on the styrene oxide ring-opening reaction with isopropanol. The high accessible Brønsted acid sites of MOF-808, leading to a 100 % conversion and regioselectivity to the primary alcohol.

The possibility of post-synthetic processes in MOFs led to the sulfation of the zirconium cluster in MOF-808 (Juncong Jiang et al., 2014). Thus, the final material enhanced its Brønsted acidity of the terminal or bridging hydroxyl groups, and also, authors noticed the acidity increment of the proton on the sulfate group due to the polarizing effect of the Zr (IV) (Juncong Jiang & Omar M. Yaghi, 2015). Moreover, Trickett et al. (Trickett et al., 2018) studied the origin of the acidity of the sulfated MOF-808. The authors ascribed its strong

Brønsted acidity to the hydrogen bonding interaction between water and a chelating sulfate on the zirconium nodes. Thus, the MOF dehydration leads to a decrease in its acidity. Accordingly, they tested the sulfated MOF-808 as a catalyst in the dimerization of isobutene to produce isooctene. In this process, undesired higher order alkene oligomers greater than C₈ can also be formed. The reaction was performed from room temperature up to 200 °C and MOF-808 was compared to commercial catalysts such as sulfated zirconia, Amberlyst, and H-ZSM-5. The sulfated MOF-808 was found to have a higher conversion (21.5%) at 160 °C, which surpassed the activity of the other mentioned catalysts that achieved conversions lower than 15 %. Further, the C₈ selectivity at 160 °C of sulfated MOF-808 was 92.8 %, very similar to the sulfated zirconia. On the other hand, the Amberlyst and H-ZSM-5 catalysts showed a C₈ selectivity under the 35 %. However, the sulfated MOF-808 loses its activity as the temperature rises, and the desorption of water molecules from the zirconium cluster occurs.

The sulfated MOF-808 was also tested in other reactions. Vo et al. (Vo et al., 2018) studied the performance of this material as the heterogeneous catalyst on the cyclocondensation reaction between 2-aminobenzamide and methyl acetoacetate to form 2-methylquinazolin-4(3H)-one at 100 °C for 6 h and using glycerol as a green solvent. The reaction reached 93 % and 37 % yield using sulfated MOF-808 and pristine MOF-808, respectively. Furthermore, sulfated zirconia and Amberlyst- 15 were less active, c.a. 20 % and 40 %, respectively, toward the reaction of interest. Also, Jiang et al. (Juncong Jiang et al., 2014) found that sulfated MOF-808 was catalytic active in the Friedel-Crafts acylation of anisole with 2-chlorobenzoyl chloride (100 % conversion, 110 °C for 12 h), esterification of oleic acid with methanol (80 % conversion, 65 °C for 6 h) and the limonene isomerization (100 % conversion, 60 °C for 1 h), all of them Brønsted catalyzed reactions.

Liu et al. (H. Liu et al., 2019) studied the synthesis of MOF-808 through defect engineering approach using the isophthalic acid as the defective ligand during the synthesis and the subsequent modification with sulfuric acid. The authors found that as the defects in the material increase, also its H^+ concentration rises. They tested the sulfated catalyst in the addition reaction of isobutylene with ethylene glycol to form ethylene glycol mono-tert-butyl ether (EGME, 2-1). It was found that high conversions of ethylene glycol were associated with large pore sizes, whereas high selectivity is achieved if small pore sizes are presented in the sulfated MOF-808. On the other hand, Liu et al. (P. Liu et al., 2019) reported the isomerization and oligomerization reactions of light olefins (C3-C6) under ambient pressure flow conditions. They found that different products were obtained for different olefins at the same reaction conditions. Isobutene, 2-methyl-1-butene, and 2-methoxypropene gave dimers, isomers, and heavier oligomers, respectively; thus, despite the similarity of their molecular structures. The results suggested that Brønsted acid sites in the sulfated MOF-808 exhibit oligomerization selectivity towards α -olefins with a double substitution at the second carbon atom.

Glycerol Esterification with Acetic Acid

The commercial biodiesel production has grown exponentially, leading to a massive buildup of glycerol, a co-product of biodiesel production. Hence, given the need to add value to glycerol, its esterification with acetic acid emerges as a viable option for the industry. The reaction products are mono, di, and tri acetylated esters, MA, DA, and TA, respectively. From these, DA and TA are the interest products since they serve as raw materials for biodegradable polyesters and cosmetic production (Venkatesha, Bhat, & Prakash, 2016). It is also worth mentioning that the acid-catalyzed glycerol esterification can be performed

using catalysts with Lewis or Brønsted acid sites (Kong et al., 2016). Patel et al. (Patel & Singh, 2014) synthesized two series of catalysts consisting of 12-tungstophosphoric, TPA_3 , anchored to MCM-41, and zirconia supports. Authors found that at 100 ° C for 6 h and a glycerol/acetic acid molar ratio of 1:6, the $\text{TPA}_3/\text{MCM-41}$ and $\text{TPA}_3/\text{ZrO}_2$ exhibited conversions of 87 % and 80 %, respectively. The $\text{TPA}_3/\text{MCM-41}$ catalyst also showed higher selectivity towards DA and TA of 60 % and 15 %, respectively, compared to $\text{TPA}_3/\text{ZrO}_2$, in which selectivities towards Da and TA were 36 % and 4 %, respectively. Probably, as glycerol is a highly functional molecule, it can quickly diffuse through the hexagonal channels of the $\text{TPA}_3/\text{MCM-41}$ catalyst compared to the $\text{TPA}_3/\text{ZrO}_2$ catalyst.

Furthermore, the results can be related to the acidity of the supports, being the MCM-41 more acidic than ZrO_2 . Also, Venkatesha et al. (Venkatesha et al., 2016) studied the effect of pore volume on clays with comparable acidity. For that, they treated the montmorillonite clay with organic sulfonic acids towards the modification of pore characteristics due to dealumination. They found that an increased pore volume around the acid sites enables the multiple acetylations of glycerol, favoring the triacetin formation.

The exposed literature reviewed highlighted gives a brief statement of the main points of theoretical and experimental research works that support the results obtained in this Dissertation work.

1. An Analysis of the Effect of the Zirconium Precursor of MOF-808 on its Thermal Stability, Structural and Surface Properties²

1.1 Overview

Due to their thermal and chemical stability zirconium based Metal-Organic Frameworks (Zr-MOFs) have been extensively studied in the literature. However, many details of the influence of preparation conditions are still unclear. Most papers tend to use one type of metallic precursors for synthesizing Zr-MOFs such as MOF-808. Therefore, as far as we know, a systematic analysis of the effect of the zirconium precursor on the properties of MOF-808 has not been conducted. In this work, three different metallic precursors were employed; namely, zirconium chloride, zirconyl chloride, and zirconyl nitrate for synthesizing MOF-808 keeping all other synthesis conditions constant. The results of the study indicated the following: (i) the nature of the zirconium precursor impacts the crystalline and porous structure of MOF-808. Particularly, the presence of structural water in the precursors seems to cause a detriment in these properties which was reflected in an increase of the relative percentage of amorphicity of the materials as well as on the formation of

² Adapted from: Ardila-Suárez, C., Rodríguez-Pereira, J., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). An analysis of the effect of zirconium precursors of MOF-808 on its thermal stability, and structural and surface properties. *CrystEngComm*, 21(9), 1407-1415, doi: 10.1039/C8CE01722K, **with permission from The Royal Society of Chemistry.**

disorganized mesopores. (ii) In contrast to (i), the surface properties of the materials and their thermal stability under an air atmosphere were not altered by the use of the different precursors. All materials exhibited a surface populated by free and uncoordinated carboxylates as well as inorganic zirconium structures corresponding to uncoordinated oxo-clusters. The ensemble of these findings contributes to a better understanding of the features that make MOFs interesting for diverse applications. Particularly, works on defect engineering may be benefited from the insight on surface chemistry provided in this contribution.

1.2. Experimental Section

Materials

MOFs were synthesized with the following reagents. Metallic precursors: zirconium chloride, ZrCl_4 (98%), zirconyl chloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99%), and zirconyl nitrate, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.9%), were obtained from Sigma-Aldrich, Merck, and Alfa Aesar, respectively. The organic linker; Benzene-1,3,5-tricarboxylic acid (H_3BTC , 95%), was obtained from Aldrich Chemistry. The solvent; N,N-dimethylformamide (99.8%), the modulator; acetic acid (99.8%), and the washing solvents; acetone (99.8%) and methanol (99.9%), were all purchased from Merck. Reactants were used as received.

Synthesis the of materials

Zirconium MOFs were synthesized using a solvothermal method based on a modification of the synthesis reported by Liang et al. (W. Liang et al., 2014). Typically, 0.5 mmol of the corresponding zirconium salt were put in a 25 ml screw-capped glass jar reactor. Then, 2.8 mL of acetic acid and 4 ml of DMF were introduced in the reactor, and the obtained solution was put under stirring. After 15 min, 0.168 mmol of H_3BTC were dissolved in 6 ml of DMF

and added dropwise to the solution containing the dissolved zirconium precursor. The mixture was stirred for additional 10 min and later sonicated for 20 min. Subsequently, the mixture was sealed and heated at 120 °C for 24 h. After cooling down to room temperature, the as-synthesized MOFs were recovered by filtration and washed twice with DMF, twice with methanol and twice with acetone. The resulting powder was dried at 80 °C for 2 h. An activation procedure was performed overnight at 110 °C under a vacuum pressure of 0.06 mbar. For the sake of brevity, the materials synthesized from ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ were named as ZrBTC1, ZrBTC2, and ZrBTC3, respectively.

Assessment of physicochemical properties of ZrBTC MOFs

The assessment of the synthesized materials was: The morphology, elemental composition, crystallinity, porous structure, thermal stability, and surface chemistry state. Thermal profiles of the synthesized materials were measured by TGA. Tests were performed on a TA2050 instrument. Samples were heated to 900 °C at a rate of 5 °C/min under an air (Linde, 4.7, 99.997% purity) flow of 30 mL/min. SEM images were taken on a Quanta FEG 650 equipment. The acceleration voltage was set to 2.5 kV. Samples were prepared by spreading them on a carbon tape. Elemental analysis via EDX was performed with an accelerating voltage set to 7 KV so that both zirconium ($L\alpha = 2.042$) and chlorine ($K\alpha = 2.621$ KeV) could be reliably quantified. The crystalline structure of the materials was assessed by XRD. XRD patterns were recorded using a Bruker AXS D8 Advance DaVinci geometry instrument equipped with monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418\text{\AA}$) operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ value range from 3.0 to 50.0° (with a step time of 0.6 s). The unit cell parameters were obtained from the Le Bail fitting, and the calculation of the relative crystallinity of the synthesized materials are displayed in

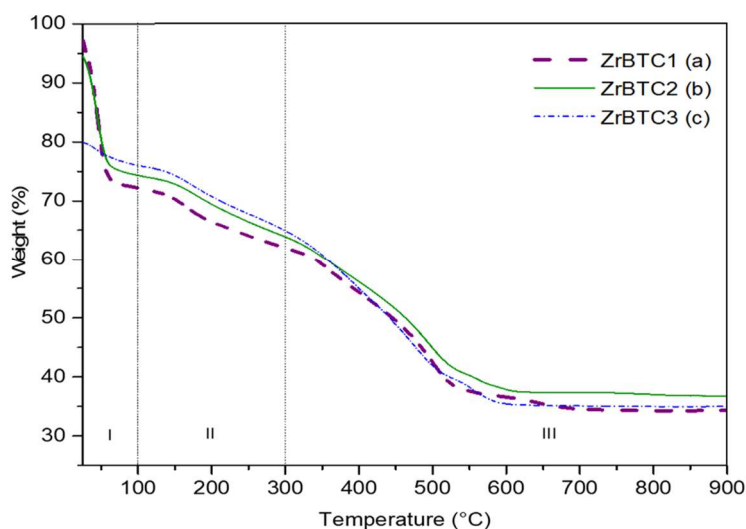
Section A-1.1. of the Supplementary Information. Textural properties of synthesized materials were evaluated after recording Ar adsorption-desorption isotherms at 87 K using a 3Flex (Micromeritics) apparatus. The relative pressure range went from 1.82×10^{-5} to 0.998 with equilibrium intervals of 10 s. Isotherms for the materials were recorded twice in independent experiments. Before measurements, the materials were degassed at a temperature of 110 °C under vacuum for 12 h. Surface area calculations were performed using the methods based on the χ (James B Condon, 2006) and BET theories (Brunauer, Emmett, & Teller, 1938). The latter was applied considering the consistency criteria proposed by Rouquerol et al. (Rouquerol, Llewellyn, & Rouquerol, 2007). Details on how pore size distributions were calculated are presented in Section A-1.2 of the Supplementary Information. Quantification of surface elements and chemical species was carried out by XPS. Analyses were performed on the XPS/ISS/UPS-A.Centeno surface characterization platform (SPECS). The C-(C, H) component of the C 1s peak at 284.8 eV as a calibration reference of Binding Energy (BE) scale (Rouxhet & Genet, 2011). More information related to the operation conditions of the instrument, the data analysis at CasaXPS program and the peak decomposition for the quantification of surface chemical species can be found in Section A-1.3 of the Supplementary Information.

1.3. Results and Discussion

This section discusses the effects of the use of different zirconium precursors on the properties of the materials. First, the thermal stability of the materials is discussed. Second, the crystalline structure and morphology of the Zr-MOFs is analyzed. Afterwards, the porous structure is discussed followed by an assessment of the surface chemistry.

The thermograms for the as-synthesized materials under an air atmosphere are presented in Figure 5 (also see Section A-2.1 of the Supplementary Information). In general, the thermal profiles of all three materials were similar. Taking the literature as a reference (Shearer et al., 2016; Shearer et al., 2014), three different weight loss regions can be identified. The first region, I, is within the temperature range between 25 and 100°C. The weight loss observed in region I is ascribed to the volatilization of adsorbed water. The second region, II, goes from 100 to 300 °C and is attributed to the removal of the modulator (acetic acid), the solvent (DMF), and the dehydroxylation of the zirconium cluster (Shearer et al., 2014). And, the third region, III, goes from 300°C and up to 700°C. The weight loss, in this case, is ascribed to the thermal decomposition of MOFs and further formation of zirconium oxide. According to the results presented in Figure 5, one may not affirm the existence of strong differences either on the thermal stability of the materials or on their zirconium content. Therefore, the use of different precursors did not seem to affect this property.

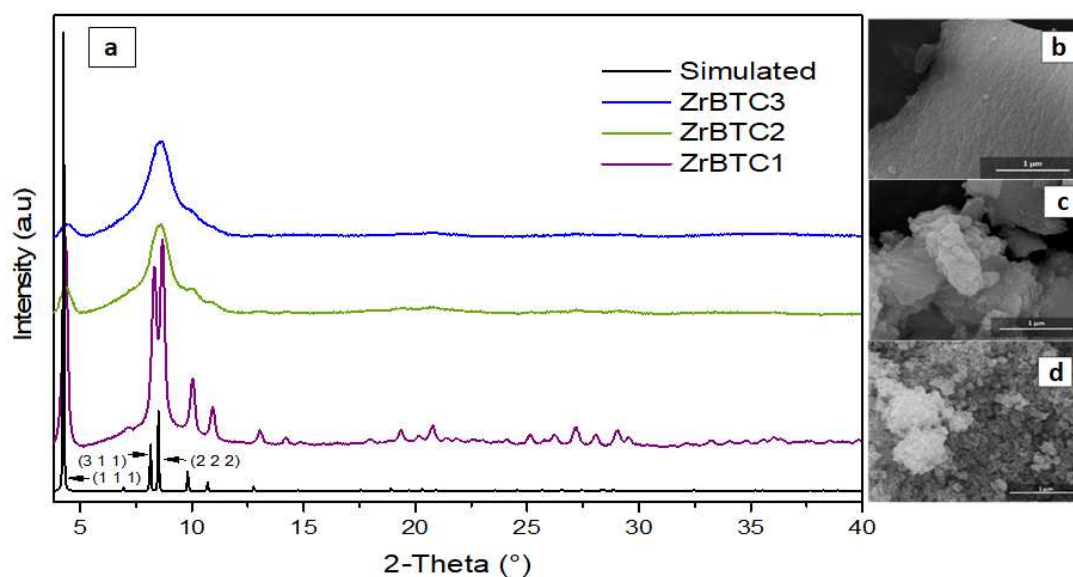
Figure 5 Thermogravimetric analysis (TGA) in air atmosphere of ZrBTC MOFs from precursors: (a) ZrCl_4 (ZrBTC1), (b) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2) and (c) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3).



The XRD patterns of the synthesized materials and their corresponding SEM images are shown in Figure 6. The XRD pattern of ZrBTC1, synthesized using ZrCl_4 as precursor, showed a full set of reflections from the crystalline phases of MOF-808 (Hiroyasu Furukawa et al., 2014). The diffraction peak at $2\theta = 4.34^\circ$ was assigned to the (111) plane of MOF-808. The peaks at $2\theta = 8.32^\circ$ and 8.69° were assigned to diffraction from the planes (311) and (222) of MOF-808, respectively (W. Liang et al., 2014). Indexation of the powder diffraction pattern of synthesized materials using DICVOL06 program at Fullprof Software and resulted Le Bail indexation powder diffraction patterns are presented in Table A-1. SEM images showed a powder composed of agglomerated fine particles, Figure 6d, which, according to XRD, have a crystallinity similar to that reported for MOF-808 (W. Liang et al., 2014). Concerning ZrBTC2, synthesized using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, the XRD pattern, Figure 6a, exhibited a very broad peak in the range from 5 to 12.5° which exhibited sharp shoulders at ca. 10.0° and 10.9° where reflections from other planes of ZrBTC1 were found. Such broadening and the lower intensity of the diffraction peaks indicate a lower crystallinity of ZrBTC2 as compared to ZrBTC1.

Figure 6

(a) XRD patterns of ZrBTC MOFs and SEM images from precursors (b) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3), (c) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2), and (d) ZrCl_4 (ZrBTC1), respectively.



SEM images for ZrBTC2, Figure 6c, showed larger ill-defined particles in this case. Finally, ZrBTC3, synthesized from $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, exhibited an XRD pattern very similar to the one found for ZrBTC2. SEM images, Figure 6b, showed larger particles than those of ZrBTC2. Further structure Le Bail treatment of XRD data are shown in Table A-2 and Figures A-2 to A-4. In general, regardless of the Zr precursor, all synthesized materials crystallized in the cubic space group $\text{Fd}\bar{3}\text{m}$. Changing the zirconium precursor modified the corresponding cell parameters and cell volumes. Particularly, smaller but similar cell parameters were obtained for materials synthesized with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ as compared to the material synthesized with ZrCl_4 , Table A-2. Accordingly, a larger cell volume was estimated for ZrBTC1 as compared to ZrBTC2 and

ZrBTC3. This agrees well with obtaining finer more crystalline particles from ZrCl_4 as evidenced by SEM (Figure 6d). Considering the differences in the XRD patterns, it was deemed important to assess the degree of amorphicity of the synthesized materials. After comparing the XRD pattern for ZrBTC1 with previous literature reports (Hiroyasu Furukawa et al., 2014; W. Liang et al., 2014) it was assumed that this material can represent a 100% crystalline MOF-808. Therefore, the XRD pattern of ZrBTC1 was taken as a reference for performing the calculation of the degree of amorphicity of ZrBTC2 and ZrBTC3. Following this procedure, the relative crystallinity of ZrBTC2 and ZrBTC2 were 73% and 62%, respectively. This tendency correlated with the cell volume since as the materials became more amorphous, the cell volume decreased. The above observations allow reaching a first conclusion which is that the Zr metallic precursor has an important effect on the crystalline structure and morphology of the Zr-MOFs. Such a trend may be explained considering the crystallization kinetics of the materials. Particularly, the effect of water during MOFs synthesis is to be considered. Ragon et al. (Ragon et al., 2014) established that water may enhance the kinetics of crystallization of Zr-based UiO-66 MOFs. According to their interpretation of results, the presence of coordination water in the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ precursor favors the formation of $\text{Zr}^{4+}\text{oxo/hydroxo}$ clusters hence boosting the crystallization rate. According to Sang et al. (Sang et al., 2017), the mechanism of a Zr-MOF formation using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as the precursor, includes a first step of solvation of the precursor that causes hydrolysis and hydration to yield the corresponding polymeric hydroxide. Similar arguments were presented by Zahn et al. (Zahn et al., 2014) who studied the effect of the content of water on the modulated synthesis of Zr-based MOFs using DMF as solvent. They found that since the precursor molecules must be hydrolyzed first for the oxo-cluster formation, the reaction proceeds faster if more water is added. Such a process is followed by a complexation

of the zirconium with the modulator and further chemical exchange between the carboxylic modulator and the BTC linker. However, a faster rate of crystallization does not necessarily mean obtaining a more crystalline material. Indeed, the rapid formation of crystallites during synthesis might result in disordered particle size growth due to phenomena such as Ostwald ripening. In the case of precursors such as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, water makes part of the structure of these salts. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is reported to possess rings of four eight-coordinated zirconium atoms connected by bridging hydroxide groups and terminal water molecules (Clearfield & Vaughan, 1956; Macdermott, 1973). Meanwhile, for $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Bénard et al. [38] found that the value of x in the formula is ca. 4.7 and that the structural formula of this salt should be given as $\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 4.7\text{H}_2\text{O}$. ZrCl_4 is instead an anhydrous precursor, and its water content could be related to the air moisture exposition due to its hygroscopic behavior (Ragon et al., 2014).

It is also worth mentioning that traces of water might also be present in the acetic acid used as modulator. Thus, it is possible that the water from of the above compounds may lead to higher rates of crystallization (Ragon et al., 2014) as well as to the formation of Zr^{4+} oxo/hydroxo clusters hindering the coordination of the organic ligand to zirconium (Low et al., 2009; Stavitski et al., 2011). On the other hand, in the case of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, it is reported that the NO_3^- anion readily forms complexes with zirconium (Nielsen & Wilfing, 2000). Such complexes may be deleterious for crystallinity (Bai et al., 2016). Conversely, Cl^- anions do not tend to form such complexes (Nielsen & Wilfing, 2000). As we mentioned before, the different water content during the MOFs synthesis could obstruct the coordination with the organic ligands and also, increase the crystallization kinetics in a disordered way, leading to almost no long-range order within the structure (Bennett & Cheetham, 2014),

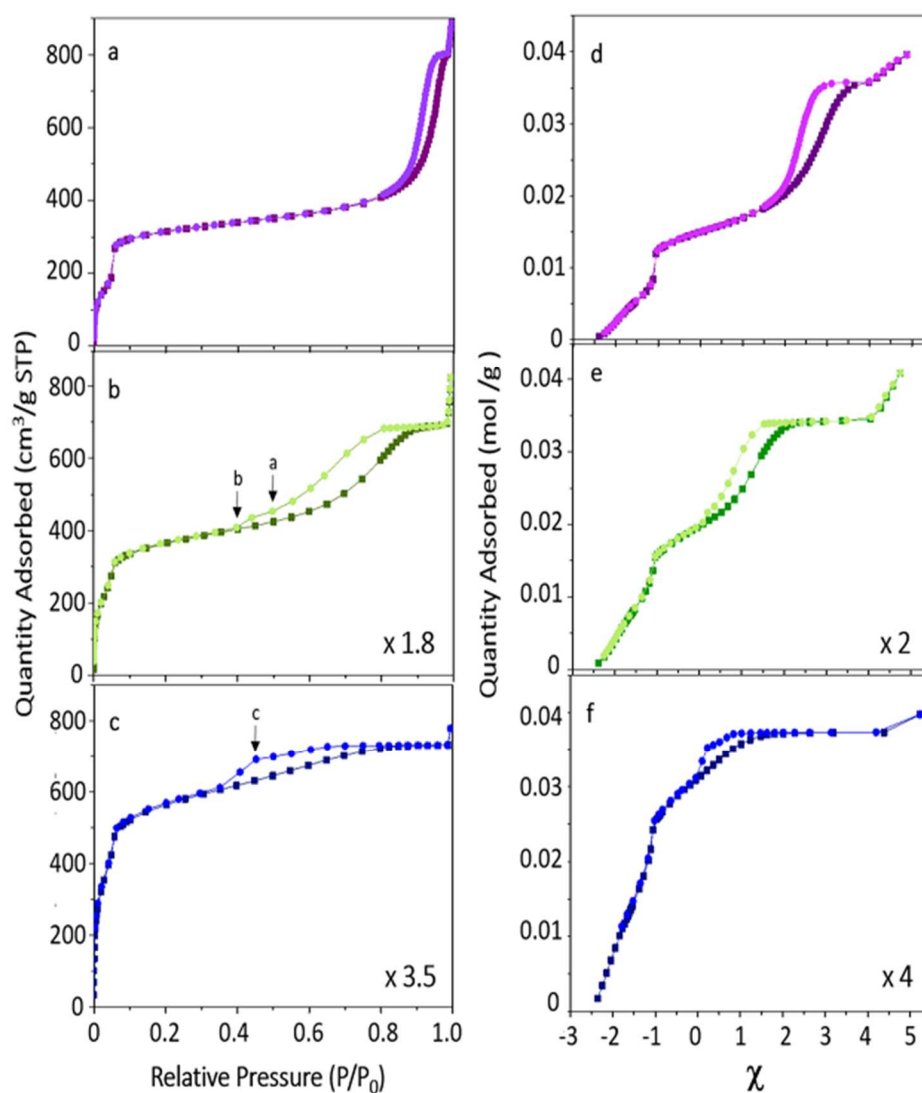
resulting in the reduction of Bragg peaks in the X-ray diffraction patterns that are observed in the ZrBTC2 and ZrBTC3 materials.

The Ar adsorption-desorption isotherms for the synthesized materials are shown in Figure 7. Figures 7a to 7c show the recorded isotherms and Figures 7d to 7f feature χ -plots of the isotherms. According to IUPAC classification (Thommes et al., 2015), the recorded isotherms are a combination of type I and type IV isotherms. Type I isotherms are related to microporous solids whereas, a Type IV isotherm corresponds to mesoporous materials. Therefore, all materials displayed both micropores and mesopores. ZrBTC1 from ZrCl₄ exhibited an isotherm with a type H1 hysteresis loop with sharp adsorption and desorption branches, Figure 7a. This is usually associated with narrow mesopore size distributions and pore connectivity (Cychosz, Guillet-Nicolas, García-Martínez, & Thommes, 2017; Thommes & Cychosz, 2014). On the other hand, the materials synthesized from the hydrated precursors, ZrBTC2 and ZrBTC3, showed type H2 hysteresis loops which are ascribed to disordered mesoporous solids with cavities interconnected by narrow necks (Thommes et al., 2015). It is interesting to notice that ZrBTC2, Figure 7b, and ZrBTC3, Figure 7c, exhibited an initial “knee-shaped” decrease of its hysteresis curvature (see arrows a and c in Figures 7b and 7c respectively) which is related to pore blocking caused by a superposition of the evaporation in blocked pores that are connected through small channels (Nguyen, Fan, Do, & Nicholson, 2013; Reichenbach, Kalies, Enke, & Klank, 2011). ZrBTC2 also exhibited the features of cavitation. Cavitation is evidenced by an abrupt decrease of the desorption branch of isotherms within a relative pressure of ca. 0.38, arrow b in Figure 7b. Cavitation inside a porous network results from delayed evaporation of the liquid probe whose vapor is forced

to pass through very narrow necks (Thommes, Smarsly, Groenewolt, Ravikovitch, & Neimark, 2006). This hints to the presence of ink-bottle pores in ZrBTC2.

Figure 7

Ar (87 K) adsorption/desorption analysis of ZrBTC MOFs from precursors: (a) ZrCl_4 (ZrBTC1) (b) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2), and (c) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3), in the all range of the linear P/P_0 . χ -method adsorption/desorption isotherms of the same materials (d) ZrBTC1, (e) ZrBTC2 and (f) ZrBTC3.



Surface areas for the synthesized materials were initially calculated using the method from the BET theory (SA_{BET}) (Brunauer et al., 1938). However, the BET method is built on assumptions not applicable to microporous solids such as MOFs (Rouquerol et al., 2007) and its results are thus very debatable (K. S. Walton & Snurr, 2007). The application of the BET-Rouquerol Consistency Criteria method and the results of its application are disclosed in the Section A-2.3.1 of the Supplementary Information. In general, the procedure was not satisfactory. It is proposed to use an alternative method, the method derived from the χ -theory (James B. Condon, 2002), for the surface area calculation. The surface area calculations must be consistent throughout this work and to compare the surface areas of the synthesized materials, avoiding discrepancies in the measurements of their surface area, since some of them could meet all the consistency criteria while others do not.

Previous reports have successfully used this method for surface area calculation where the BET has also been found to yield inconsistent results (Baldovino-Medrano, Farin, & Gaigneaux, 2012). The reader can find in the Section A-2.3.2 of the Supplementary Information details on how the χ -method calculations were performed. Table 1 summarizes the calculated surface areas, SA_{χ} , for ZrBTC1, ZrBTC2, and ZrBTC3. Notice that in the microporous range, two surface areas were calculated; namely, Surface 1 and Surface 2, which can be associated with two different families of pores. The first family corresponds to the smallest pores of the materials and further surfaces correspond to families of larger pores. Accordingly, all solids showed three different families of pores; two in the micropore range and one in the mesopore range.

The former can be associated with the changes in slope observed in the P/P_0 range near 0.1 in the corresponding isotherms, Figures 7a to 7f. Both Surface 1 and Surface 2 were

modified as a function of the zirconium precursor as follows: ZrCl_4 (Surface 1 = $875 \text{ m}^2/\text{g}$) > $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Surface 1 = $657 \text{ m}^2/\text{g}$) > $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Surface 1 = $569 \text{ m}^2/\text{g}$) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Surface 2 = $146 \text{ m}^2/\text{g}$) > ZrCl_4 (Surface 2 = $119 \text{ m}^2/\text{g}$) > $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($15 \text{ m}^2/\text{g}$). Accordingly, MOFs prepared from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ decreased ca. 25% and 35% Surface 1 as compared to the MOF prepared from ZrCl_4 . The same trend cannot be described for Surface 2 since ZrBTC2 from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ displayed a ca. 18% larger Surface 2 as compared to ZrBTC1 from ZrCl_4 . In contrast, ZrBTC3 from $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ displayed the lowest Surface 2 value which was ca. 90% lower as that found for ZrBTC2. In general, the total microporous SA_χ (Micro- SA_χ) for the materials decreased following the same order as Surface 1: ZrCl_4 (Micro- $\text{SA}_\chi = 994 \text{ m}^2/\text{g}$) > $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Micro- $\text{SA}_\chi = 803 \text{ m}^2/\text{g}$) > $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Micro- $\text{SA}_\chi = 751 \text{ m}^2/\text{g}$). Relative deviations from the Micro- SA_χ for ZrBTC1 from ZrCl_4 amounted to ca. 19 and 24% for ZrBTC2 and ZrBTC3, respectively. The trend in Micro- SA_χ coincided with the trend in Meso- SA_χ : ZrCl_4 (Meso- $\text{SA}_\chi = 325 \text{ m}^2/\text{g}$) > $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Meso- $\text{SA}_\chi = 293 \text{ m}^2/\text{g}$) > $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Meso- $\text{SA}_\chi = 182 \text{ m}^2/\text{g}$). In this case, Meso- SA_χ for MOFs prepared from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ decreased ca. 10% and 40% as compared to the MOF prepared from ZrCl_4 . In general, the total SA_χ of the materials diminished ca. 17 and 42% for MOFs from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ($\text{SA}_\chi = 1096 \text{ m}^2/\text{g}$) and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($\text{SA}_\chi = 766 \text{ m}^2/\text{g}$), respectively, as compared to the MOF from ZrCl_4 ($\text{SA}_\chi = 1319 \text{ m}^2/\text{g}$). This trend is qualitatively consistent with the one found when estimating surface area with the BET method. However, comparing both sets of surface areas, the BET method estimated total surface area values 20 to 30% lower as compared to the χ -method (see Table A-3, Section A-2.3.1 of the Supporting Information).

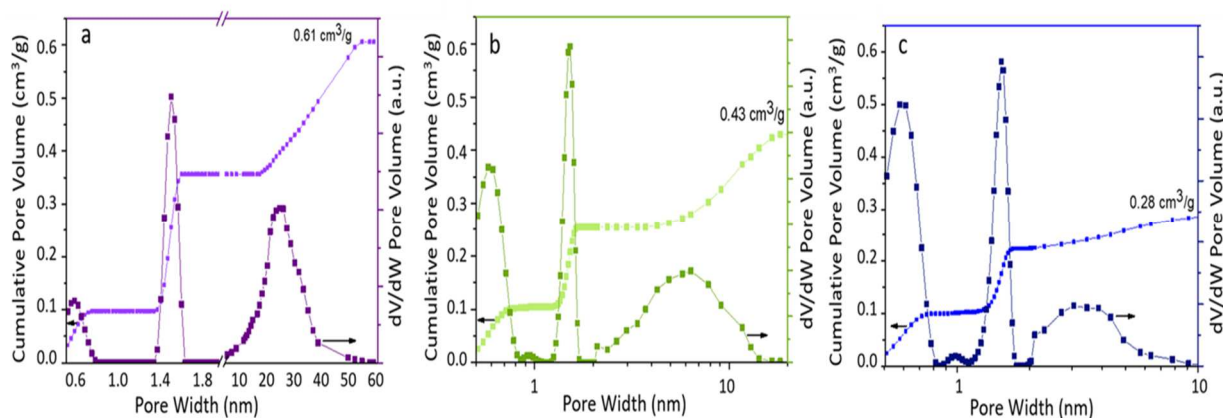
Table 1

Summary of the textural properties calculated by the χ method of the ZrBTC1, ZrBTC2, and ZrBTC3 materials, synthesized from ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ precursors, respectively.

	Microporous Range					Mesoporous Range			Total χ surface area m ² /g
	Surface 1		Surface 2		Total				
	χ surface area m ² /g	Rsq	χ surface area m ² /g	Rsq	Microporous χ surface area m ² /g	Mesoporous χ surface area m ² /g	Rsq		
ZrBTC1	875	0.9963	119	0.9729	994	325	0.9917	1319	
ZrBTC2	657	0.9975	146	0.9768	803	293	0.9802	1096	
ZrBTC3	569	0.9993	15	0.9902	584	182	0.9936	766	

Figure 8

Cumulative pore volume and pore-size distribution of ZrBTC MOFs from precursors: (a) ZrCl_4 (ZrBTC1) (b) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2), and (c) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3). The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by BJH desorption method, respectively.



The trends found for surface areas as a function of the zirconium precursor matches well the already discussed tendencies in crystallinity. The higher the degree of crystallinity of the MOFs, the higher were both their micro and meso surface areas. Concerning pore size distributions, Figure 8 shows both the micro and mesoporous pore size distributions as calculated from the NLDFT and BJH methods, respectively. Figure 8 also features the cumulative pore volume plots as a function of pore size.

All materials displayed multiple families of pores whose presence led to stepped cumulative pore volume curves, see section A-2.3.3 of the Supplementary Information. As shown in Figure 8, the ensemble of these results evidenced two things: (i) the structure of the microporous network of MOF-808 is relatively insensitive to the nature of the zirconium precursor and is related to the previously reported tridimensional microporous framework which contains tetrahedral cages with internal pore diameters of 0.48 nm formed by a tetrahedron with inorganic secondary building units at the vertices and the trimesic acid linkers at the faces of the tetrahedron. These tetrahedral cages are sharing vertices that forms a large adamantane cage with internal pore diameter of 0.18 nm (H. Furukawa et al., 2014). Furthermore, Liang et al. (W. Liang et al., 2014) reported micropores with average sizes of 1.52 and 0.63 nm for MOF-808 synthesized with acetic acid as the modulator. It is remarkable though that the MOFs synthesized from zirconyl chloride, and zirconyl nitrate, produced an additional family of micropores whose sizes are between two families conventionally accepted for MOF-808. (ii) The mesoporous structure of MOF-808 strongly depends on the zirconium precursor. According to results, ZrCl_4 leads to more regular mesopores as compared to zirconyl chloride and zirconyl nitrate. However, these mesopores have a more heterogeneous distribution of sizes and could be related to the inclusion of

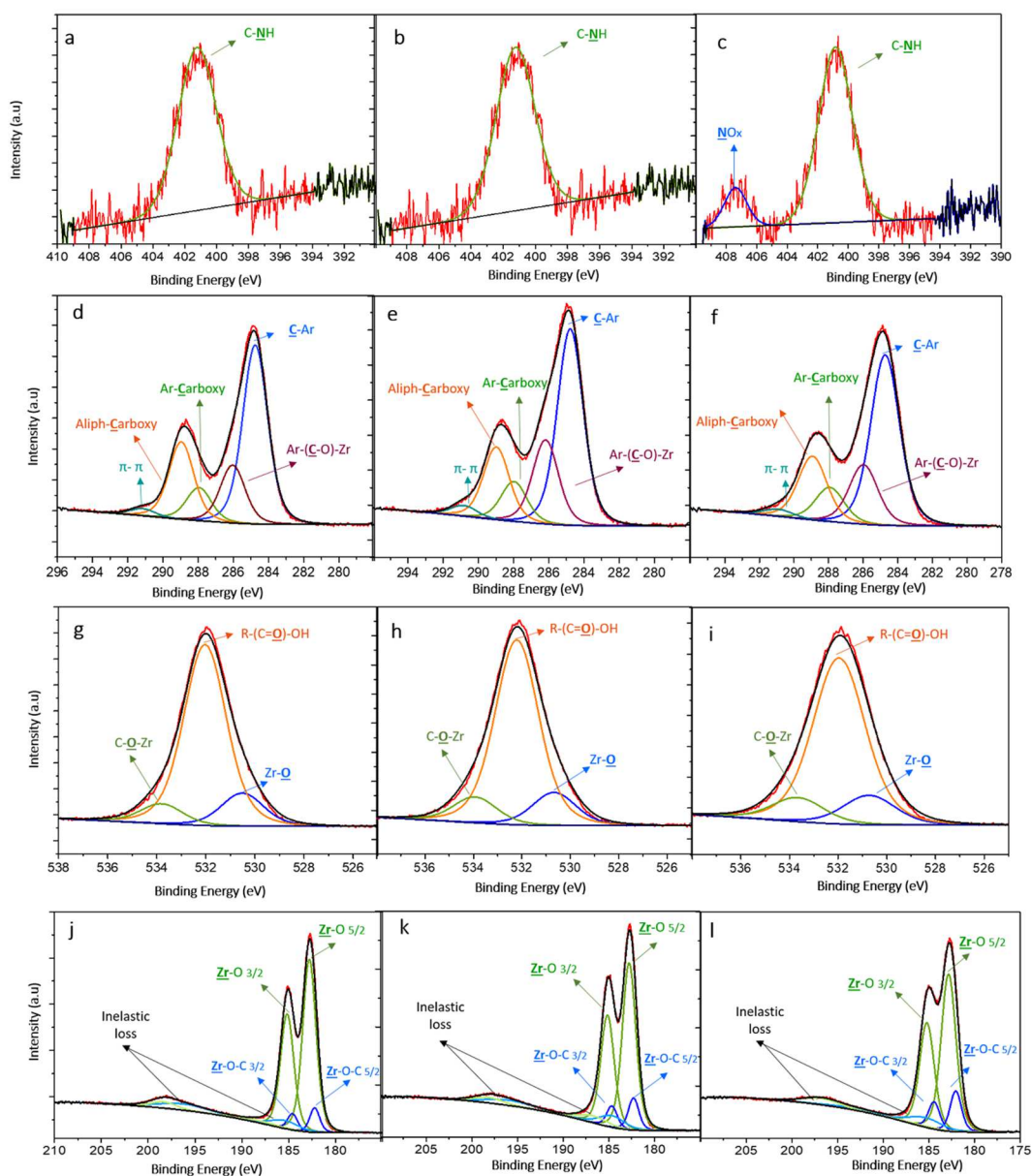
missing linker defects (Cai & Jiang, 2017). An in-depth discussion on missing linker defects caused by the addition of modulators will be shown in Chapters 3 and 4.

The evidence discussed in this section demonstrates the impact that the modification of the type of zirconium precursor has on the development of different networks of mesopores in MOF-808. As in agreement with what was discussed for the crystallinity and morphology of the materials, these changes might be associated with differences in relative concentration of structural water linked to the precursors. Indeed, one may qualitative classify the complexity of the porous network of the synthesized MOFs as a function of the metallic precursors as follows: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} > \text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} > \text{ZrCl}_4$.

The decomposition of the N 1s, C 1s O 1s and Zr 3d peaks recorded in XPS analysis are displayed in Figure 9. Table A-4 presents the relative concentration of the elements found on the surface of the synthesized materials. Besides carbon, oxygen, and zirconium; the expected components of MOFs, traces of nitrogen, silicon, and aluminum were detected and quantified. In the case of nitrogen (See section A-2.3.4 of the Supplementary Information), its presence can be associated with the deposition of residual dimethylamine from the hydrolysis of the DMF solvent (Wißmann et al., 2012). It is interesting to notice that, for the MOF prepared with zirconyl nitrate, traces of NO_x species (Breen, 1991) were also found on the surface of the corresponding ZrBTC3 material; Figure 9c.

Figure 9

N 1s, C 1s, O 1s and Zr 3d peaks decomposition recorded in XPS analysis of ZrBTC MOFs from precursors: (a,d,g,j) ZrCl_4 (ZrBTC1), (b,e,h,k) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2) and (c,f,i,l) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3). The C-(C,H) component at 284.8 eV was taken as reference for the binding energy calibration.



According to the chemical composition of the surface of the materials reported in Table 4, the following empirical formulas were estimated: $\text{ZrBTC1} = \text{CO}_{0.846}\text{Zr}_{0.160}\text{N}_{0.002}\text{Si}_{0.013}$, $\text{ZrBTC2} = \text{CO}_{0.788}\text{Zr}_{0.128}\text{N}_{0.002}\text{Si}_{0.012}\text{Al}_{0.026}$, and $\text{ZrBTC3} = \text{CO}_{0.847}\text{Zr}_{0.146}\text{N}_{0.003}\text{Si}_{0.008}\text{Al}_{0.025}$. These formulas are determined in a hydrogen free basis, since this element does not have core electrons and its photoionization cross section is only 0.0002 hence impeding its detection by XPS (Stojilovic, 2012). According to Furukawa et al. (Hiroyasu Furukawa et al., 2014), the chemical formula of the parent MOF-808 is $\text{CO}^{1.848}\text{Zr}_{0.25}\text{H}_{0.25}$. Conversely, in the case of the MOFs synthesized in this work, the mean of the surface molar ratio of oxygen was within the $\text{C.I.}_{t0.05;2} = [0.747, 0.894]$. This implies an oxygen deficiency of ca. 50% as compared to the molar ratio of oxygen reported by the mentioned authors. Concerning the molar ratio of zirconium, its mean was within the $\text{C.I.}_{t0.05;2} = [0.105, 0.184]$ which implies a ca. 40% deficiency of this element on the surface as compared to MOF-808. According to these findings, the chemical composition of the surface of the MOFs synthesized herein differs strongly from the expected composition of the crystalline core of MOF-808. These results thus beg the question: why is the chemical composition of the surface of the synthesized MOFs so different from that postulated for the crystalline core?

Table 2 shows the quantification of the different chemical species of carbon, oxygen, and zirconium. Taking these values into account, Table 3 displays molar ratios between the different species considered for peaks decomposition. When performing peaks decomposition in XPS, it is crucial to confer chemical sense to the different components assigned to represent chemical species. For doing so, stoichiometric relationships between these species must be calculated and contrasted to the stoichiometry of the chemical compounds under consideration (Dufrêne, Boonaert, & Rouxhet, 1999; Rouxhet & Genet,

2011). In this case, the molar ratios C-Ar/Ar-Carboxy refer to the proportion between the carbon atoms of the aromatic ring of H₃BTC and those of the carboxylate functional groups in H₃BTC, see Figure A-1. In the H₃BTC case, the stoichiometry of the compound leads to a C-Ar/Ar-Carboxy = 6/3 = 2. The values presented in Table 3 for this ratio are close to 2 hence corroborating that the proposed decomposition has a good chemical sense.

Furthermore, the assignment of components ascribed to carboxylates for the decomposition of the peaks corresponding to the C 1s and O 1s core levels also keeps chemical sense, Table 3. The stoichiometry of a carboxylate is carbon/oxygen = 0.5. In Table 3, the ratio: “Free”-[Carboxy/CarbOxy] and [Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH₃] corresponds to carbon and oxygen atoms involved in the carboxylate functional group. Particularly, the “Free”-[Carboxy/CarbOxy] was calculated from the ratio of the components: [(Ar-Carboxy)+Aliph-Carboxy]/[R-(C=O)-OH] and, the [Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH₃] was calculated from the ratio of the components [Ar-(C-O)-Zr]/{[Ar-(C-O)-Zr]-[2×C-NH]} presented in Figures A-1 and 1.5. According to results, “Free”-[Carboxy/CarbOxy] and coordinated [Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH₃] ~ 0.5 for each one of the studied materials thus demonstrating that the proposal presented herein makes chemical sense. Therefore, based on the results presented in Table 3, it seems safe to ascertain that the surface of the synthesized MOFs is enriched by unreacted carboxylates from the H₃BTC linker, Ar-Carboxy, and by residual carboxylates, Aliph-Carboxy, from either the acetic acid modulator or the formic acid produced by the hydrolysis of the DMF solvent. In general, the mean for the total concentration of surface free carboxylates was within the C.I._{t0.05;2} = [17.0, 22.2]. Hypothesis testing, using a t-Student distribution with 4 degrees of freedom. Assuming equal variances (Navidi, 2006), for the mean of both species showed no

significant difference, $p\text{-value} = 0.776$, between their relative surface concentrations. Regarding the molar ratio $\text{Zr-O}/\text{Zr-O}$ corresponding to the inorganic bonds of the zirconium oxoclusters of the materials, results showed that its mean was within the $\text{C.I.}_{t0.05;2} = [0.88, 1.34]$ which contains to the theoretical oxygen to zirconium ratio of 1.33, i.e. Zr_6O_8 , determined for MOF-808 (Bai et al., 2016; Hiroyasu Furukawa et al., 2014).

According to the results in Table 2, the surface of the synthesized MOFs has a higher concentration of zirconium species belonging to the zirconium oxocluster than of zirconium coordinated to the H_3BTC linker. The latter trend is particularly reflected on the low concentration of species ascribed to the coordination of zirconium to the H_3BTC linker; namely, Ar-(C-O)-Zr , C-O-Zr , and Ar-(C-O)-Zr (Figures A-1 and 1.5 and Table 2) as well as the ratios $[\text{Ar-(C-O)-Zr}]/[\text{Ar-(C-O)-Zr, C-NH}_3]$ and $[\text{Ar-(C-O)-Zr}/\text{Ar-(C-O)-Zr}]$ (Table 3). The fact that the molar ratios for the coordinated zirconium species are well below the 1:2 stoichiometric molar ratio of the species suggests that these bonds are rather associated to defective structures and not to the crystalline core of the MOFs.

Table 2

C 1s, O 1s and Zr 3d peaks contributions concentration for ZrBTC1, ZrBTC2, and ZrBTC3 materials. The species are coded as C-Ar: Carbon belonging to an aromatic ring, Ar-(C-O)-Zr, C-NH₃: Carbon from the carboxylic acid group linked to the Zr cluster, Ar-Carboxy: carbon belonging to the carboxylic acid group of H₃BTC, Aliph-Carboxy: Carbon from the carboxylic acid group linked to an aliphatic chain, Zr-O: oxygen linked to Zr in the organic cluster, R-(C=O)-OH: oxygen belonging to a carboxylic acid functional group, C-O-Zr: oxygen belonging to the C-O-Zr bonds, Zr-O: zirconium belonging to inorganic cluster and, Zr-O-C: zirconium coordinated to an organic group through oxygen.

Sample			
Relative Molar %	ZrBTC1	ZrBTC2	ZrBTC3
C 1s			
C-Ar	25.5	25.5	25.6
Ar-(C-O)-Zr, C-NH ₃	4.7	5.2	5.1
Ar-Carboxy	8.6	10.9	8.9
Aliph-Carboxy	11.0	9.7	9.6
O 1s			
Zr-O	5.9	5.5	5.5
R-(C=O)-OH	32.4	30.5	31.6
C-O-Zr	3.6	4.3	4.6
Zr 3d			
Zr-O	7.2	5.7	6.0
Zr-O-C	0.8	0.8	1.2

Table 3

Species molar ratios for ZrBTC1, ZrBTC2, and ZrBTC3 materials synthesized from ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ precursors, respectively.

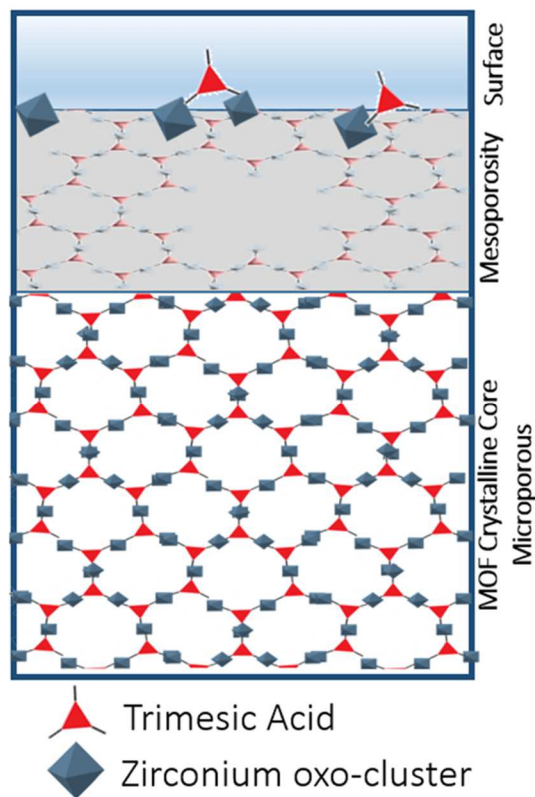
Species molar ratios	Sample		
	ZrBTC1	ZrBTC2	ZrBTC2
C-Ar/Ar-Carboxy	1.97	1.58	1.82
"Free"-[Carboxy/CarbOxy]	0.49	0.48	0.47
Coordinated			
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]	0.43	0.39	0.51
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH3]	0.09	0.08	0.13
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]	0.21	0.20	0.26
Inorganic			
Zr-O/Zr-O	1.22	1.05	1.07

Considering these findings, Figure 10 sketches a proposal for describing the surface chemistry of the synthesized MOFs. However, other structures could be possible to imagine according to the presented results.

According to the above findings, the surface chemistry of MOFs belonging to the 808 family is quite different from what would be expected from its bulk chemical structure reported in the literature (Hiroyasu Furukawa et al., 2014; W. Liang et al., 2014). From the present results, this phenomenon does not depend on the nature of the zirconium precursor as in contrast to the morphology, crystallinity, and porosity of the materials. It is interesting to observe that such a behavior is similar to the trend found for the thermal stability of the materials. The thermal stability of a given material is strongly defined by its surface chemistry since surface species are first decomposed under thermal stresses.

Figure 10

Proposed structure of synthesized materials from the crystalline core of MOF 808 to a defective surface.



1.4. Conclusions

This study illustrates the effect of using different zirconium precursors on the physicochemical properties of Zr-MOFs of the MOF-808 series. Results showed that using different precursors impacts the morphology, crystallinity, and porosity of MOF-808. Therefore, the employed zirconium precursors acted as structure directing agents. It seems that the presence of structural water in the zirconium precursors could be related to the structural differences found among the synthesized materials. Conversely, zirconium precursors did not affect the thermal stability and surface chemistry. Results showed that the

synthesized materials exhibited a defective structure at the surface contrary to the reported bulk chemical core of MOF 808: Zr_6O_8 clusters coordinated to the organic ligands forming the periodic structure. Particularly, an abundance of uncoordinated zirconium oxo-clusters was found besides uncoordinated carboxylate functional groups belonging to the aromatic structure of the organic linker. In addition, the detection of carboxylates attached to an aliphatic chain indicated the presence of unreacted modulator molecules on the surface of MOF-808. The evidenced defective surface of MOF-808 presents opportunities for applications that make use of defect engineering.

2. Enhanced Acidity of Defective MOF 808: Effects of Activation Process and Missing Linker Defects on Reactivity³

2.1. Overview

Among the zirconium-based Metal-organic frameworks, the MOF -808 has been reported as a promising heterogeneous catalyst due to its inherent missing linker defects. In this work, we perform state-of-the-art density functional theory calculations along with ab initio molecular dynamics and classical reactive molecular dynamics studies of the activation processes of the MOF-808 material and correlating them to the type and strength of the proposed active sites. By starting with a defect-free structure, we added formic acid as modulator and evaluated the effect of its removal after an activation process using adsorption calculations of ammonia molecules. Results show that the activation process induces proton mobility on the zirconium node leading to its rearrangement and the release of water molecules. We calculate the strength of the acid sites accompanied by Bader charge analysis, vibrational frequency data, and density of states calculations. The dehydroxylation and modulator removal that occur during the activation process affects the acidity of the MOF-

³ Adapted from: Ardila-Suarez, C., Perez-Beltran, S., Ramirez-Caballero, G. E., & Balbuena, P. B. (2018). Enhanced acidity of defective MOF-808: effects of the activation process and missing linker defects. *Catalysis Science & Technology*, 8(3), 847-857. doi: 10.1039/C7CY02462B, with permission from The Royal Society of Chemistry.

808. This theoretical rationalization of the activation process can serve as a basis for engineering of defects in MOF-808 materials.

2.2. Computational and System Details

2.2.1. Computational Details

DFT and AIMD

The Vienna ab initio simulation package (VASP) is used to perform both the DFT optimizations and the AIMD simulations (Kresse & Furthmüller, 1996; Kresse & Hafner, 1994). For all calculations, the core-electron interactions are described using the Projector Augmented Wave (PAW) pseudopotentials provided in VASP databases (Blöchl, 1994; Kresse & Joubert, 1999), and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) is selected as the exchange-correlation functional (Perdew, Burke, & Ernzerhof, 1996). The plane wave is expanded up to a cutoff energy of 400 eV, with the convergence criteria for ionic relaxation loop and the self-consistent electronic iteration set to 10^{-2} and 10^{-4} eV, respectively. The partial occupancies of the wavefunctions approximated with a Gaussian smearing set to 0.01 eV. K-point mesh sampling for the Brillion zone performed with the Monkhorst-Pack method at $1 \times 1 \times 1$ on each side for the DFT optimizations and AIMD simulations, whereas the density of state calculations (DOS) use a $2 \times 2 \times 2$ sampling. Moreover, the Bader charge analysis method is employed for charge calculations (Tang et al., 2009), and the dynamical matrix method is used for the vibrational frequency calculations.

The equation below allowed us the calculation of binding energy of ammonia molecules for the quantification of acidity strength (Lee, 2016):

$$\Delta E = E_{(MOF808/adsorbate)} - [E_{MOF808} + E_{adsorbate}] \quad (1)$$

Where the $E_{(MOF808/adsorbate)}$, the E_{MOF808} , and the $E_{adsorbate}$ terms are the total energy of adsorbed molecule, the bare MOF-808 structure, and the gas-phase molecule, respectively.

Following an earlier experimental report on the activation process of the MOF-808 material (W. Liang et al., 2014), AIMD simulations are performed to show the structural rearrangement of zirconium node occurring during activation at a temperature of 383 K using the NVT ensemble. The employed time step is 1.0 fs for about 12 ps long with the Nose-mass parameter set to 0.5, corresponding to 176 time steps per oscillation.

ReaxFF

For studying the dynamics of the activation process of the MOF-808 material, we used reactive classical molecular dynamics with the ReaxFF method developed by van Duin *et al.* and implemented in the LAMMPS code (Aktulga, Fogarty, Pandit, & Grama, 2012; van Duin, Merinov, Jang, & Goddard, 2008). This force field is developed to accurately simulate chemical reactions in large nanoscale systems, which cannot be performed by classical nonreactive force fields that do not allow bond breaking and bond forming. Compared to them, ReaxFF determines the bond order directly from the interatomic distances that are updated every MD iteration, and thus it does not need initial data of chemical bonding (van Duin, Dasgupta, Lorant, & Goddard, 2001). Our ReaxFF MD simulations effectively show the dehydroxylation and modulator agent removal during the activation process in MOF-808 structures. For the ReaxFF simulations, we use the MOF-808 supercell that contains 1344

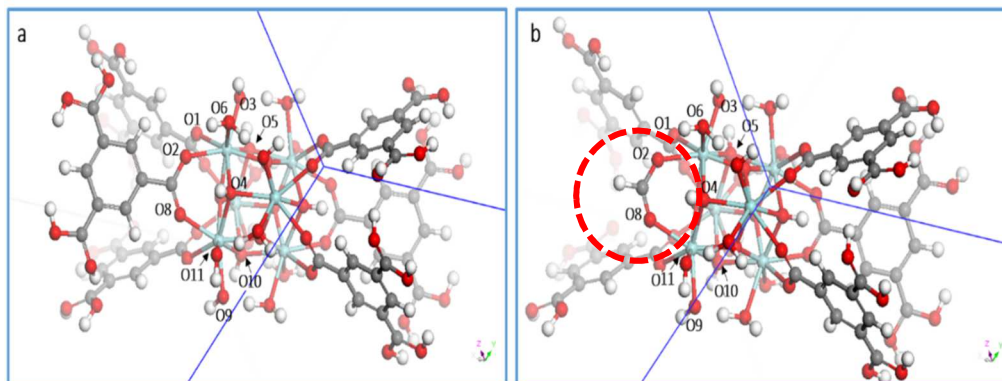
atoms with the NVT ensemble at 383 K for about 150 ps using a time step of 0.035 fs as recommended by Davis et al. (Davis, Belonoshko, Rosengren, Duin, & Johansson, 2010). For the sake of stability during simulations, we fixed the carbon atoms belonging to the trimesic acid (the organic ligand) to their initial positions for the entire simulation run. The trajectory of water molecules during the dehydroxylation process on the ReaxFF simulation was extracted using the OVITO Software (Stukowski, 2009).

2.2.2. System Details

The proton mobility and the dehydroxylation process of the MOF-808 material is investigated with the DFT and the AIMD methods by using a cluster model, whereas the dynamics of the activation process is studied with the ReaxFF method. Both cluster and ReaxFF models are based on the periodic structure reported elsewhere (Gomez-Gualdron et al., 2014). The cluster model (See Figure 2.1a) has one zirconium node with six hydroxyl and six water molecules attached to it ($[Zr_6(\mu_3 - O)_4(\mu_3 - OH)_4(OH)_6(H_2O)_6]^{+6}$), plus six trimesic acids acting as the organic linkers. Saturation of dangling bonds is achieved with hydrogen atoms attached to the ends of the organic linkers. A unit cell box of 28 Å x 28 Å x 28 Å on each side encloses the whole cluster in order to eliminate interactions with periodic images inherent of using the VASP package. The formation of defects is simulated by substitution of a trimesic acid (organic ligand) with a monodentate ligand. To accomplish this, Figure 2.1b shows how we replaced one of the organic linkers with a formate ion.

Figure 11

(a) Defect-free and (b) defective structures before activation process. Colour code: C, gray; O, red; H, white and Zr, cyan.



2.3. Results and Discussion

DFT Optimizations

Figure 11a shows the DFT optimized defect-free cluster. The distances $Zr - O_{\mu 3}$, $Zr - OH_{\mu 3}$, and $Zr - Zr$ are 2.09 Å, 2.30 Å, and 3.56 Å, respectively. EXAFS measurements performed for MOF UiO-66 structures are $2.09 \pm 0.01 \text{ Å}$, $2.232 \pm 0.009 \text{ Å}$, and $3.515 \pm 0.007 \text{ Å}$, for the $Zr - O_{\mu 3}$, $Zr - O$ and $Zr - Zr$ interactions, respectively (Valenzano et al., 2011). This agreement between our theoretical results and these experimental measurements evidences the DFT capability for handling this cluster structure even with the need of enclosing it into a periodic unit cell.

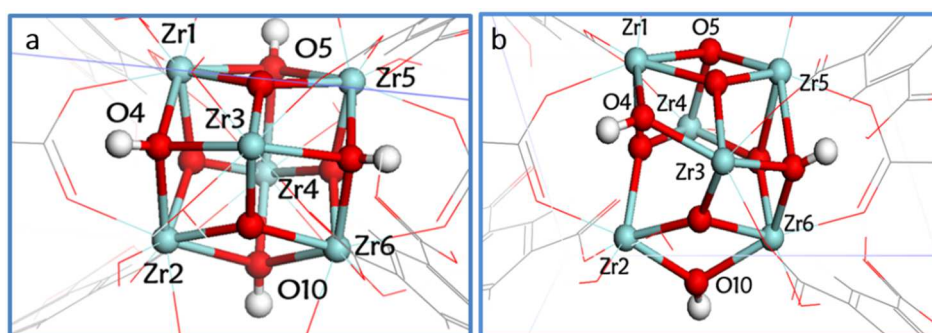
AIMD simulations

The AIMD simulations evidence desorption of some of the six water molecules initially attached to the cluster structure, which induces the remaining deprotonated oxygen atoms to get closer to the surface, in agreement with an earlier report from De Vos et al. (De Vos,

Hendrickx, Van Der Voort, Van Speybroeck, & Lejaeghere, 2017). We believe this desorption of water molecules is in close relation with thermal activation processes reported for this material at 383 K, as we will discuss in a future publication. Figure 12 shows how the oxygen atom labeled as O5 ($\mu_3 - OH$) gets deprotonated during the AIMD simulation. Upon deprotonation, the Zr4-O5 distance decreases from 2.36 Å to 2.017 Å, whereas the distance Zr5-O5 goes down from 2.273 Å to 2.083 Å. The distance Zr1-O5, however, increases from 2.311 Å to 2.470 Å. On the other hand, the oxygen O4 remains protonated with only slight changes in its distance to the Zr1 and Zr3 atoms going from 2.314 Å and 2.256 Å to 2.332 Å and 2.1632 Å, respectively. The Zr2-O4 bond, however, gets broken. Based on an earlier work (De Vos et al., 2017), we suggest the coordination changes of the oxygen O4 promotes the redistribution of the charge associated with the Zr2 atom, helping the zirconium node to get more stable upon deprotonation.

Figure 12

Zirconium oxo/hydroxo cluster (a) before (b) after the activation process.



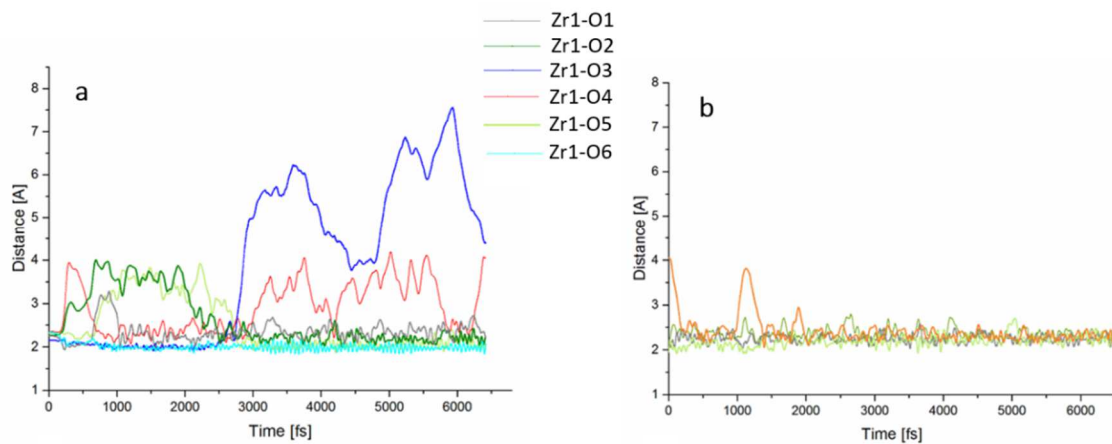
As Figure 13a outlines, the AIMD simulation also reveals changes in the Zr1-O distances. We observed the Zr1 atom constantly changes its distance to the O4 atom until the Zr1-O4 bond gets broken. The O5 atom, however, remains bonded to the Zr1 atom despite the

existence of oscillations, but in comparison to the O4 atom, the O5 atom loses an H atom to become an μ_3 -O oxygen. In agreement with Vandichel *et al.* (Vandichel *et al.*, 2016) for the UiO-66 MOF, we believe this process is related to the removal of a water molecule. We also observed a proton transfer process involving the O6 and O3 atoms, along with a H₂O molecule coordinated with an adjacent Zr atom, which is in agreement with a report from Ling *et al.* for the UiO-66 MOF (Ling & Slater, 2016). The H atom moves from the O6 atom to the O3 one, after which, as the blue line on Figure 13a evidence, the O3 atom migrates to an adjacent Zr. Finally, the H₂O molecules get removed as free water. At the end of the simulation, we observe a total of five water molecules removed from the cluster surface. Figure 13b shows the results from a second AIMD simulation performed after deleting the five water molecules that got detached from the first AIMD simulation. Besides the cluster stabilization, we observe now how the O4 atom bonds back to the Zr1 atom. At the end of the simulation, the Zr1-OH distance gets close to 2.05 Å, which happens to be in agreement with the 2.0 Å distance reported elsewhere (Trickett *et al.*, 2015).

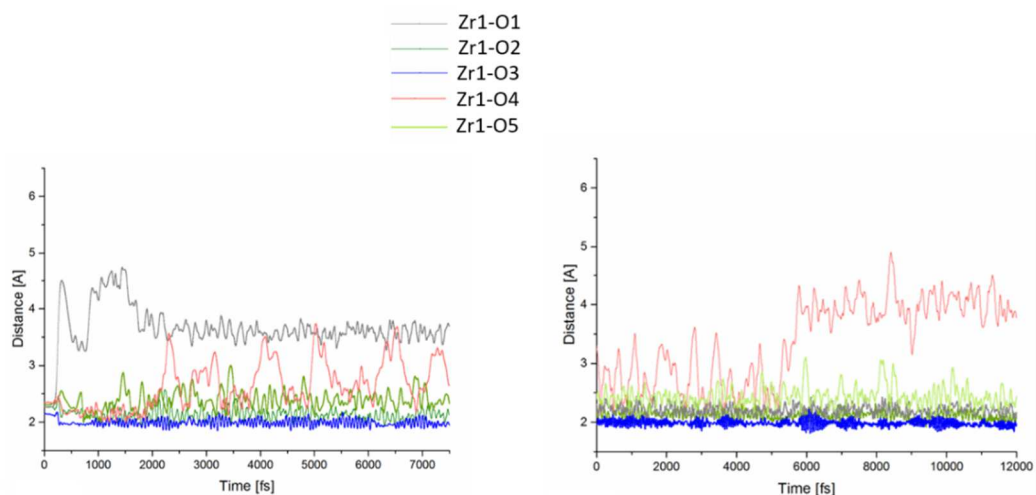
Figure B-1 in the Supplementary Information shows how the Zr2 atom interacts with the surrounding oxygen atoms. The distance Zr1-O8 fluctuates until stabilization, and the O9 oxygen receives a proton from the O11 atom, which in turn, receives another proton from a water molecule coordinated to an adjacent zirconium. After this sequence of events, the O11 atom gets removed as a water molecule. After the removal of free water molecules, the AIMD simulation shows no significant changes related to the Zr2-O distances. However, for this second simulation, the proton attached to the O9 atom migrates to an oxygen of an adjacent zirconium atom, after which the Zr2-O9 distance gets close to 2.05 Å.

Figure 13

Zr1...O distance changes in defect-free structure (a) initial steps (b) after removal of surrounding water molecules at 383 K.

**Figure 14**

Zr1 ...O distance changes in defect structure (a) initial steps (b) after removal of surrounding water molecules at 383 K.



We proceed to investigate the effect of activation process on a defective structure in which one organic linker has been replaced a formate ion during synthesis. In our simulation, we observe how the structure keeps the zirconium cluster electrically neutral thanks to the similar

chemical functionality between the organic ligand and the formate ion, see Figure 11b. During the activation process that we see during the AIMD simulation, we observe changes in the distance $\text{Zr1}\cdots\text{O}$ (Figure 14a), which ends up with the O1 going away from Zr1 atom. This O1 atom exchanges its position with the other oxygen belonging to the organic ligand, the latter being the one that ends up coordinated to the Zr1 atom. The O2 oxygen from the formate ion also tries to move away from the Zr1, but contrary to the O1 atom, the Zr1-O2 bond remains intact, and the O2 atom keeps close to the Zr1 atom. Also, we observe that the O4 atom gets trapped in a back and forth oscillation with the Zr1. The O6 oxygen, which is initially coordinated as water molecule with the Zr1 atom (not showed), gets removed as a free water molecule instead.

After this AIMD simulation, it is observed that six water molecules separate from the zirconium cluster. Once the free water molecules are removed, the AIMD simulation (Figure 14b) shows that the O4 oxygen moves away from Zr1. In addition to the above, no significant changes occur in Zr1-O distances. Afterwards, the Zr1-O3 distance is 1.92 Å. Furthermore, as shown above, the formate is not removed from the structure since it remains coordinated to the Zr1 atom by the O2 oxygen. After the removal of free water molecules, the AIMD simulation shows no significant changes for the Zr1-O distances. If a defect is included, none of the $(\mu_3 - \text{OH})$ is deprotonated after activation process. However, the coordination arrangement is more drastic. Both O4 and O5 go from $(\mu_3 - \text{OH})$ atoms to Zr-OH and remain coordinated to Zr2 and Zr1 (defect sites), respectively. At the same time both Zr1-O5 and Zr2-O4 distances decrease from 2.304 to 2.214 and 2.332 to 2.057 Å, respectively, which is according to the De Vos *et al.* (De Vos et al., 2017). Furthermore, as reported by Vandichel

et al. (Vandichel *et al.*, 2016) for a zirconium-based MOF, the dehydroxylation process could lead the decrease of a zirconium atom coordination number from 8 to 6.

Table 4

Partial Charges Calculated for the Zr and O atoms in MOF-808 Cluster after AIMD simulations.

	Average charge e				
	Zr	O – L ^a	$\mu_3/\mu_2 - OH$	$\mu_3 - O$	OH
Defect-Free Cluster	2.586	-1.177	-1.324	-1.227	-1.272
Defective Cluster	2.592	-1.176	-1.434	-1.255	-1.326

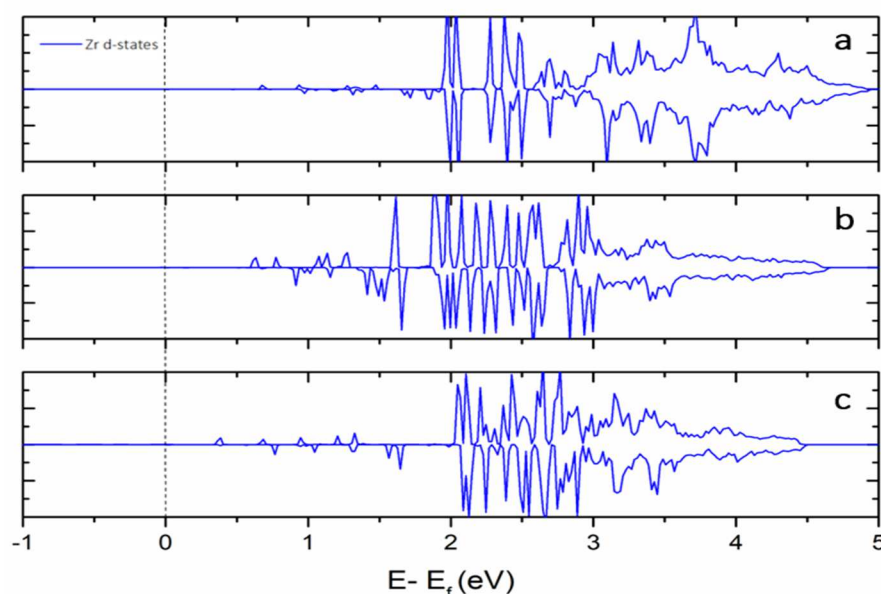
Table 4 and Figure B-2 in Supplementary Information present a Bader charge analysis performed to determine the electronic charge distribution before and after the AIMD simulation. The eightfold coordinated Zr^{4+} ions have a positive charge corresponding to +2.616 |e| (Figure B-1). Similar results were obtained using Hirshfeld charge analysis for the UiO-66 family (L.-M. Yang, Ganz, Svelle, & Tilset, 2014).

After ~12 ps of AIMD simulation, the Zr atoms only suffered a slight decrease in their coordination numbers, which we associate to a partial reduction process. As demonstrated before for metal complexes with aquo, hydroxo and oxo ligands (Ramos-Cordoba, Postils, & Salvador, 2015), small variations in partial charge can reflect pronounced changes in formal metal oxidation states. Furthermore, the Zr_6O_8 cluster exhibits a redistribution of its oxygen atoms belonging to $\mu_3 - OH$ and to $\mu_3 - O$ species. The average charge on $\mu_3 - O$ oxygen atoms decreases from -1.209 |e| to -1.227 |e| and -1.255 |e| for the defect free and defective structures respectively, after the activation process. Also, the average charge on $\mu_3 - OH$ oxygen atoms decreases from -1.257 |e| to -1.324 |e| and -1.434 |e| for the final $\mu_3/\mu_2 - OH$ in defect free and defective structures respectively, after the activation process.

Both the activation process and the inclusion of missing linkers modify the zirconium node structure. Since MOF-808 inherently exhibits ligand defects, its calculated density of states (see Figure B-3) differs from the twelve –fold coordinated structure of UiO-66 zirconium MOF. As reported by Flage-Larsen *et al.* (Flage-Larsen, Røyset, Cavka, & Thorshaug, 2013) the dehydroxylation that occurs during the activation process alters the zirconium cluster that is evidenced by the differences in their total DOS plot. Accordingly, de Vos *et al.* (De Vos et al., 2017) pointed out that the DOS of the zirconium d-states reflects the inclusion of defects in zirconium MOFs. Thus, in dehydroxylated structures (defect-free and defective structures) the d orbitals are more localized than in the node of the hydroxylated one.

Figure 15

Partial Zr d-states DOS of hydroxylated-defect free, dehydroxylated-defect free and defective dehydroxylated MOF 808 structures. The defect-free MOF808 exhibits inherently six missing linker defects per cluster. The dashed line stands for the Fermi-level.



According to Vieira Soares *et al.* (Vieira Soares et al., 2016), a high density of zirconium states in the conduction band nearby to the Fermi level, is related to the tendency of the MOF to receive electronic density. Thus, in the activated structures, the d states are localized in lower energy sites in where the organic linker has been removed (see Figure 15). The PDOS of the defect-free structure after the activation process (Figures B-4 and B-5) were plotted following the nomenclature reported by Yang *et al.* (L.-M. Yang et al., 2014) and allows to disaggregate the electronic states in both valence and conduction bands. The zirconium d-states are the main contributors to the conduction band followed by both s- and p-states of carbon and oxygen atoms. The covalent bonding in the metal-organic framework is evidenced by overlaps in the valence band. Thus, the s-states of H I overlap with the p-states of O III between -8.9 to -3.0 eV, as well as the s-states of H II, overlap with the p-states of C I in the energy range between -10 and -3.0 eV. Also, the p-states of C III can overlap with the p-states of O I in the range from -9.0 to -3.0 eV.

ReaxFF MD

Further calculations with the ReaxFF method allowed us to follow up the diffusion of the water molecules throughout the framework structure (Boyd, Moosavi, Witman, & Smit, 2017; X. Y. Liu, Pai, & Han, 2017). Figure 16 outlines the structural changes of the fully hydroxylated MOF-808 structure during its activation process at 383 K. We observe how the water molecules get detached from the surfaces of the zirconium clusters followed by their migration throughout the pore structure, reaching an average of 4.8 water molecules removed per zirconium cluster. It is remarkable the agreement between this average and the value reported earlier for the AIMD simulations, where we detected the detachment of five water

molecules, which indicates the accuracy of the ReaxFF parameterization used here. Figure 17 shows the trajectory of a single water molecule during the ReaxFF simulation. After being removed from the zirconium cluster, the water molecule briefly moved randomly, and after that it traveled a significant distance through the pore structure, to finally get involved in a Brownian-like motion (Vrgas L & Snurr, 2015).

Figure 16

Activation process ReaxFF MD simulation of defect-free MOF-808 at 383 K (a) initial structure (b) beginning of the dehydroxylation process and (c) final dehydroxylated structure.

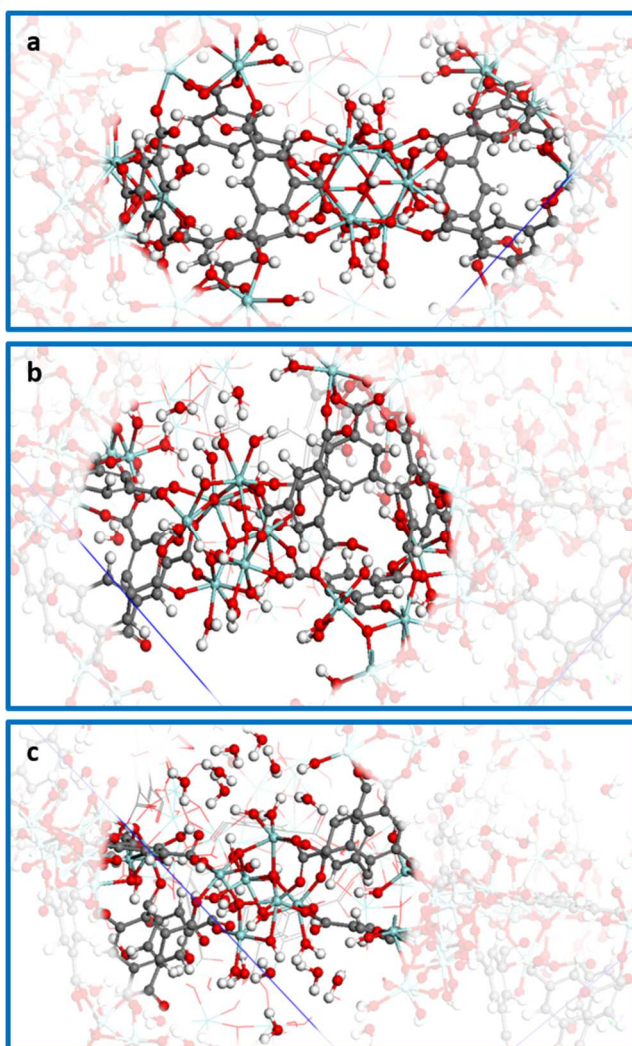
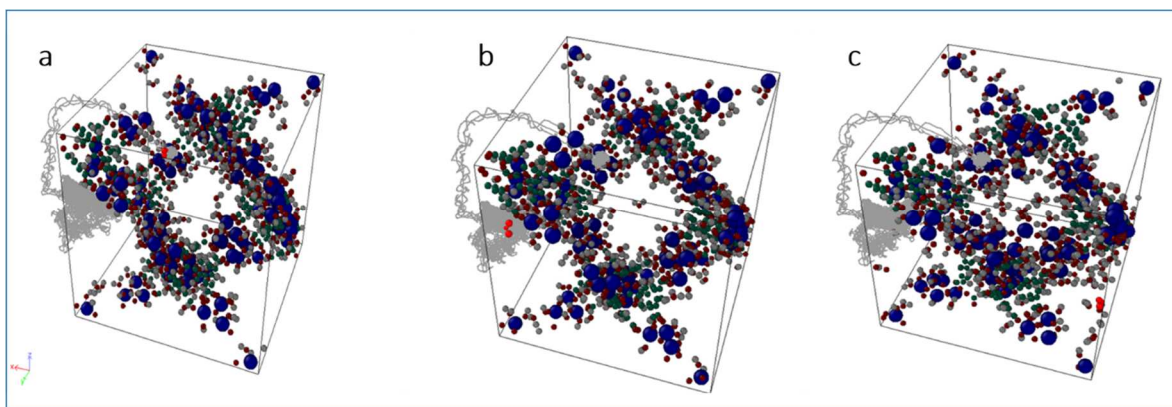


Figure 17

The trajectory of a water molecule during the activation process at 383 K at time steps (a) 15000 (b) 1839000 and (c) 3513000.



The activation process of the defective structure is also followed with the ReaxFF method by replacing one trimesic acid linker with three formate ions to get a total of three zirconium clusters with defects. Figure 18 highlights the activation process of one of these zirconium clusters. Even though the defects presence, the dihydroxylation mechanism goes similarly to the one detected for the defect-free structure. Besides this behavior, the formate ion attached to this zirconium cluster is involved in a separation process to finally get removed from the structure. Two of the added formate ions get displaced from the zirconium cluster and the third one remained coordinated. All zirconium clusters involved in this behavior also exhibit the removal of the six water molecules. This result is in agreement with the AIMD simulations for the defective structure. Thus, for the conditions at which we performed both the AIMD and the ReaxFF simulations, the modulator agent removal leads to the formation of exposed active acid sites.

Figure 18

Activation process ReaxFF MD simulation of defect MOF-808 at 383 K (a) initial structure (b) beginning of the dehydroxylation process and (c) final dehydroxylated structure.

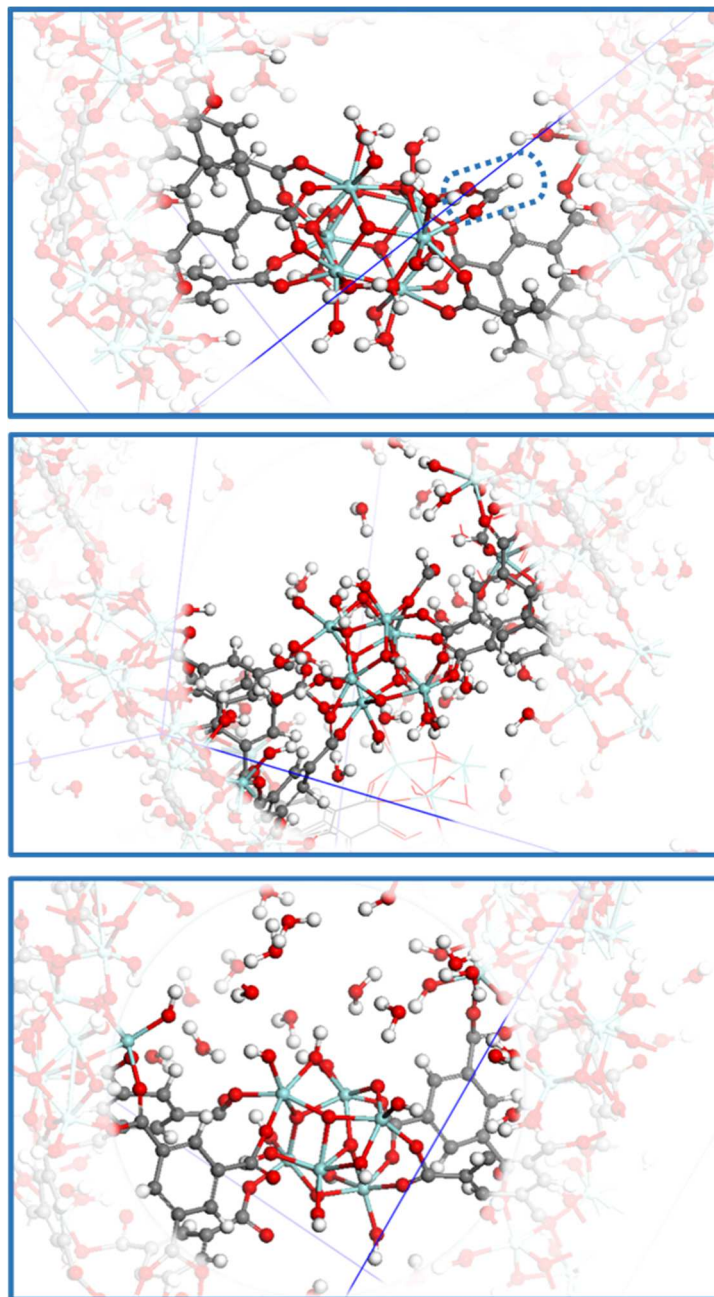
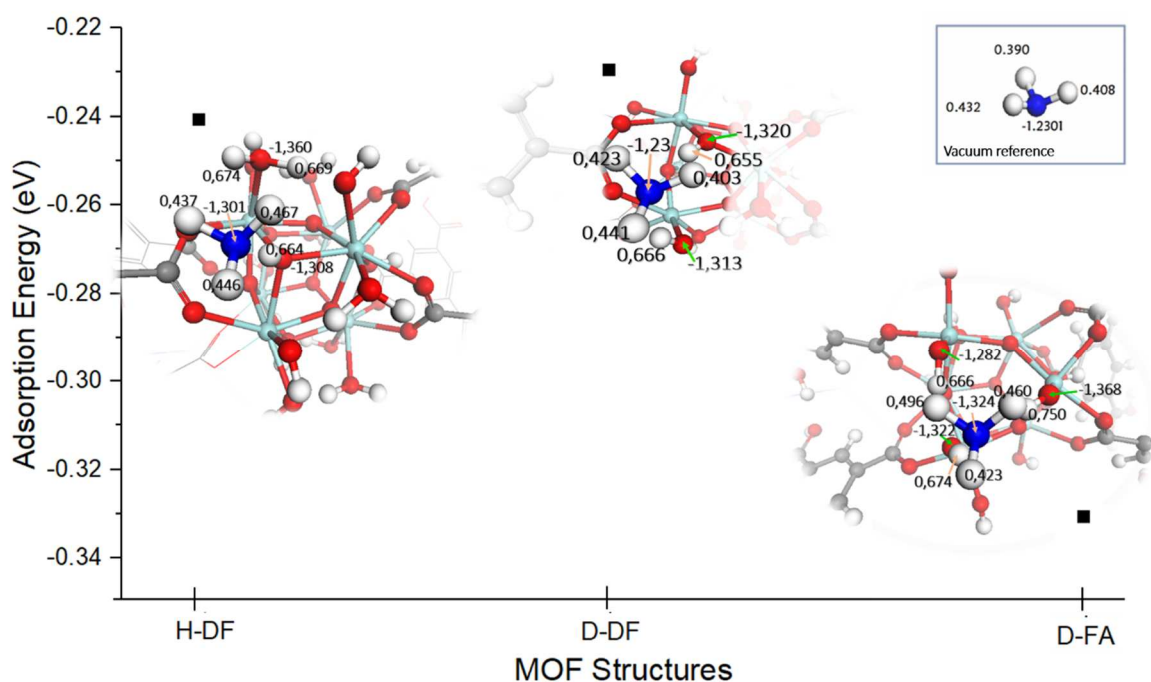


Figure 19

Energy and Bader charge of ammonia adsorption in hydrated defect-free structure (H-DF), dehydroxylated defect-free structure (D-DF), and defective dehydroxylated structure (D-FA).



NH_3 adsorption on MOF-808 structures

The acid strength of active sites on MOF-808 was quantified by DFT calculations of ammonia adsorption; a basic probe molecule experimentally used to determine the Lewis and Brønsted acidity in solid acids (Alharbi, Brown, Kozhevnikova, & Kozhevnikov, 2014; Jiménez-Morales, Moreno-Recio, Santamaría-González, Maireles-Torres, & Jiménez-López, 2015). Brønsted acidity in MOFs can be found in ligands such as hydroxyl groups, water, and alcohols coordinated to the metal node (Juncong Jiang & Omar M. Yaghi, 2015). Figure 19 shows the corresponding ammonia adsorption energies on the Brønsted acid sites of the hydrated MOF-808 cluster, the dehydrated defect-free, and defective structures (after

the activation process). After relaxation, the hydrated structure exhibited an ammonia adsorption energy of -0.24 eV. We also observed the adsorption energy slightly decreases after the activation process of the defect-free structure, but it increases for the activated defective structure. The ammonia molecule was not protonated, and it is hydrogen-bonded via its nitrogen atom to the hydroxyl groups of MOFs structures (Tsyganenko, Pozdnyakov, & Filimonov, 1975). However, the adsorption energies were significantly negative and comparable to previous studies on zirconium MOFs (Ling & Slater, 2016). The Bader charges were also computed to analyze the charge transfer between the MOF-808 structures and the guest molecule. For NH_3 , the nitrogen charge remains constant for the adsorption of the dehydroxylated defect-free structure. However, the nitrogen decreases its charge from -1.230 |e| to -1.301 |e| and -1.324 |e| for the hydroxylated defect free and the defective dehydroxylated structure, respectively. Furthermore, adsorption energies are according to the ammonia electron donation to the MOFs structures that are 0.049 |e|, 0.037 |e| and 0.055 |e| for the H-DF, D-DF, and D-FA structures, respectively.

The vibrational frequency calculations were also performed for the ammonia adsorption. The frequencies and eigenvectors of the vibrational modes were calculated using a partial dynamical matrix with atoms limited to the nearest surroundings. As studied before (Bučko, Hafner, & Benco, 2004), the employment of the partial matrix leads to results that agree with the computationally demanding of full dynamical matrix calculations. Our results are comparable to previous experimental (Špirko, 1983) and theoretical (PW:DFT-GGA-PW91 level of theory) (Erdogan, Ozbek, & Onal, 2010) results for the ammonia molecule in the gas phase. In our case, the values for asymmetric and symmetric stretching frequencies are 3491 cm^{-1} and 3377 cm^{-1} , respectively. Also, the values for asymmetric and symmetric bending frequencies are 1565 cm^{-1} and 1090 cm^{-1} for the single ammonia molecule. As reported

previously (Kung & Kung, 1985), the stretching frequencies for adsorbed ammonia decrease compared to those of gas phase; thus, the asymmetric stretching for adsorbed ammonia are 3453, 3442 and 3413 cm^{-1} for the dehydrated defect-free, the hydrated defect-free structure, and dehydrated defective structures, respectively. In the case of the symmetric stretching for the adsorbed ammonia, the calculated values are 3340, 3375 and 3332 cm^{-1} for the dehydrated defect-free, the hydrated defect-free structure, and dehydrated defective structures, respectively. Further, It is reported that those shifts of the vibrational modes of adsorbed ammonia molecule, are related with its adsorption at weak acid sites (Bučko et al., 2004). The calculated values for the asymmetric and symmetric bending frequencies of the dehydrated defective structure that exhibited the highest adsorption energy are 1507 and 1041 cm^{-1} . Thus confirming the weak nature of the hydroxyl Brønsted sites of the studied structures.

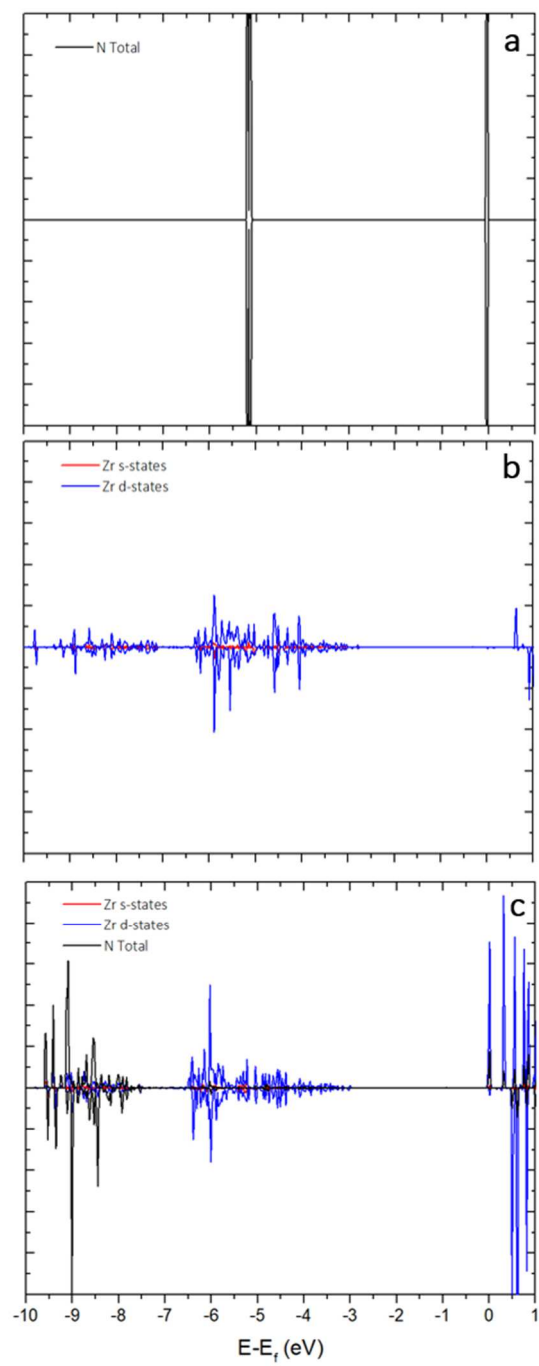
The zirconium atoms in the hydroxylated structure of MOF-808 are surrounded by hydroxyl groups and water molecules, making them inaccessible as Lewis acid sites. However, for the dehydroxylated structures, these atoms become partially accessible and exhibit Lewis acidity. The dehydroxylated defect-free and the defect structures were tested for ammonia adsorption in uncoordinated zirconium site denoted as Zr2 (see Figure 12). After relaxation, the dehydrated defect-free structure exhibited an ammonia adsorption energy of -0.33 eV whereas the dehydrated defective structure showed an adsorption of -0.11 eV. Vibrational frequency calculations were also performed for the ammonia adsorption. Compared to those mentioned above asymmetric and symmetric stretching frequencies for ammonia molecule in the gas phase, the adsorbed ammonia in dehydroxylated defect-free structure is are 3347 cm^{-1} and 3451 cm^{-1} , respectively. In the case of the adsorbed ammonia on the defective dehydroxylated structure, the asymmetric and symmetric stretching

frequencies are 3338 cm^{-1} for its asymmetric stretching and 3465 cm^{-1} for its symmetric stretching on the gas phase. As reported previously (Sälli, Martiskainen, & Halonen, 2012), the interaction between ammonia and the metal during adsorption is reflected not only in the adsorption energy but also in the vibrational energy levels of stretches by red shifts.

Comparing these results with the ammonia adsorption on Brønsted sites, we see that the dehydroxylation process leads to an increase of proton acidity in the case of the defective structure. Thus, the zirconium at which it is bonded exhibits only slight Lewis acidity. On the contrary, the defect-free structure which showed the lowest adsorption energy in its evaluated Brønsted site exhibits an increase in the adsorption energy measured at the Lewis site. In order to obtain insights into the electronic factors that control the ammonia adsorption at the zirconium site, density of states calculations were performed. Figure 20 shows the comparison of the density of states of ammonia molecule before (Figure 20a) and after (Figure 20c) adsorption on the zirconium site (Figure 20b) of the dehydroxylated defect-free structure. The total DOS of the nitrogen atom of ammonia molecule exhibited noticeable changes in its electronic structure. It is observed an interaction between states of the nitrogen atom (belonging to ammonia) and Zr states. The corresponding DOS of adsorbed ammonia showed broad bands for N atom, indicating the NH_3 -metal bonding.

Figure 20

Total DOS of N that belongs to ammonia. (b) Partial Zr DOS of dehydroxylated defect free structure and (c) NH_3 / dehydroxylated defect-free structure. (Adsorption energy: -0.33 eV).



2.4. Conclusions

The activation process for defect-free and defective structures of MOF-808 has been investigated using AIMD and ReaxFF MD methods. The activation process induces proton mobility on the zirconium oxo/hydroxo cluster leading to the release of water molecules. The rearrangement of bond distance between zirconium atoms and their coordinated oxygen atoms, which also entails some bond breaking, is related to charge balance. The removal of five water molecules is observed during the AIMD process, whereas the defect structure exhibits the release of six water molecules. Regarding this last point, the cluster model shows that the formate ion that replaces the organic linker remains only slightly bonded to the zirconium node. ReaxFF MD calculations for the MOF-808 supercell in agreement with the *ab initio* calculations evidenced the removal of the majority of the formate ions that replaced the organic linkers. Also, the number of removed water molecules of both defect-free and defective structures agrees with the results of the cluster model.

Bader charge analysis evidence the decrease of the zirconium atoms coordination environment as well as the charge differences of the different oxygen atoms types after the activation process. The inclusion of defects leads to more localized zirconium d-states which also appear at lower energy sites where the removed linkers were previously located. For the measurement of the strength of the acid sites, calculations of ammonia adsorption energy accompanied by Bader charge analysis, vibrational frequency data and density of states were performed. It is shown that the dehydroxylation process does not increase the strength of the Brønsted sites. Conversely, if the dehydroxylation is performed on the defective structure, the energy of ammonia adsorption increases. However, the reported sites only exhibit weak Brønsted acidity. Concerning Lewis acidity, it is observed that the partially coordinated

zirconium atoms on the dehydroxylated defect-free structure exhibited significantly larger ammonia adsorption energy compared to the defective structure.

It is demonstrated that the creation of defect centers might help to increase the acidity of the MOF-808. We also found out that the removal of labile coordinated species did not lead to open metal sites in the defective structure; instead, it was the redistribution of charges which induced the acidity. This theoretical rationalization of the activation process can serve as a basis for engineering of defects in MOF-808 materials.

3. Synthesis, Characterization, and Post-Synthetic Modification of a Micro/Mesoporous Zirconium-Tricarboxylate Metal-Organic Framework: Towards the Addition of Acid Active Sites⁴

3.1. Overview

Zr-MOFs are characterized by their high thermal and chemical stability which may facilitate their application in heterogeneous catalysis. However, these applications could be restricted if large reactants exceed the MOF pore sizes leading to unavailable surface areas. In this work, we study the effect of acetic acid concentration, used as the modulator, on the formation of micro/mesoporous materials. This inclusion of a modulator during synthesis and its removal by an activation process generate materials with missing linker defects. We show that an increase in the concentration of modulator leads to an improvement of calculated apparent surface area and to a modification of MOF-808 pore structure by producing mesopores at the expense of micropores. Furthermore, we perform a post-synthetic modification (PSM) of the MOF-808. We observe the expected sulfation of the zirconium oxo-cluster but also the sulfonation of the organic ligand. Also, we find that only

⁴ Adapted from: Ardila-Suárez, C., Díaz-Lasprilla, A. M., Díaz-Vaca, L. A., Balbuena, P. B., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). Synthesis, characterization, and post-synthetic modification of a micro/mesoporous zirconium–tricarboxylate metal–organic framework: towards the addition of acid active sites. *CrystEngComm*, 21(19), 3014-3030, doi: 10.1039/C9CE00218A, **with permission from The Royal Society of Chemistry.**

the families of mesopores and the larger micropores are interconnected within the material, and the ultramicropores seem to be isolated from the porous structure. The PSM process led to the addition of Lewis and Brønsted acid sites to the MOF-808. Experimental results are complemented by theoretical calculations using Density Functional Theory and Ab Initio Molecular Dynamics Simulations. The rationalization of the synthesis conditions effect and the post-synthetic sulfation process on the final properties presented in this paper can serve as a basis for engineering of defects towards the synthesis of solid acid catalysts from MOF 808

3.2. Experimental

Employed reagents

Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99%), the solvent for the synthesis of the materials: N,N-dimethylformamide (DMF, 99.8%), the acetic acid (99.8%) employed as modulator, the sulfuric acid (95-97%) used for the post-synthetic modification, the washing solvents: acetone (99.8%), methanol (99.9%), and chloroform (99.8%), were all obtained from Merck Millipore. The organic linker, Benzene-1,3,5-tricarboxylic acid (H_3BTC , 95%), was obtained from Aldrich Chemistry. Pyridine (99%); used for the analysis of acidity, was obtained from J.T. Baker. All reagents were used as received.

Synthesis and modification of zirconium-tricarboxylate MOFs

The solvothermal synthesis of Zr- MOFs was carried out in a 25 mL screw-capped glass jar by heating solutions containing the zirconium salt, the organic linker, and a modulator. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.2417 g, 0.75 mmol) and the corresponding quantity of

modulator were dissolved in 4 mL of dimethylformamide and stirred for 15 min. Trimesic acid (0.0525 g, 0.25 mmol) was dissolved in 4 mL of DMF and added dropwise to the initial solution. The mixture was stirred for additional 10 min. Later on, the mixture was sonicated for 20 min. Subsequently, the mixture was sealed and heated to 108°C for 24 h. The as-synthesized Zr-MOFs were filtered and washed once with DMF and twice with both methanol and acetone. The resulting powder was dried at 80°C for 2 h. A selected Zr-MOF was post-synthetic modified adapting the procedure presented by Jiang et al. (Juncong Jiang et al., 2014). Briefly, 50 mg of the synthesized material was treated with 50 mL of 0.05 M sulfuric acid (2.5 mmol) for 24 h. After that, the solution was solvent exchanged with 50 mL of water for three days; with the water being changed once a day, quickly exchanged with 50 mL of acetone and immersed in 50 mL of chloroform for three days. During this time, chloroform was exchanged once per day. Finally, all the synthesized materials were activated overnight at 110 °C under a vacuum pressure of 0.05 mbar. The nomenclature used for the materials followed the convention: *ZrBTC-concentration* of the modulator. For example, the sample synthesized with 114.6 equivalents of acetic acid; calculated on the basis of zirconium precursor, was denoted as ZrBTC-114.6.

Assessment of the physicochemical properties of the materials

The thermal stability of the synthesized materials was evaluated by Thermogravimetric analysis (TGA). TGA was performed on a TA2050 apparatus using a heating rate of 5 °C/min under a nitrogen flow of 15 mL/min and raising the temperature to 700°C. Quantitative analysis of the TGA data was performed following

the principles of the method reported by Shearer et al. (Shearer et al., 2016; Shearer et al., 2014) and considering the thermal decomposition in an inert environment of a dehydroxylated MOF-808.

The porosity and surface area of the materials were assessed by calculations derived from N₂ and Ar adsorption-desorption isotherms at 77.4 and 87.3 K, respectively, using a 3Flex equipment (Micromeritics). For the measurements, the relative pressure range went from 1.82×10^{-5} to 0.998 P/P₀. Equilibration intervals of 10 s were employed. Isotherms were recorded twice in independent experiments. Before measurements, the materials were degassed at a temperature of 110 °C under vacuum for 12 h. The vacuum pressure reached after the latter procedure was ca. 0.05 mbar. Surface area calculations were performed using the methods based on the χ (James B Condon, 2006) and BET theories (Brunauer et al., 1938). The latter was applied for comparison purposes and considering the consistency criteria proposed by Rouquerol et al. (Rouquerol et al., 2007), according to our previous work (Ardila Suárez, Rodríguez Pereira, Baldovino Medrano, & Ramírez Caballero, 2019) (see Table C-1). Microporous pore size distributions were calculated with Non-Local Density Functional Theory (NLDFT) routines assuming cylindrical pores. A regularization factor of 0.0316 was employed. Mesoporous pore size distributions were calculated by the Barret-Joyner-Halenda (BJH) method (Ardila Suárez, Rodríguez Pereira, et al., 2019). The calculation routines for these procedures were provided in the *MicroActive* software of the instrument.

The crystalline structure of the materials was assessed by powder X-ray diffraction (XRD). XRD patterns were recorded using a Bruker AXS D8 Advance DaVinci

geometry instrument equipped with monochromatized Cu K α radiation ($\lambda = 1.5418\text{\AA}$) and operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ value range from 3.0 to 50.0° with a step time of 0.6 s⁻¹. Le Bail treatment of the structures was performed using the FullProf software (Rodríguez-Carvajal, 2001). An approximate percentage of crystallinity was calculated using the DIFFRAC EVA software, and it was based on the ratio between the area that represents the crystalline contribution and the total area of the diffractogram as related to the integrated intensities of the corresponding amorphous and crystalline contributions (DIFFRAC; Giencke).

The identification of functional groups from the as-synthesized and modified MOFs was performed by Infrared spectroscopy on a Thermo Scientific Nicolet iS50 FTIR spectrometer after MOFs activation under a dynamic vacuum at 110°C. The latter was carried out in a VacPrep 061 unit (Micromeritics). The identification of surface acid sites was performed by FTIR analysis of adsorbed pyridine. This basic nitrogen aromatic is frequently used as a probe molecule to characterize solid acid catalysts due to its ability to interact with both Lewis and Brønsted sites (Sushkevich, Vimont, Traver, & Ivanova, 2015). Pyridine chemisorption was performed following the procedures reported by authors such as Breen et al. (Breen, Deane, & Flynn, 1987) and Reddy et al. (Reddy, Bhat, Nagendrappa, & Jai Prakash, 2009). Briefly, samples of ca. 0.05 g were placed in stainless steel reactors of 0.5 and 1.2 in diameter and height, respectively. For each sample, two different reactors were employed. 0.1 mL of pyridine was added to the sample contained in one of the reactors, while the other sample was left as a blank. The reactors were heated up to 120 °C for 24 h. After that,

they were opened, during 20 min under room conditions, for the remotion of physisorbed pyridine. The infrared spectra were recorded before and after the pyridine chemisorption.

Quantification of surface elements was carried out by X-ray photoelectron spectroscopy (XPS). Analyses were performed on the A. Centeno-XPS/ISS/UPS surface characterization platform (SPECS). The platform is provided with a PHOIBOS 150 2D-DLD energy analyzer package. A monochromatized Al K α X-ray source (FOCUS 500) operated at 200 W. The pressure in the analysis chamber was approximately 1×10^{-7} Pa. The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and to 60 eV for high-resolution spectra. Samples were mounted on carbon conductive tape over metallic sample holders for analysis. Surface charge compensation was controlled with a flood gun (FG 15/40-PS FG500) operated at 58 μ A and 1.0 eV. General spectra were recorded for all samples followed by high-resolution spectra: C 1s, O 1s, Zr 3d, N 1s, and S 2p. Data analysis was performed with the CasaXPS program (Casa Software Ltd) using the SPECS Prodigy library for R.S.F. values. A U3 Tougaard baseline (J. Walton, Alexander, Fairley, Roach, & Shard, 2016) was employed for background modeling together with a Lorentzian line shape, LA(1.53,243) for peak decomposition. The methodology for analyzing surface chemical functional groups was adapted from our previous work (Ardila Suárez, Rodríguez Pereira, et al., 2019). For the C 1s peak, the following chemical species were considered: (i) Carbon belonging to an aromatic ring, labeled as C-Ar, which is indistinguishable from the peak from the C-(C,H) species from aliphatic hydrocarbons. Both the latter peaks were considered to be centered at 284.8 eV

(Rouxhet & Genet, 2011) and used as a reference for the calibration of the binding energy (BE) scale of the spectra (Rouxhet & Genet, 2011). (ii) Carbon from the carboxylic acid group linked to the Zr cluster, labeled as Ar-(C-O)-Zr. For the unmodified and PSM submitted samples, the mean BE for this component was found between the range 286.20 and 286.68 eV, respectively. (iii) Carbon belonging to the carboxylic acid group of H₃BTC, labeled as Ar-Carboxy. The peak for this component was fixed at 288.0 eV following the literature (Genet, Dupont-Gillain, & Rouxhet, 2008; Rouxhet & Genet, 2011). (iv) Carbon from the carboxylic acid group linked to an aliphatic chain labeled as Aliph-Carboxy and fixed at 289.0 eV (Genet et al., 2008). For the PSM treated samples, an additional component was considered. Namely, (v), Carbon linked to a sulfonic group, labeled as C-S-O (Kumar, Mamlouk, & Scott, 2014). Moreover, finally (vi), the peak corresponding to the $\pi - \pi^*$ transition in the aromatic rings was taken into account to peak decomposition (Briggs & Beamson, 1992). The mean BE for this component was 290.85 and 291.00 eV for the unmodified and sulfated samples, respectively. For this component, the R.S.F. value was set to 0 during chemical species quantification. The same FWHM was set for all carbon species. For the O 1s peak of the ZrBTC-114.6 material, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) Oxygen linked to Zr in the inorganic cluster, labeled O-Zr, and centered at 530.76 eV (Y. Wang et al., 2017). (ii) Oxygen belonging to a carboxylic acid functional group, R-(C=O)-OH (Rouxhet & Genet, 2011) and (iii) oxygen belonging to the Zr-O-C bonds in the MOF (Ardila Suárez, Rodríguez Pereira, et al., 2019). For the material submitted to PSM, oxygen bound to the sulfate group O-S chemical species was also considered. Its position was set at 530.9 eV following the literature (Poo-arporn,

Thachepan, & Palangsantikul, 2015). The separation of this contribution from the O-Zr was aimless, nonetheless. For the Zr 3d core level, two different species were considered. The first was Zr belonging to the inorganic cluster; labeled Zr-O. For this species, the average of the Zr 3d_{5/2} peak was located at 182.49 eV. The second was Zr coordinated to an organic group through oxygen, labeled Zr-O-C. The Zr 3d_{5/2} peak for this species was located at an average BE of 183.77 eV. For the PSM submitted sample, two additional contributions were considered. Namely, a species for zirconium linked to the sulfate group and labeled as Zr-O-S. The average position of the Zr 3d_{5/2} peak for Zr-O-S was 185.18 eV. In this case, the following constraints were imposed during peak decomposition: a) the area of the Zr 3d_{3/2} core level is equal to two-thirds the area of the Zr 3d_{5/2} core level, and, b) a separation of 2.37 eV between both core levels (Moulder, Chastain, & King, 1995). Finally, for the S 2p peak of the PSM treated sample, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) O-S-C from sulfur linked to the organic constituents of the MOF. The S 2p_{3/2} contribution of this species was found at an average BE of 167.34 eV. (ii) “Free S” that is associated with residual sulfate ions. The average position of the S 2p_{3/2} peak of this species was 169.41 eV. (iii) S-O-Zr corresponding to sulfur linked to inorganic Zr moieties. In this case, the average of the S 2p_{3/2} peak was centered at 170.26 eV. All of the aforementioned binding energies are associated with S-O bonds in (SO₄)²⁻ species in which sulfur remains in a hexavalent oxidation state (S⁶⁺) (Zhichao Miao et al., 2017). The proposed chemical shifts are assumed to be associated with the chemical environment of the sulfur atom. For the S 2p core level, the following constraints were imposed during peak decomposition: a) the area of the S 2p_{1/2} core level is equal to half the area of the S

2p_{3/2} core level, and, b) A separation of 1.16 eV between these two peaks was assumed ("Thermo Scientific XPS,"). In general, stoichiometric relationships between species were used as a rational guide providing stoichiometric consistency to the adopted methodology (Ardila Suárez, Rodríguez Pereira, et al., 2019; Dufrêne et al., 1999; Rouxhet & Genet, 2011).

3.3. Theoretical studies

Assessment of the activation stage

The Vienna ab initio simulation package (VASP)(Kresse & Furthmüller, 1996; Kresse & Hafner, 1994) was used to perform both Density Functional Theory (DFT) optimizations and ab initio Molecular Dynamics (AIMD) simulations. A cluster model containing one zirconium node surrounded by five trimesic acids as organic linkers, and one acetate as modulator agent, were selected to analyze the proton mobility and dehydroxylation of the defect-free MOF-808, according to our previous work (Ardila-Suarez, Perez-Beltran, Ramirez-Caballero, & Balbuena, 2018). The MOF molecular cluster was extracted from the corresponding MOF-808 3D structure reported elsewhere (Gomez-Gualdron et al., 2014). Hydrogen atoms were added to ensure a valence saturation of the unsaturated bonds, see Figure 21a. The dimensions of the cells were 28 Å x 28 Å x 28 Å to eliminate possible interactions with the periodic images. Core-electron interactions were described using the Projector Augmented Wave (PAW) pseudopotentials provided in the VASP databases (Blöchl, 1994; Kresse & Joubert, 1999). The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) (Perdew et al., 1996) was selected as the exchange-correlation functional.

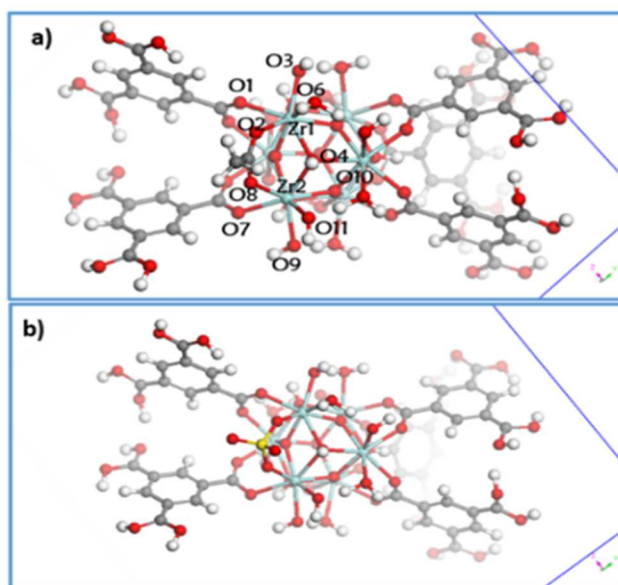
The plane wave was expanded up to a cutoff energy of 400 eV. The convergence criteria for the ionic relaxation loop and the self-consistent electronic iteration were set to 10^{-2} and 10^{-4} eV, respectively. A Gaussian smearing with a width of 0.01 eV was employed, and a $1 \times 1 \times 1$ k -points Monkhorst-Pack (Monkhorst & Pack, 1976) mesh sampling was used in the surface Brillouin zone. AIMD simulations were carried out on the optimized MOF-808 clusters using the NVT ensemble at 110 °C to match the temperature employed during the synthesis of the materials. The simulations were performed with a time step of 1.0 fs, and the Nose thermostat with a Nose-mass parameter of 0.5 was used to control temperature oscillations. This parameter gives a frequency of oscillation corresponding to 176-time steps.

Assessment of a sulfated cluster

The inclusion of one sulfate ion into the structure of the MOF-808 material was simulated by replacing the initial acetate ion by a sulfate ion (see Figure 21b) in the MOF-808 cluster. The procedure was based on a previous literature report (Juncong Jiang et al., 2014). The parameters used for DFT calculations were the same as for the unmodified structure. The dynamical matrix method was used for calculating vibrational frequencies. DFT calculations of pyridine adsorption quantified the acid strength of the active sites on the sulfated MOF-808, a basic probe molecule experimentally used to determine the acidity of solid acids (Chakraborty & Viswanathan, 1999; Zaki, Hasan, Al-Sagheer, & Pasupulety, 2001). The adsorption of pyridine on the sulfated MOF-808 structure was assessed following Equation 1. The latter allowed calculating the binding energy of the adsorbed pyridine molecule and was used for the theoretical estimation of the acidity strength (Lee, 2016).

Figure 21

Cluster models for the zirconium-based MOF-808 (a) Defect (b) sulfated structures. Color code: C, gray; O, red; H, white; Zr, cyan, and S, yellow. The hydrogen atoms were added to ensure a valence saturation of unsaturated bonds.



3.4. Results and Discussion

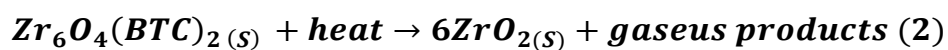
Influence of the concentration of modulator on the properties of zirconium tricarboxylate MOFs

This section discusses the influence of the concentration of the modulator on the thermal stability, porous structure and surface area, crystallinity, and molecular structure before and after activation of the synthesized Zr-MOF.

Thermograms for the as-synthesized samples ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 are displayed in Figure 22a. In general, the TGA profile of these samples exhibited the same shape only differing strongly in the initial drop in weight for a temperature up to 100°C.

Following the methodology proposed in previous publications (Ardila Suárez, Rodríguez Pereira, et al., 2019; Shearer et al., 2016), three different weight loss regions were defined in the thermograms. Region I, from 25 to 100° C, was associated with the volatilization of adsorbed water. In this region, the weight loss of the materials followed the trend: ZrBTC-52.4 (16.61%) < ZrBTC-83.5 (19.28%) < ZrBTC-114.6 (24.52%). These differences suggest that an increase in the concentration of the modulator enhances the capacity for retaining adsorbed water. According to the literature (Araujo & Jaroniec, 2000; Pan, Jaroniec, & Klinik, 1996), this is a consequence of a modification of the porous structure and the surface area of the materials. Indeed, we will show later that ZrBTC-114.6 had the highest surface area among the synthesized MOFs. The weight loss in Region II, from 100 to 400 °C, was attributed to the removal of monocarboxylate linkers, DMF (solvent), and the dehydroxylation of the zirconium cluster. As the removal of the acetate ion and the dehydroxylation of the zirconium cluster occur within the same range, their differentiation is aimless. In this case, the recorded weight losses were basically the same: namely, ZrBTC-83.5 (17.8%) ~ ZrBTC-114.6 (18.7%) ~ ZrBTC 52.4 (19.4%). Therefore, the concentration of the modulator did not seem to induce an effect on the events occurring when submitting the samples to these conditions.

Finally, Region III, defined between 400 and 700°C, was considered to correspond to the thermal decomposition of the MOFs. Hence, this region was assumed to involve the complete degradation of the organic constituents of the materials resulting in the formation of zirconium oxides (equation 2) (Shearer et al., 2014)



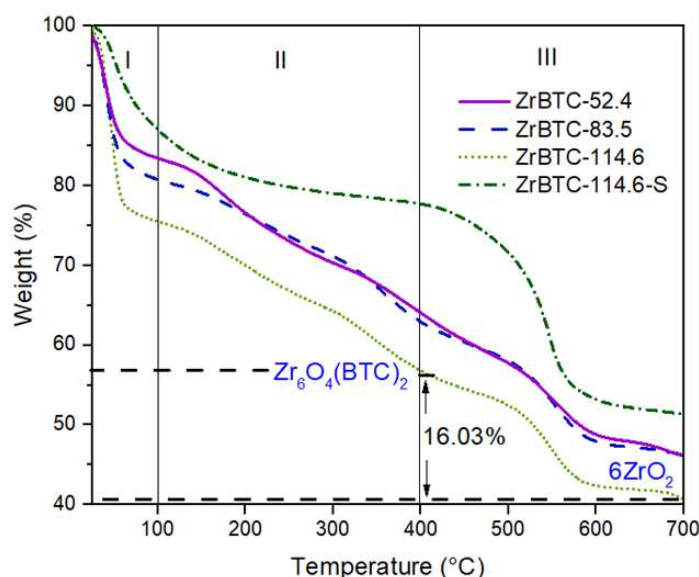
For the analysis of the thermal profile recorded for Region III, the relative weight loss due to the decomposition of the material was evaluated after performing a mass balance considering the stoichiometry of equation 2. Consequently, assuming a basis of 100 g of the initial $\text{Zr}_6\text{O}_4(\text{BTC})_2$ ($M = 1025.57$ g/mol) the mass of solid residue -6 moles of ZrO_2 ($M = 739.34$ g/mol)- should be 72.11 g which corresponds to a relative weight loss of 27.89%. The recorded weight losses for the Zr-MOFs were always below such a theoretical value: namely, 17.89% for ZrBTC-52.4, 16.68% for ZrBTC-83.5, and 16.03% for ZrBTC-114.6. The observed tendency hence suggests that the structure of the Zr-MOFs synthesized herein differs from the one postulated for the fully crystalline parent material regardless of the concentration of the acetic acid modulator. Shearer et al. (Shearer et al., 2016; Shearer et al., 2014) proposed that the deviations in the weight loss from the theoretically expected values for the fully crystalline MOFs in this Region are proportional to the number of missing organic linkers in the structure. Therefore, such departures would be produced by defective MOF structures. Based on this assumption, the Zr-MOFs synthesized in this work are defective with a relatively similar percentage of missing organic linkers in their structure despite the variations in the concentration of the acetic acid linker used for their synthesis.

To summarize, TGA analysis showed that the concentration of the acetic acid linker did not produce an appreciable effect on the shape of the thermal profiles of the synthesized Zr-MOFs. The thermal processes leading to the removal of structural species and further Zr-MOF decomposition did not seem to be modified by the concentration of the organic linker either. Conversely, an increase in the concentration of the latter led to a stronger weight loss due to the volatilization of adsorbed water

hence suggesting the formation of a material with a larger surface area. In general, all of the synthesized Zr-MOFs seemed to be defective due to missing organic linkers. The results and discussion that follows provide support for the above interpretations.

Figure 22

Thermogravimetric analysis (TGA) in a nitrogen atmosphere of MOFs at different modulator concentrations and missing linker defects calculation on ZrBTC-114.6 sample.

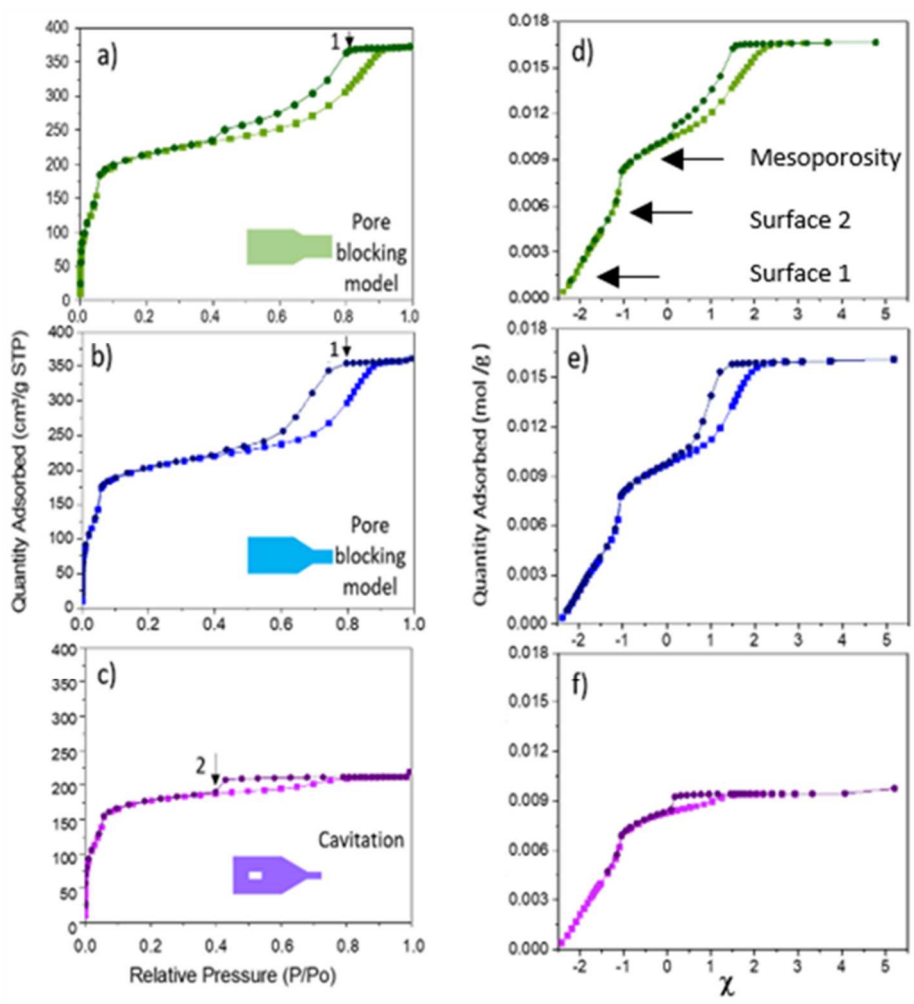


Ar adsorption-desorption isotherms for ZrBTC-114.6, ZrBTC-83.5, ZrBTC-52.4 are shown in Figure 23. The N₂ adsorption-desorption isotherms is shown in Figure C-1. The recorded isotherms are a combination of IUPAC's (Sing, 1985) types I and IV isotherms. Therefore, the synthesized materials possessed micropores and mesopores (Thommes et al., 2015). Hysteresis loops provide information related to the distribution, shape, and connectivity of mesopores (Lowell, Shields, Thomas, & Thommes, 2012; Thommes et al., 2015). All materials exhibited H2 type hysteresis (see Figure 23a-c). For these loops, the samples exhibited a plateau at the desorption branch which (see arrow 1) surpassed the plateau recorded for the adsorption branch

of the loop. Such behavior is characteristic of a hindered evaporation process and is usually interpreted as if narrow connections between pores block the transit of the evaporated probe molecule through the porous network of the material (Thommes et al., 2006). Larger plateaus were found with the decrease in the concentration of acetic acid, Figure 23. Besides this trend, the decrease in the concentration of the modulator also seemed to alter the mesoporous network of the material up to a point where cavitation takes place (Thommes et al., 2006). This is suggested by the presence of a step followed by an abrupt drop in the amount of the adsorbed probe in the hysteresis loop at lower relative pressures; ca. 0.4-0.42 and ca. 0.49-0.44 for argon at 87.3 K and nitrogen at 77.4 K, respectively; see arrow 2 in Figures 23c and C-1c. The morphology of the mesopores can be correlated with the shape of the hysteresis loop of the isotherm. Indeed, materials presenting pore blocking effects are characterized by having pores interconnected through channels with a medium size; while materials that exhibit cavitation have narrow channels that interconnect their pores, see Figure 23. These channels are known as bottlenecks. Thus, the cavitation phenomena is an indication of a weak connection between pores (Ragon et al., 2015). A schematization of these systems is shown in the insets of Figures 23 and C-1.

Figure 23

Ar adsorption/desorption isotherms of (a) ZrBTC-114.6 (b) ZrBTC-83.5 and, (c) ZrBTC-52.4, in the all range of the linear P/P_o . χ -method adsorption/desorption isotherms of the same materials (d) ZrBTC-114.6, (e) ZrBTC-83.5, and (f) ZrBTC-52.4.



Wu et al. (Wu et al., 2013) reported that the use of acetic acid as the modulator in the synthesis of Zr based UiO-66 MOFs. The porosity of the materials synthesized by these authors was evaluated by N₂ physisorption. Though the authors showed evidence for the formation of mesopores, unfortunately, their N₂ physisorption results limited themselves to the adsorption branch of the isotherms hence preventing a qualitative

assessment of the hysteresis loops. The authors ascribed the formation of mesopores to a lower connection between zirconium nodes that propitiated their formation. On the other hand, Liang et al. (W. Liang et al., 2014) reported the synthesis of a series of Zr-BTC MOFs whose porosity was modified by changing the chain length of the modulator by using formic, acetic, and propionic acid. However, these authors did not make any reference to the formation of mesopores for their materials. Finally, Furukawa et al. (Hiroyasu Furukawa et al., 2014) reported a type I isotherm; i.e., no mesopores were found, for a MOF-808 synthesized with the same Zr metallic precursor employed herein and using formic acid as the modulator. Comparing these reports to our work, not only a strong influence of the nature of the modulator on the porous structure of Zr-MOFs is evidenced, but also the role of the concentration of a given modulator takes a central stage in controlling this property as well. The characteristics of the recorded isotherms show that the synthesized Zr-MOFs are micro/mesoporous materials whose pore network is affected by the concentration of the acetic acid modulator. The lower the concentration of the modulator, the more complex the corresponding porous network becomes. Such a complexity seems to be related to the formation of narrow necks interconnecting the mesopores. The narrowness of these necks seemed to increase with the decrease of the acetic acid modulator concentration.

According to calculations, the synthesized materials possess various families of pores whose distributions are reflected in the corresponding stepwise cumulative pore volume curves, See Figure 24a-c. Particularly, ZrBTC-52.4, Figure 24a, showed three different families of micropores. The average sizes of these families were ca.: 0.58, 0.88, and 1.53 nm. Among them, the one whose average size was 0.88 nm represented

the lowest increase in cumulative pore volume. Furthermore, such a family of pores tended to disappear with the increase in the concentration of the modulator. Concerning mesopores, the increase in the concentration of the modulator led to displacement and widening of the pore size distributions in this range. The total pore volumes calculated for ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 were 0.50, 0.48, and 0.30 cm³/g, respectively with corresponding pore volumes related to mesopores of 42.0, 41.7, and 13.3 %. Thus, an increment in the concentration of modulator enhanced both the total and mesopores pore volume of the synthesized Zr-MOFs.

Table 5 presents the results for the calculated surface areas by the method derived from the χ -theory (Ardila Suárez, Rodríguez Pereira, et al., 2019). In general, the total surface area of the materials increased with the concentration of the organic modulator. This trend was qualitatively consistent with the one found when estimating surface area with the BET method, Table C-1. Such a trend concurs with the fact that TGA tests pointed out to larger free volume spaces available for Zr-BTC114.6 (previous section). On the other hand, the χ -method allows calculating the surface area for the different families of pores of the material (James B Condon, 2006; James B. Condon, 2001, 2002). Therefore, it was possible to determine that the surface areas corresponding to both the micropores and mesopores of the materials increased with the concentration of the organic modulator. The relative percentages of the mesopore surface area were ca. 30% for both ZrBTC-114.6 and ZrBTC-83.5, and ca. 17% for ZrBTC-52.4.

Table 5

Summary of the textural properties calculated by the χ method of the ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 materials

	Microporous Range					Mesoporous Range		Total χ surface area m ² /g
	Surface 1		Surface 2		Total			
	χ surface		χ surface		Microporous χ	Mesoporous χ		
	area	Rs _q	area	Rs _q	surface area	surface area	Rs _q	
	m ² /g		m ² /g		m ² /g	m ² /g		
ZrBTC-114.6	669	0.99	143	0.99	812	238	0.99	1050
ZrBTC-83.5	630	0.99	139	0.98	769	225	0.99	994
ZrBTC-52.4	610	0.99	33	0.99	643	107	0.99	750
ZrBTC-114-S	664	0.98	-	-	664	40	0.99	704

Therefore, the value of this percentage seems to reach a plateau after reaching a certain value of concentration for the organic modulator. On the other hand, χ -method calculations accounted for the surface area of two families of pores; namely, surfaces 1 and 2 in Table 5, in the microporous region of the isotherm. Therefore, the contribution of the family of pores with an average size of 0.88 nm could not be differentiated from the others. Correlating the calculated pore size distributions with those for the surface areas of the microporous structure of the materials, surface 1 was ascribed to the family of pores with an average size of 0.58 nm, while surface 2 was assumed to represent the family of micropores measuring 1.53 nm. An estimation of the relative percentage area surface 2/surface 1 yielded: ca. 22% for ZrBTC-83.5 ~ 21% for ZrBTC-114.6 > 5.0% for ZrBTC-52.4. This trend resembles the one found before for the relative mesopores to micropores surface areas. Therefore, it seems that there is a critical concentration of organic modulator that promotes the formation of Zr-MOFs structures with larger pores in both the micro and mesoporous size ranges. The results presented in this section agree with literature reports (Z. Hu et al., 2016;

Shearer et al., 2016), showing that the modulator serves to control the porosity of Zr-MOFs. However, as far as we know, these previous reports have not explored the role of the concentration of the organic modulator as presented herein. In this sense, one of the contributions of this work was establishing how the concentration of an organic modulator alters the porosity and surface area of Zr-MOFs of the 808 type in particular ways.

Diffraction patterns recorded for samples of ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 are shown in Figure 25. All samples had the following set of reflections: $2\theta = 4.34^\circ$, 8.32° , and 8.69° assigned to the (111), (311), and (222), respectively, planes of MOF-808 (Hiroyasu Furukawa et al., 2014) and crystallized in the cubic space group $Fd\bar{3}m$, Table C-2. The differences in the diffraction patterns of the samples suggest a change in crystallinity, nonetheless. In general, the structural parameters of the crystallites of the material did not seem to be affected by the concentration of modulator, Table C-2. Therefore, the atomic arrangement of crystallites can be assumed to be the same regardless of the studied range of concentration of the organic modulator which agrees with the fact that the thermal stability was found to be similar for the synthesized MOFs. Further crystal structure treatment aiming to determine a relative percentage of crystallinity of the materials is shown in the Supporting Information (See Figures C-2-4 and Table C-2). The estimated relative crystallinity percentages are included in Figure 25. These percentages indicated, first, that the synthesized Zr-MOFs are partly amorphous and, second, that an increase in the concentration of the modulator promotes the formation of a larger fraction of crystallites of MOF-808 above 83.5 equivalents of acetic acid; i.e., for ZrBTC-114.6. Such a result can be interpreted considering that Schaate et al. (Schaate et al., 2011) reported that the concentration of

the modulator influences the coordination between the metal component and the organic linker of MOFs hence promoting order in the arrangement of the framework. Herein, the characterization of the porosity of the materials discussed in the previous section indicated that the concentration of the modulator altered the relative proportions (i.e., pore volumes and surface areas) between the different families of pores of the materials hence evidencing how this factor impacts the structural arrangement of the Zr-MOFs.

Figure 24

Cumulative pore volume and pore-size distribution of (a) ZrBTC-52.4, (b) ZrBTC-83.5, (c) ZrBTC-114.6, and (d) ZrBTC-114-S. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range

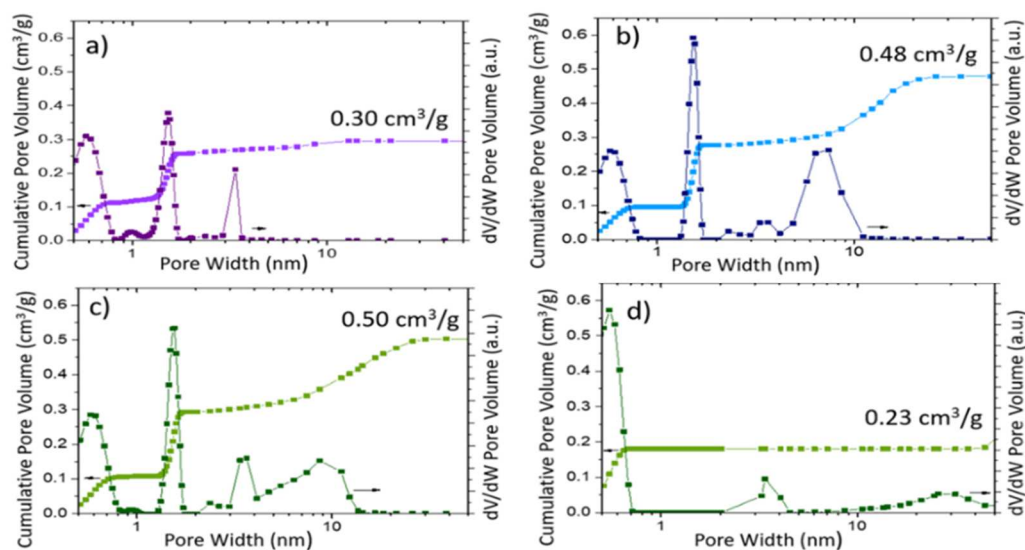
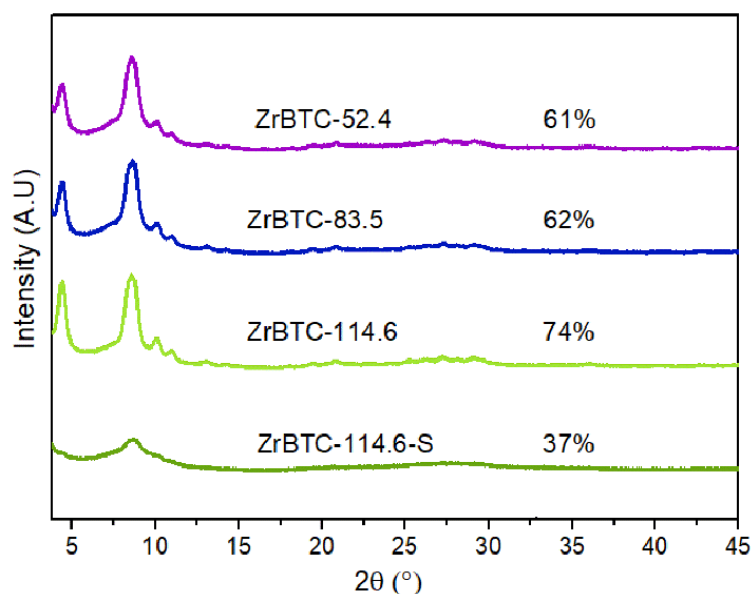


Figure 25

Experimental PXRD data and calculated relative crystallinity of synthesized MOFs.



FTIR spectra of ZrBTC-114.6 MOFs taken at room temperature and after heating at 110 °C; i.e., the activation temperature, and under vacuum are shown in Figure 26. A broadband was observed at around 3300 cm^{-1} , i.e., in the OH region, indicating significant perturbations by H-bonding as usually observed for the OH groups of carboxylic acids and also interactions with adsorbed water (Ragon et al., 2015). After heating at 110°C, only this broadband disappeared. Therefore, the removal of hydroxylated species after activation was established as in agreement with TGA results as well. On the other hand, Figure 27 presents the IR spectra for the activated materials within the region between 400 and 1800 cm^{-1} . Particularly, the band at 1710 cm^{-1} was ascribed to free acid acetate (W. Liang et al., 2014). In the spectra of the activated samples, the bands around 1600 -1500 cm^{-1} were related to the stretching modes of the carboxylate group (COO^-) (F. Yang, Li, & Tang, 2018). Meanwhile, the

weak band in the region of $1480\text{--}1420\text{ cm}^{-1}$ was attributed to the C=C bonds in the aromatic compound of the organic linker (Wißmann et al., 2012). The bands observed in the region of $750\text{--}655\text{ cm}^{-1}$ were attributed to the asymmetric vibration of the Zr-(μ_3 -O) bridges in the framework building blocks (Piszczyk, Radtke, Grodzicki, Wojtczak, & Chojnacki, 2007). Also, the band at 640 cm^{-1} was assigned to a vibration of the hexanuclear cluster, and the band around $545\text{--}555\text{ cm}^{-1}$ was associated with the asymmetric stretching vibration of Zr-(OC) bonds (Y. Wang et al., 2017). Finally, the coordination of the oxo-cluster with the modulator was confirmed by the detection of a band at 1660 cm^{-1} which is ascribed to coordinated acetate groups in MOFs. In general, all the above spectra showed corresponded to the usual bands for MOFs carboxylates (Atzori et al., 2017; Shearer et al., 2016); namely, vibrations from C-O-Zr, Zr-O, C=C, and C-O bonds. This implies that despite the structural differences between the materials presented herein and those parent Zr-MOFs reported in the literature (W. Liang et al., 2014), they all share the same bulk molecular structure.

Figure 26

Infrared spectra of synthesized MOFs ZrBTC-114.6 at 25°C (red) and after activation under dynamic vacuum at 110 °C (black).

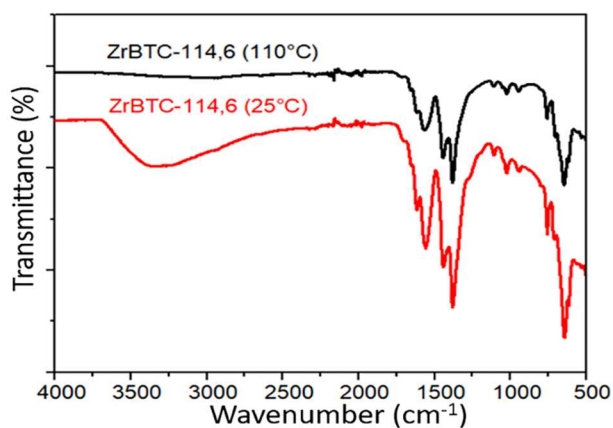
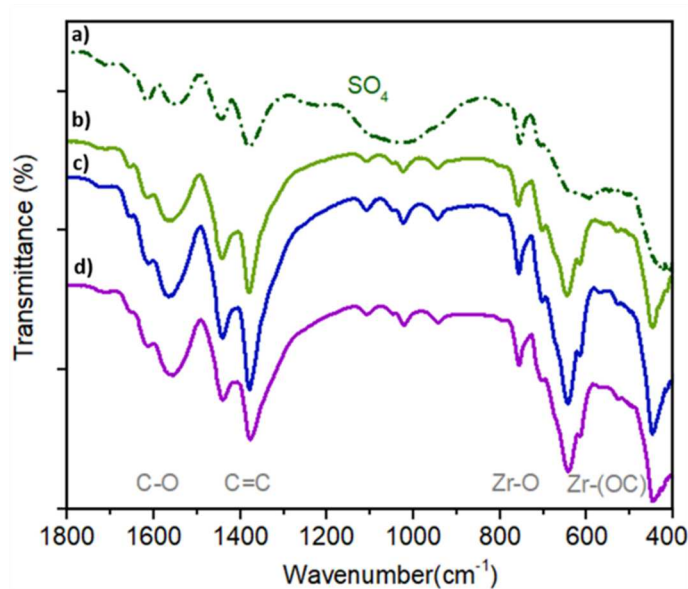
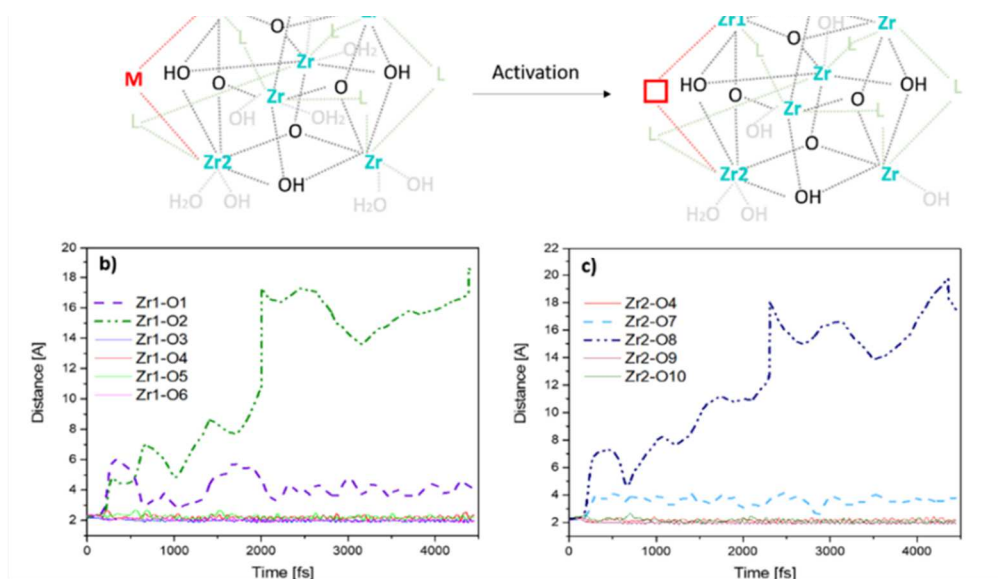


Figure 27

Infrared spectra of synthesized of (a) ZrBTC-114.6-S, (b) ZrBTC-114.6, (c) ZrBTC-83.5, and (d) ZrBTC-52.4

**Figure 28**

a) Schematic representation of the activation process. b) Zr1 •••O and, c) Zr2 •••O distance changes in defect structure during activation process at 110 °C.



To gain insight into the processes occurring at the molecular level during the activation stage of the materials, AIMD-NVT simulations were carried out. The considered scheme for the removal of the modulator (denoted as M) during such a process is schematized in Figure 28a. The simulation was performed at 110°C in agreement with the activation conditions. Figures 28b-c show the changes in the distance between zirconium and oxygen atoms during the simulation. The zirconium atoms denoted as Zr1 and Zr2 are coordinated to the acetate ion of the framework. According to calculations, the activation process leads to modulator agent removal. Thus, O2 and O8, the oxygen atoms belonging to the acetate ion, move away from Zr1 and Zr2, respectively, leading to bond breaking after 200 fs. It is also observed that the O1 and O7 oxygen atoms belonging to different organic linkers and connected to the Zr1 and Zr2 atoms, respectively, try to separate from the structure, but at the end of the simulation, they remained close to the zirconium atoms. Moreover, the activation process was found to promote dehydroxylation. During such dehydroxylation, four water molecules are removed from the zirconium cluster. These results agreed with the experimental evidence collected by TGA and FTIR.

To summarize the findings concerning the effect of the concentration of acetic acid on the physicochemical properties of the synthesized Zr-MOFs belonging to the MOF-808 family, the following can be said: (i) organic linkers can be replaced by modulator molecules. The latter can, in turn, be removed from Zr-MOFs during activation during which adsorbed water is also removed. (ii) The thermal stability of the Zr-MOFs was not affected by the modifications in the concentration of the organic modulators. Such finding can be associated with the fact that the crystalline structure of the materials was unaltered. (iii) Regardless of the concentration of acetic acid, all

synthesized Zr-MOFs exhibited an amorphous fraction and a porous structure consisting of families of pores in both the micro and mesopore ranges of pore sizes. The data suggested that increasing the concentration of the organic modulator up to a critical point promoted the crystallinity of the materials as well as the formation of a larger relative fraction of mesopores of wider diameters.

Considering the results discussed above, a sample from ZrBTC-114.6; which exhibited the highest crystallinity, surface area, pore volume, and average mesopore diameter while having the least tortuous mesopore system and keeping the same microporous structure and thermal stability of the other materials, was selected for further modification via a post-synthetic exposure to sulfuric acid.

This section discusses first the thermal stability of the modified ZrBTC-114.6 material. Second, an assessment of the effect of the modification process on the surface area and porosity of the material is conducted. Third, the effects on crystallinity are discussed. Fourth, the molecular structure of the material is evaluated through FTIR analysis. Fifth, XPS and FTIR analyses of adsorbed pyridine serve to cast light into the molecular structure of the surface of the material. Finally, a theoretical analysis of the adsorption of pyridine over the surface of the PSM MOF is made.

Thermograms from samples of ZrBTC-114.6 before and after the post-synthetic modification, ZrBTC-114.6-S, are shown in Figure 22. In general, the performed analysis indicated that the thermal stability of the material increased after PSM. On the other hand, ZrBTC-114.6-S showed a 13% less of weight loss than the untreated parent materials in Region I of the thermogram. As it was showed in the previous

section, this region reflects changes in surface area and porosity. Therefore, the PSM MOF is expected to have a reduction in both its total pore volume and surface area as compared with the untreated sample. This is consistent with the occupation of its free volume by sulfate groups. Concerning the thermal decomposition of the organic structure, Region II, the PSM MOF was relatively more stable than its untreated counterpart; namely, ZrBTC-114.6-S lost ca. 8% less of weight loss than ZrBTC-114.6. Such behavior hints to the replacement of acetate ions by sulfates which are more thermally stable (Alhassan, Rashid, Al-Qubaisi, Rasedee, & Taufiq-Yap, 2014; Constantino & Pinnavaia, 1995). Finally, regarding the decomposition of the inorganic part of the materials, ZrBTC-114.6-S exhibited a higher, ca. 10%, weight loss than the unmodified material. This result is coherent with the proposal of the replacement of acetate ions by sulfates.

The argon adsorption-desorption isotherms and the corresponding χ -plots for ZrBTC-114.6 and ZrBTC-114.6-S are shown in Figure 29. After PSM, the isotherm of the material changed. The hysteresis loop became most like a type H4 one (Thommes et al., 2015), in which the adsorption branch resembles a combination of Types I and II isotherms and the lower limit of the desorption branch is usually located at the cavitation-induced relative pressure. This behavior suggests that mesopores became clogged by sulfate groups hence inducing pore blocking and cavitation effects. Furthermore, the pore size distribution, Figure 24, of ZrBTC-114.6-S was starkly different from the one calculated for ZrBTC-114.6.

Particularly, mesopores were enlarged while the family of micropores with an average size of 1.53 nm disappeared. These trends were consistent with the surface areas calculated through the χ -method, Table 5. Indeed, the total surface area of the

PSM MOF decreased ca. 33 % ($SA_{\chi} = 704 \text{ m}^2/\text{g}$) as compared to ZrBTC-114.6 ($SA_{\chi} = 1050 \text{ m}^2/\text{g}$). Furthermore, the surface area corresponding to microporous from the family with an average size of 1.53 nm amounted to zero whereas the mesoporous surface area dropped ca. 83%.

Also, the total pore volume exhibited a reduction of ca. 54 % after PSM. These results suggest that sulfate ions are hindered from entering ultramicropores in Zr-MOFs. It also suggests that the families of pores corresponding to the largest micropores and the mesopores of the synthesized MOFs are not connected to the ultramicropores of the materials. The latter proposal is partly supported by the fact that PSM did not change the surface area of the ultramicropores. Figure 31 illustrates the above proposals. The results reported herein differ from previous literature (Juncong Jiang et al., 2014) showing that there was no effect of performing the same sulfuric acid based PSM for a parent MOF-808. However, the MOF was fully crystalline and fully microporous according to the authors (Juncong Jiang et al., 2014). Thus, in principle, only the external surface of that material could be sulfated since the sulfate ions would not access its internal structure.

After the post-synthetic modification process, the crystallinity of the treated material decreased by ca. 37% (Figure 25). Indeed, almost all the peaks displayed by ZrBTC-114.6 disappeared from the diffractogram except for the one assigned to the (2 2 2) plane. This trend, along with the changes found for the thermal stability and porous structure of ZrBTC-114.6-S, suggests that the material was chemically attacked by sulfuric acid during PSM. In this regard, Trickett et al. (Trickett et al., 2018) determined that sulfate groups in MOF-808 are coordinated in both a bridging and chelating mode to the zirconium nodes in a similar fashion to previously reported

sulfated zirconia (Ben Chaabene, Bergaoui, Ghorbel, Lambert, & Grange, 2004; Hammache & Goodwin, 2003). MOFs synthesized from high-valent metal ions such as zirconium and carboxylate ligands have been reported as stable materials in aqueous acidic conditions (Morris et al., 2012; Piscopo et al., 2015). This suggests that our conclusions may not apply to some other defective microporous/mesoporous Zr-MOFs. One may argue that the defects of the material promote the degradation of their inner crystalline structure during the PSM process due to a competition between protons and metal ions for the coordination with the organic ligand (Yuan et al., 2018). Furthermore, there is a probability that an additional sulfonation of the aromatic ligands may occur. In this sense, Hajipour et al. (Hajipour, Mirjalili, Zarei, Khazdooz, & Ruoho, 2004) reported the sulfonation of aromatic structures using silica sulfuri acid as a catalyst and under mild reaction conditions. As discussed later, there is experimental evidence to support the sulfonation hypothesis.

Figure 29

(a) Argon adsorption-desorption isotherms of MOF ZrBTC-114.6 without and with PSM, in all range of the linear P/P_o . (b) χ -method adsorption/desorption isotherms of the same materials.

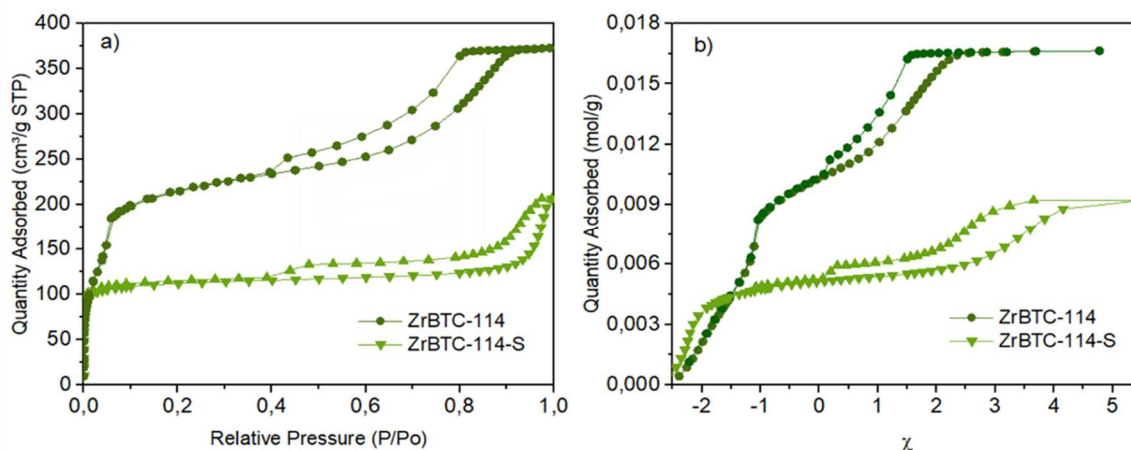
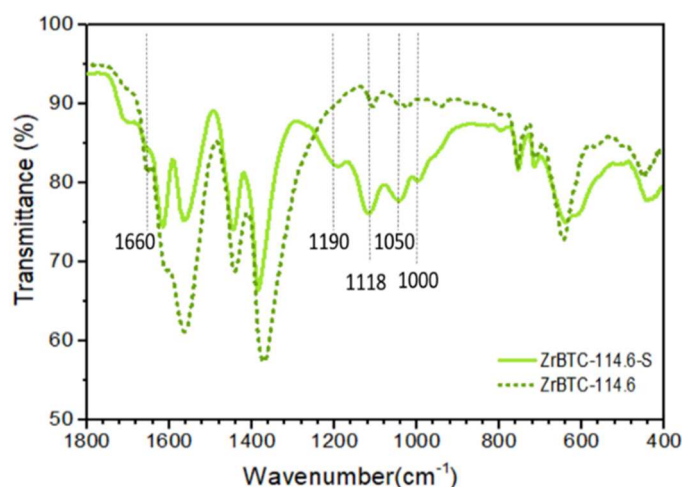


Figure 30

Infrared spectra zoom-in between 1800 and 400 cm^{-1} of synthesized MOFs ZrBTC-114.6 before and after the PSM.

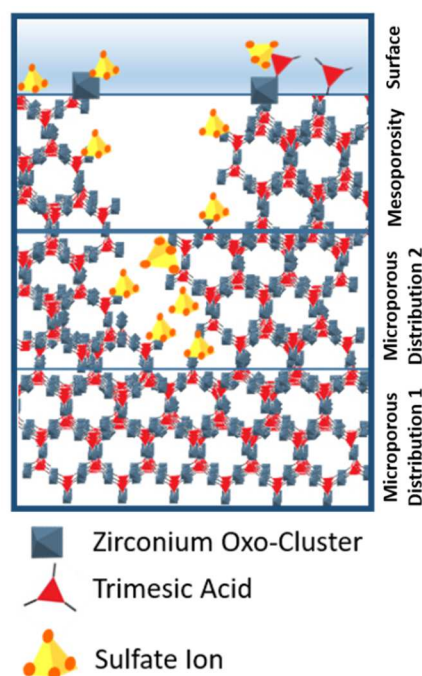


FTIR spectra for ZrBTC-114.6-S is shown in Figure 30. After the post-synthetic modification process, the characteristic functional groups of the current Zr-MOFs were preserved. However, a decrease in the intensity of the bands assigned to the coordinated acetates was observed. Conversely, an additional band from 1000 to 1200 cm^{-1} was recorded for ZrBTC-114.6-S. This band was assigned to sulfate functional groups. Jiang et al. (Juncong Jiang et al., 2014) found evidence for metal-bound sulfate groups with bands observed between 800 and 1500 cm^{-1} in the spectra of sulfated MOF-808. On the other hand, Chen et al. (J. Chen et al., 2014a) obtained sulfonic acid-functionalized MOFs and reported bands for the symmetric and asymmetric stretching modes of $\text{O}=\text{S}=\text{O}$ at 1137 and 1294 cm^{-1} , respectively. Therefore, FTIR spectra recorded for ZrBTC-114.6-S support the hypothesis of a

chemical attack of the structure of the material leading to both sulfation and sulfonation.

Figure 31

Proposed structure of the sulfated material. The defective structure seems to be interconnected from the external surface to the second microporous distribution. However, the first microporous distribution seems to be isolated.



The relative concentration of the elements and the components found on the surface of the synthesized materials is presented in Table 6. In agreement with a previous report (Ardila Suárez, Rodríguez Pereira, et al., 2019), the presence of traces of nitrogen could be related to the deposition of residual dimethylamine from the hydrolysis of the DMF solvent (Shearer et al., 2016). The empirical formulas for the

surface of ZrBTC-114.6 and ZrBTC-114.6-S were $\text{CO}_{0.825}\text{Zr}_{0.166}\text{N}_{0.002}$ and $\text{CO}_{1.432}\text{Zr}_{0.286}\text{N}_{0.005}\text{S}_{0.145}$, respectively. Both these formulas differ from what has been reported for pure crystalline MOF-808. Indeed, Furukawa et al. (Hiroyasu Furukawa et al., 2014) estimated that the latter has the formula $\text{CO}_{1.848}\text{Zr}_{0.25}\text{H}_{0.25}$. Accordingly, the defective MOFs synthesized herein have an oxygen deficiency at the surface of ca. 55 % and a deficiency of ca. 34 % of zirconium. The same kind of behavior was found before for a series of Zr-MOFs prepared from various zirconium precursors (Ardila Suárez, Rodríguez Pereira, et al., 2019). Concerning ZrBTC-114.6-S, Jiang et al. (Juncong Jiang et al., 2014) reported that a parent purely crystalline MOF 808 submitted to the same PSM yielded the chemical formula: $\text{CO}_{1.736}\text{Zr}_{0.330}\text{H}_{0.714}\text{S}_{0.127}$. In this case, the sulfated material synthesized herein exhibited lower oxygen, ca. 18 %, and zirconium, ca. 13 %, concentrations at the surface.

Table 6

C 1s, O 1s, Zr 3d, S 2p and N 1s peaks contributions concentration C 1s, O 1s, Zr 3d, S 2p and N 1s peaks contributions concentration for ZrBTC-114.6 and ZrBTC-114.6-S materials. The species are coded as C-Ar: Carbon belonging to an aromatic ring, Ar-(C-O)-Zr, C-NH₃: Carbon from the carboxylic acid group linked to the Zr cluster, Ar-Carboxy: carbon belonging to the carboxylic acid group of H₃BTC, Aliph-Carboxy: Carbon from the carboxylic acid group linked to an aliphatic chain. Zr-O: oxygen linked to Zr in the inorganic cluster, R-(C=O)-OH: oxygen belonging to a carboxylic acid functional group, C-O-Zr: oxygen belonging to the C-O-Zr bonds. Zr-O: zirconium belonging to the inorganic cluster and, Zr-O-C: zirconium coordinated to an organic group through oxygen. For sulfated sample additional species are noted as C-S-O: Carbon belonging to the sulfonic group, Zr-O/ S-O, oxygen belonging to zirconium oxo-cluster or sulfate group, Zr-O-S, zirconium linked to the sulfate group

and the sulfur species: $\underline{\text{S}}\text{-O-Zr}$, $\text{O-}\underline{\text{S}}\text{-C}$ and $\underline{\text{S}}_{\text{free}}$ that corresponds to sulfur belonging to the sulfate group, to the aromatic sulfonation and free sulfur, respectively.

Relative Molar %	Sample	
	ZrBTC-114.6	ZrBTC-114.6-S
C 1s		
$\underline{\text{C}}\text{-Ar}$	24.38	12.29
$\text{Ar-(}\underline{\text{C}}\text{-O)-Zr, } \underline{\text{C}}\text{-NH}_3$	5.83	6.62
$\underline{\text{C}}\text{-S-O}$	-	1.51
$\text{Ar-}\underline{\text{C}}\text{arboxy}$	9.91	9.79
$\text{Aliph-}\underline{\text{C}}\text{arboxy}$	10.05	4.65
Total	50.17	34.86
O 1s		
$\text{Zr-}\underline{\text{O}}/\text{S-}\underline{\text{O}}$	4.62	16.76
$\text{R-(C=}\underline{\text{O}}\text{)-OH}$	31.75	21.71
$\text{C-}\underline{\text{O}}\text{-Zr}$	5.02	11.45
Total	41.39	49.92
Zr 3d		
$\underline{\text{Zr}}\text{-O}$	5.55	3.97
$\underline{\text{Zr}}\text{-O-C}$	2.82	2.49
$\underline{\text{Zr}}\text{-O-S}$	-	3.52
Total	8.37	9.98
S 2p		
$\underline{\text{S}}\text{-O-Zr}$	-	1.55
$\text{O-}\underline{\text{S}}\text{-C}$	-	1.84
$\underline{\text{S}}_{\text{free}}$	-	1.68
Total	-	5.07
N 1s		
N 1s	0.08	0.18
Empirical formula (Surface)*	$\text{CO}_{0.825}\text{Zr}_{0.166}\text{N}_{0.002}$	$\text{CO}_{1.432}\text{Zr}_{0.286}\text{N}_{0.005}\text{S}_{0.145}$

In contrast, the defective MOF presented herein showed a higher concentration (ca. 15%) of sulfur at its surface as compared to the one synthesized by Jiang et al. (Juncong Jiang et al., 2014). Such differences remark how the chemistry of the surface of defective MOF-808 differs from that of the pure crystalline material.

The decomposition of the C 1s, O 1s, Zr 3d, N 1s, and S 2p peaks recorded for samples ZrBTC-114.6 and ZrBTC-114.6-S are displayed in Figure 32. In general,

strong peak widening was observed on all the high-resolution spectra after the post-synthetic modification process. Such a feature is a symptom of differential charging effects occurring during XPS (Cazaux, 1999, 2000). Differential charging can be caused by both electronic and geometric factors (Baldovino-Medrano, Ospina, & Gaigneaux, 2019; Landoulsi et al., 2016) and is considered a nuisance for identifying true chemical shifts in XPS. Despite all efforts, this effect could not be prevented under the current analysis conditions. However, peak decomposition was carried out following the methodology reported earlier (Ardila Suárez, Rodríguez Pereira, et al., 2019) strictly aiming to make a qualitative assessment of the spectra. Taking the latter into account, values for the relative concentrations of the chemical species presented in Table 6 for the sample of ZrBTC-114.6-S are considered to be somehow inaccurate but valid for a qualitative comparison with those calculated for ZrBTC-114.6 over which charging effects were effectively controlled. Stoichiometric ratios between the chemical species considered for peak decomposition (Dufrêne et al., 1999; Rouxhet & Genet, 2011) were further calculated and are shown in Table 7. These ratios allow checking the consistency of the proposed decomposition as well as detecting changes in the chemistry of the surface (Ardila Suárez, Rodríguez Pereira, et al., 2019). For the untreated ZrBTC-114.6, the estimated molar ratios for the different chemical species had a fair agreement with the values expected from stoichiometry (Ardila Suárez, Rodríguez Pereira, et al., 2019). First, the $\frac{\text{C-Ar}}{\text{Ar-Carboxy}}$ ratio, which refers to the proportion between the carbon atoms of the aromatic ring of H₃BTC and those of the carboxylate functional groups in H₃BTC, was 1.55 which is close to the expected stoichiometry of 2.0 between these species. Second, the ratio "Free"- $\frac{[\text{C-Ar}]}{[\text{Carboxy}]}$; referred to the quotient between the components ascribed to free

carboxylate species, i.e. $[(\text{Ar}-\underline{\text{C}}\text{arboxy})+\text{Aliph}-\underline{\text{C}}\text{arboxy}]/[\text{R}-(\text{C}=\underline{\text{O}})-\text{OH}]$, was 0.63 which is also close enough to a stoichiometric ratio of 0.5 representative of the proportion between the carbon and oxygen atoms participating in a carboxylic acid functional group. Third, the $[\text{Ar}-(\text{C}-\text{O})-\underline{\text{Zr}}]/[\text{Ar}-(\underline{\text{C}}-\text{O})-\text{Zr}, \underline{\text{C}}-\text{NH}_3]$ ratio; representing the proportion between zirconium and carbon in a coordinated cluster, corresponds to the quotient: $[\text{Ar}-(\text{C}-\underline{\text{O}})-\text{Zr}]/\{[\text{Ar}-(\underline{\text{C}}-\text{O})-\text{Zr}]-[2\times\text{C}-\underline{\text{NH}}]\}$ where the contribution from the organic nitrogen species was subtracted after decomposing the N 1s peak.

Table 7

Estimated molar ratios for the chemical species of ZrBTC-114.6 and ZrBTC-114.6-S MOFs.

Species molar ratios	Sample	
	ZrBTC-114.6	ZrBTC-114.6-S
$\underline{\text{C}}-\text{Ar}/\text{Ar}-\underline{\text{C}}\text{arboxy}$	1.55	0.75
"Free"- $[\underline{\text{C}}\text{arboxy}/\text{Carb}\underline{\text{O}}\text{xy}]$	0.63	0.52
Coordinated		
$[\text{Ar}-(\underline{\text{C}}-\text{O})-\text{Zr}]/[\text{Ar}-(\text{C}-\underline{\text{O}})-\text{Zr}]$	0.51	1.21
$[\text{Ar}-(\text{C}-\text{O})-\underline{\text{Zr}}]/[\text{Ar}-(\underline{\text{C}}-\text{O})-\text{Zr}, \underline{\text{C}}-\text{NH}_3]$	0.57	0.26
$[\text{Ar}-(\text{C}-\text{O})-\underline{\text{Zr}}]/[\text{Ar}-(\text{C}-\underline{\text{O}})-\text{Zr}]$	0.56	0.22
Inorganic		
$\underline{\text{Zr}}-\text{O}/\text{Zr}-\underline{\text{O}}$	0.61	0.33
Sulfur-containing groups		
$\underline{\text{Zr}}-\text{O}-\text{S}/\text{Zr}-\text{O}-\underline{\text{S}}$	-	2.27
$\underline{\text{C}}-\text{S}-\text{O}/\text{O}-\underline{\text{S}}-\text{C}$	-	0.82

The calculated ratio was 0.57 which is close enough to the 0.5 ratio imposed by stoichiometry. The same kind of comparisons can be made for the rest of the ratios designated for the representative chemical species of the synthesized Zr-MOF. After PSM, the molar ratios for the carbon atoms of the aromatic ring of H₃BTC and those

of the carboxylate functional groups in H₃BTC (C-Ar/Ar-CCarboxy), the zirconium and carbon ([Ar-(C-O)-Zr]/[Ar-(C-O)-Zr,C-NH₃]) and oxygen ([Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]) in a coordinated cluster, and the zirconium and oxygen (Zr-O/Zr-O) in the inorganic moieties of the studied MOF decreased. Meanwhile, the ratio between carbon and oxygen implied by the organic coordinated zirconium clusters ([Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]) increased, whereas the ratio between carbon and oxygen in the free carboxylates remained rather constant. On the other hand, the presence of surface species related to the formation of sulfate zirconium species and sulfonated organic moieties was evidenced (Table 6), and the ratios between zirconium and sulfur (Zr-O-S/Zr-O-S) for the former and carbon and sulfur (C-S-O/O-S-C) for the latter estimated. The calculated value for the ratio Zr-O-S/Zr-O-S is close to the expected stoichiometric ratio of 2 in sulfated zirconia. Conversely, the value of the (C-S-O/O-S-C) ratio was fourfold higher than the one expected for sulfonated aromatic rings; ca. 0.17, hence suggesting that other kind of carbon species are involved in this type of chemical bonding. According to these results, the modification process with sulfuric acid applied to the defective Zr-MOF synthesized herein causes a strong modification of the chemistry of the surface of the material. Furthermore, the induced chemical modification is far from being as selective as expected from works performed on fully crystalline Zr-MOFs (Hiroyasu Furukawa et al., 2014; W. Liang et al., 2014). This is because a mixture of zirconium sulfates, sulfonated organic moieties, and even free sulfur species were present at the surface of ZrBTC-114.6-S. The susceptibility of the surface of ZrBTC-114.6 to a chemical attack by sulfuric acid is coherent with the aforementioned changes in its thermal stability, porous structure, and crystallinity.

Figure 33 features the FTIR spectra of adsorbed pyridine over ZrBTC-114.6 and ZrBTC-114.6-S. Both spectra exhibited vibrations from C-O-Zr, Zr-O, C=C, and C-O bonds (Atzori et al., 2017; Shearer et al., 2016). They also showed a weak band in the region between $1480\text{--}1420\text{ cm}^{-1}$ that corresponds to the C=C bonds in the aromatic ring of the organic linker (Wißmann et al., 2012), and bands in the region between $750\text{--}655\text{ cm}^{-1}$ (not shown) attributed to the asymmetric vibration of the Zr- ($\mu_3\text{-O}$) bridges in the framework building blocks (Piszczyk et al., 2007). These bands serve to corroborate the molecular structure of the Zr-MOFs. Additional peaks in the spectra were found between $1400\text{ and }1800\text{ cm}^{-1}$ after the adsorption of pyridine. Despite the overlapping of the bands from pyridine, the carboxylate groups, and the aromatic ring of the organic linkers of the MOFs (Juncong Jiang & Omar M. Yaghi, 2015), small shoulders at 1650 , 1620 , and 1450 cm^{-1} were detected for the unmodified MOF material after adsorbing the probe molecule.

Figure 32

C 1s, O 1s and, Zr 3d peaks decomposition recorded in XPS analysis of MOFs (a,b,c) ZrBTC-114.6 and (d,e,f) ZrBTC-114.6-S, respectively. N 1s peak decomposition of MOFs (g) ZrBTC-114.6 and (h) ZrBTC-114.6-S, respectively. S 2p peak of ZrBTC-114.6-S is shown in (i).

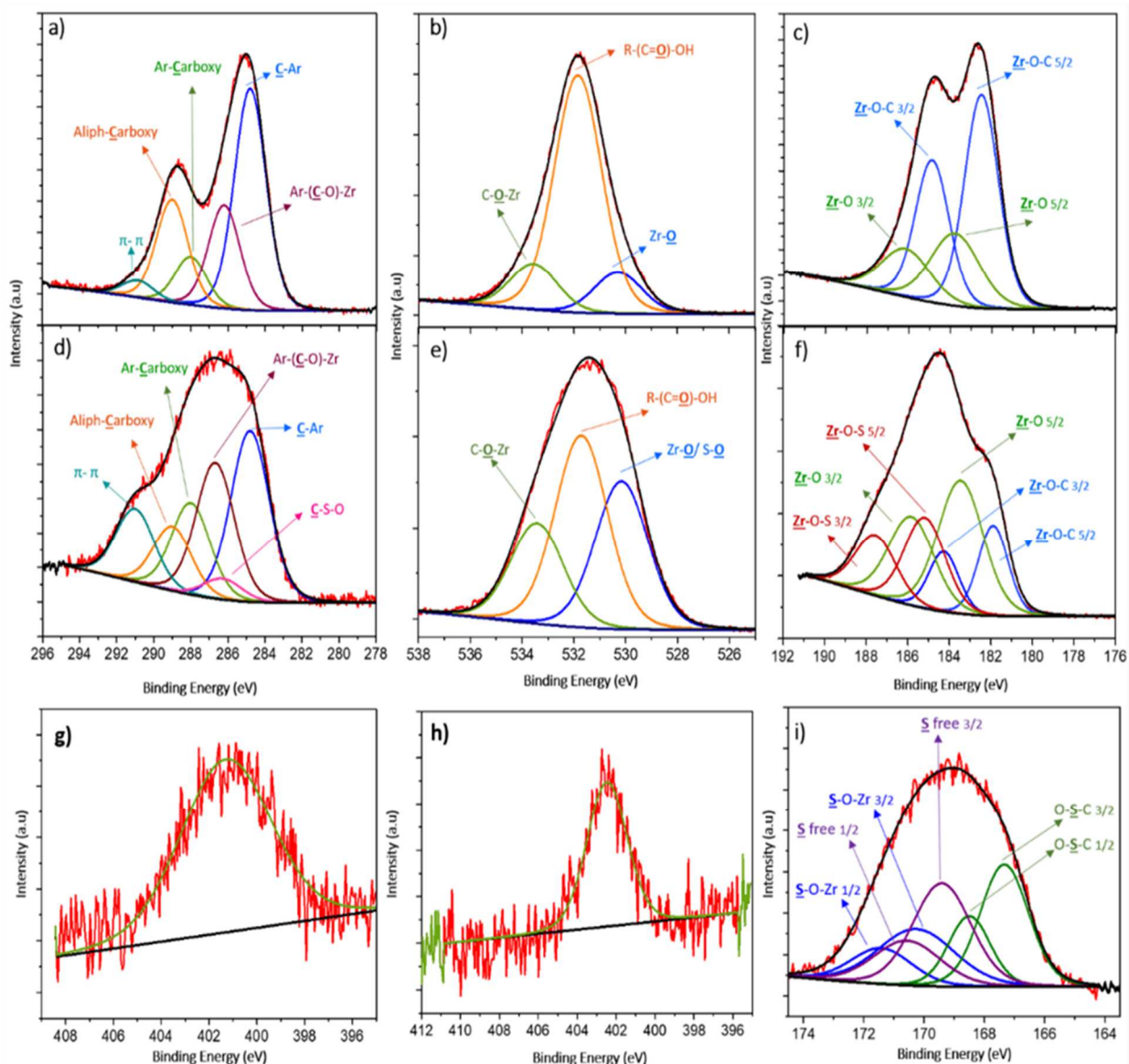
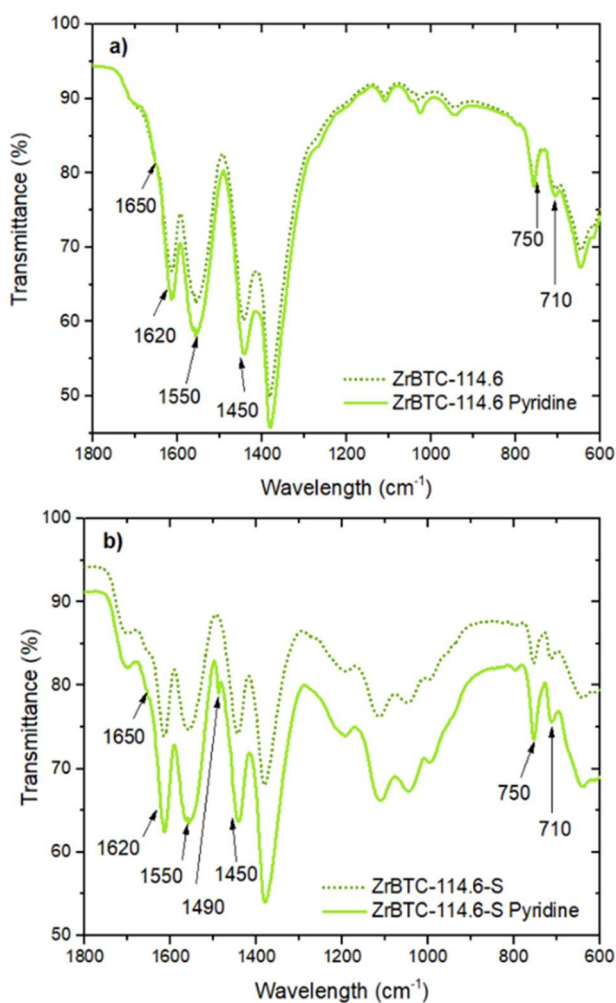


Figure 33

Infrared Spectra of (a) ZrBTC-114.6 and (b) ZrBTC-114.6-S samples with and without pyridine impregnation.

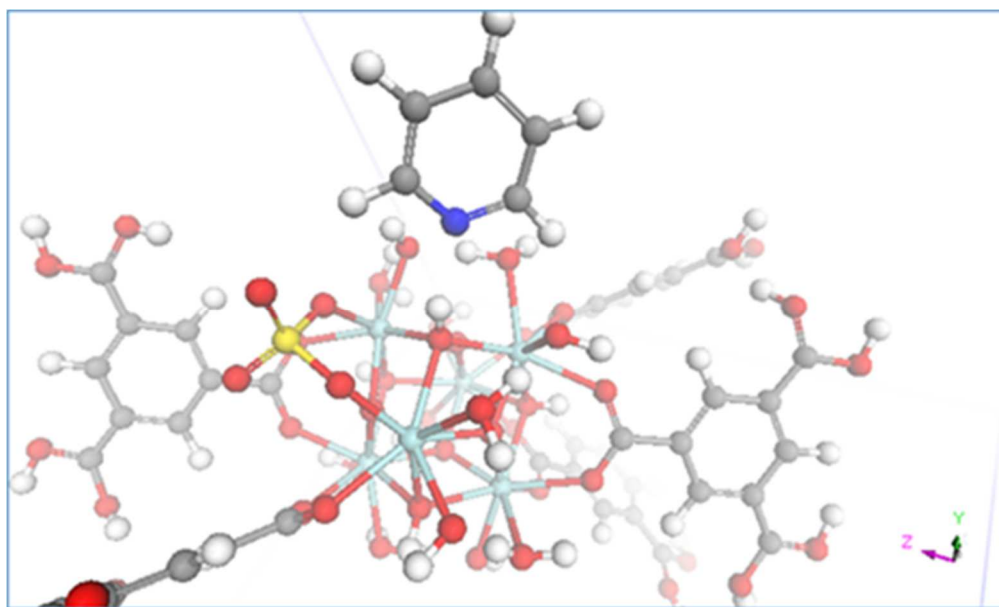


Therefore, pyridine was interacting with acid sites on the surface of ZrBTC-114.6. For the PSM sample, the signals of the shoulders mentioned above were more intense. Furthermore, two additional bands located around 1450 and 1620 cm^{-1} ; usually assigned to Lewis acid sites (Reddy et al., 2009; Weglarski, Datka, He, & Klinowski, 1996), were found. These bands could be related to unsaturated metal clusters (Babou,

Coudurier, & Védrine, 1995) whose catalytic activity on the esterification of carboxylic acids with several alcohols has been tested (Cirujano et al., 2015a, 2015b). Bands at 1550 and 1650 cm^{-1} also appeared. They were ascribed to pyridine interacting with Brønsted acid sites (Castellà-Ventura, Akacem, & Kassab, 2008; Jacobs & Von Ballmoos, 1982). Klet et al. (Klet et al., 2016b) determined; through potentiometric acid-base titration, the presence of Brønsted acidity in MOF-808. Finally, a peak found at 1490 cm^{-1} appeared after pyridine adsorption over ZrBTC-114.6-S. This peak was attributed to the adsorption of the probe over both Lewis and Brønsted sites (Chakraborty & Viswanathan, 1999; Zaki et al., 2001).

Figure 34

Pyridine molecule adsorbed on Brønsted acid site of sulfated MOF-808. Color code: C, grey; O, red; H, white; Zr, cyan; S, yellow and N, blue.



Theoretical assessment of the adsorption of pyridine

DFT calculations for the adsorption of pyridine over a sulfated MOF-808 cluster were carried out. Particularly, pyridine adsorbed on a Brønsted site from this cluster as it is shown in Figure 34. The calculations showed the formation of a hydrogen bond between the nitrogen atom of pyridine and the hydrogen atom of the hydroxyl group proposed as a Brønsted acid site, see Figure 30. The calculated C-H stretching vibration of pyridine in the gas phase was 1465 cm^{-1} . Once the pyridine molecule was adsorbed, this vibrational frequency shifted to 1496 cm^{-1} .

Such a shift is characteristic of the formation of a surface bonded complex formed between pyridine and a proton moiety and usually denoted as usually denoted as PyH^+ in studies devoted to the analysis of the acidic properties of zeolites (Buzzoni et al., 1996; Castellà-Ventura et al., 2008), silica (Parry, 1963), and sulfated zirconia (Stevens, Chuang, & Davis, 2003). After relaxation, the adsorption energy of pyridine on the sulfated cluster was -0.56 eV . This adsorption energy is comparable to the adsorption energy calculated for pyridine hydrogen bonded to a Brønsted site in a zeolite (Castellà-Ventura et al., 2008). It has been suggested that the donation ability of the hydroxyl group was strengthened by the electron-inductive effect of the $\text{S}=\text{O}$ bonds of the sulfate group (Ben Chaabene et al., 2004). Furthermore, the theoretical vibrational frequency calculations of adsorbed pyridine on sulfated MOF-808 agreed with the experimental FTIR spectra for the PSM treated Zr-MOF.

3.5. Conclusions

This study analyzed the effect of varying the concentration of acetic acid used as modulator during the synthesis of defective Zr-MOFs of the MOF-808 type. The key findings in this regard were: (i) all the synthesized materials displayed a certain degree of amorphicity related to the formation of a mesoporous structure. (ii) Increasing the concentration of the employed modulator promoted the formation of a more crystalline structure without affecting the thermal stability of the material. At the same time, the porous structure of the materials was also modified as a function of the concentration of the modulator. Particularly, wider and more numerous mesopores were formed at the highest acetic acid concentration without affecting the relative proportion between the two families of micropores belonging to the inner structure of the material. (iii) Evidence suggests that the activation stage of the materials synthesis encompasses the removal of adsorbed water and organic linkers replaced by molecules of the modulator.

On the other hand, an analysis of the effects produced by performing a conventional post-synthetic modification with sulfuric acid of a selected sample from the synthesized defective Zr-MOFs led to conclude the following: (i) sulfuric acid chemically attack the surface structure of the defective Zr-MOF leading to a sulfation of the Zr moieties and to a sulfonation of the organic functional groups in addition to depositing residual sulfate ions on the surface. (ii) The attack performed by sulfuric acid enhanced the thermal stability of the Zr-MOF, but it degraded its porous and crystalline structure. The collected evidence for the PSM treated Zr-MOF suggested that only the families of mesopores and the larger micropores are interconnected within the material. Therefore, the ultramicropores in the defective Zr-MOF seemed

isolated from the rest of the porous structure. (iii) Finally, the PSM procedure led to the formation and enhancement of both Lewis and Brönsted surface acid sites in the studied Zr-MOFs.

4. Synthesis of Ordered Microporous/Macroporous MOF-808 through Modulator-Induced Defect-Formation, and Surfactant Self-Assembly

4.1. Overview

Ordered materials with interconnected porosity allow the diffusion of molecules within their inner porous structure to access the active sites located in the microporous core. As a follow-up of our work on engineering of MOF-808, in this contribution, we study the synthesis of defective MOF-808 using two different strategies: the use of modulators and the surfactant-assisted synthesis to obtain materials with ordered and interconnected pores. The results of the study indicated that (i) the use of modulators of different chain length led to the formation of microporous/mesoporous MOFs through the formation of missing linker defects. However, the use of the acetic acid contributes to the formation of MOFs with larger mesoporous size distributions compared to materials synthesized with formic and propionic acids as modulators, and (ii) the self-assembly of CTAB surfactant produced ordered microporous/macroporous network which enhanced crystallinity. However, the surface properties of the materials seem to be unaffected by the use of surfactants during synthesis. These results contribute to the development of ordered materials with a broad range of pore size distributions and give rise to new opportunities to extend the applications of MOF-808.

4.2. Experimental Section

Materials

MOFs were synthesized with the following reagents. Zirconium precursor: zirconium chloride, ZrCl_4 (98%), from Merck. The organic ligand, Benzene-1,3,5-tricarboxylic acid (H_3BTC , 95%), and the surfactant hexadecyltrimethylammonium bromide, CTAB (>98%) were obtained from Sigma-Aldrich. The solvent N, N-dimethylformamide (99.8%), the modulators: formic acid (98 -100%), acetic acid (99.8%) and propionic acid (99%) and the washing solvents: acetone (99.8%) and methanol (99.9%) were all purchased from Merck. Reactants were used as received.

Synthesis of the materials

Zirconium MOFs were synthesized using a solvothermal method based on a modification of the synthesis reported by Liang et al. [9]. Typically, 9.99 mmol of zirconium chloride was put in a 250 mL screw-capped glass jar reactor. Then, 98 equivalents (related to the zirconium precursor) of modulator agent (formic, acetic or propionic acid) and 80 mL of DMF were introduced in the reactor, and the solution was stirred. After 20 min, 3.34 mmol of H_3BTC and the required amount of CTAB (0, 3.34 or 6.67 mmol) (S. Hu et al., 2017) were dissolved in 120 mL of DMF and added dropwise to the solution containing the dissolved zirconium precursor. The mixture was stirred for an additional 15 min and later sonicated for 30 min. The resulting mixture was distributed among twenty 50 mL screw-capped glass jar reactors and remained at 25°C for 24 h and after that at 120°C for an additional 24 h. After cooling down to room temperature, the contents of the reactors were combined, and the as-

synthesized MOFs were recovered by filtration and washed twice with DMF, twice with water, and twice with acetone. The resulting powder was dried at 120°C for 12 h. An activation procedure was performed overnight at 120°C under a vacuum pressure of 0.06 mbar. The materials synthesized using formic, acetic, and propionic acid as modulators were named as ZrBTC-F, ZrBTC-A, and ZrBTC-P, respectively. Furthermore, the materials synthesized by adding the CTAB surfactant were named as ZrBTC-AER (R = the CTAB: H₃BTC molar ratio = 1 or 2). Under the above conditions, the yields for the syntheses were 38.2 ± 10.9 , 54.6 ± 1.34 , 42.8 ± 3.07 , 55.1 ± 1.18 , and 75.6 ± 5.25 % for ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2, respectively. These yields are based on the overall weight of the ligand and of the metallic salt (Z. Hu, Peng, Kang, Qian, & Zhao, 2015).

Assessment of the physicochemical properties of ZrBTC MOFs

The thermal stability, morphology porous structure, crystallinity, molecular structure, and surface chemistry of the materials were assessed. Thermal stability was studied by recording thermal gravimetric analysis profiles. Tests were performed in a Discovery 5500 TA instrument. Samples were heated to 900 °C at a rate of 5°C/min under an air (Linde, 4.7, 99.997% purity) flow of 25 mL/min. Morphology was studied by recording scanning electron microscopy images in a Quanta FEG 650 equipment. The acceleration voltage was set to 2.5 kV through an everhart Thornley detector (secondary electrons detector). Samples were prepared by spreading them on a carbon tape in a Quorum 150ES equipment. Also, transmission electron microscopy images were recorded with a Philips CM200 microscope operating at 200 kV and equipped with an Energy-dispersive X-ray spectrometer. The porosity and surface of the materials were evaluated after recording Ar adsorption-desorption isotherms at 87 K using a 3Flex (Micromeritics) apparatus. The relative pressure range went from 1.82×10^{-5} to 0.995, with equilibrium intervals of 10 s. Isotherms for the materials were

recorded twice in independent experiments. Before measurements, the materials were degassed at a temperature of 120°C under vacuum for 12 h. Surface area calculations were performed using the methods based on the χ theory (James B Condon, 2006). For some selected materials that were post-synthetically modified, pore connectivity was tested according to our previous work (Juncong Jiang et al., 2014). The test consists on performing a sulfation procedure, which is like the one proposed by Jiang et al. (Juncong Jiang et al., 2014) followed by an assessment of porosity by Ar physisorption. For sulfation, 50 mg of the synthesized material is treated with 50 mL of 0.05 M sulfuric acid (2.5 mmol) for 24 h. The supernatant liquid is then solvent exchanged with 50 mL of water for three days changing the water once a day. Afterward, the liquid is quickly exchange with 50 mL of acetone, and the recovered solid is immersed in 50 mL of chloroform for three days. During this time, chloroform was exchanged once per day. The crystalline structure of the materials was assessed by recording X-ray diffraction patterns with a Bruker AXS D8 Advance DaVinci geometry instrument equipped with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). This instrument was operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ value range from 3.0 to 50.0° (with a step time of 0.6 s). For gaining further insight into the molecular structure of the materials, we wanted to identify and quantify the concentration of the modulators coordinated to the zirconium node. This was made by dissolution/¹H NMR spectroscopy. For this purpose, MOFs are digested in a deuterated medium (Shearer et al., 2016). During the experiment, hydroxide ions digest the organic part of the MOF, i.e., the organic linker, the modulator, and the solvent that may still be trap inside the pores of the materials. The digested product can thence be analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy, while the inorganic component, namely ZrO₂, of the material precipitates. Further details for this experiment are included in Section D-1.1. of the

Supporting information. Liquid ^1H NMR spectra were recorded on a Bruker Ultrashield 400 MHz (Avance III, 400) using a relaxation delay (D1) of 20 s and 64 scans (Shearer et al., 2016). The identification of functional groups of the as-synthesized and modified MOFs was performed by Infrared spectroscopy on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. The surface chemistry of the materials was analyzed by X-ray photoelectron spectroscopy. Analyses were performed in the XPS/ISS/UPS-A.Centeno surface characterization platform (SPECS). The platform is provided with a PHOIBOS 150 2D-DLD energy analyzer package. A monochromatized Al $K\alpha$ X-ray source (Focus 500) operated at 100 W was employed. The pressure in the analysis chamber was approximately 1×10^{-7} Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 54° . Samples were mounted on carbon conductive tape over metallic sample holders for analysis. Surface charge compensation was controlled with a flood gun (FG 15/40-PS FG500 device) operated at 58 μA and 1.0 eV. Spectra were collected in the Fixed Analyzer Transmission mode. The spot area for analyses was $3.5 \times 1.0 \text{ mm}^2$. The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and to 15 eV for high-resolution spectra. The energy step for the acquisition was set to 0.050 eV. General spectra were recorded first for all samples followed by high-resolution spectra. The C 1s peak was recorded both at the beginning and the end of the measurements for checking the evolution of surface charge during the analyses. High-resolution spectra were recorded following elements identification in the general spectra and according to samples chemistry and history. Data analysis was performed with the CasaXPS program (Casa Software Ltd) using the SPECS Prodigy library for R.S.F. values. A U 3 Tougaard baseline (J. Walton et al., 2016) was employed for background modeling together with a Lorentzian line shape, LA(1.53,243) in CasaXPS, for peak decomposition. The peak decomposition for the quantification of surface chemical

species was performed according to our previous works (Ardila Suárez, Díaz, et al., 2019; Ardila Suárez, Rodríguez Pereira, et al., 2019). For the C 1s peak, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) Carbon belonging to an aromatic ring, labeled as C-Ar. Under the analysis conditions employed herein, this component is indistinguishable from the peak from the C-(C,H) species from aliphatic hydrocarbons. In consequence, a single component centered at 284.8 eV (Rouxhet & Genet, 2011) was assumed for both species. This component was employed as a reference for correcting the BE scale of the spectra (Rouxhet & Genet, 2011). (ii) Carbon from the carboxylic acid group linked to the Zr cluster labeled as Ar-(C-O)-Zr, [286.14, 286.54] eV. (iii) Carbon belonging to the carboxylic acid group of H₃BTC, labeled as Ar-Carboxy. Based on literature references (Genet et al., 2008; Rouxhet & Genet, 2011), Ar-Carboxy was fixed at 288.0 eV. (iv) Carbon from the carboxylic acid group linked to an aliphatic chain labeled as Aliph-Carboxy and fixed at 289.0 eV (Genet et al., 2008). An additional peak corresponding to the $\pi - \pi^*$ from the aromatic ring was considered for peak decomposition (Briggs & Beamson, 1992), [290.6, 291.0] eV. For this component, the R.S.F. was set to 0 for quantification. The same FWHM was considered for all carbon species and the $\pi - \pi^*$ transition peak. For the O 1s peak, three species were considered. The first was oxygen linked to Zr in the inorganic cluster, labeled O-Zr, [530.5, 531.2] eV. The second was oxygen belonging to a carboxylic acid functional group, [531.9, 532.4] eV. In the O 1s peak, this component, labeled as R-(C=O)-OH, cannot be further decomposed into carboxylates linked to an aromatic or aliphatic chain (Rouxhet & Genet, 2011). The third oxygen component, [533.8, 534.2] eV, was ascribed to oxygen belonging to the Zr-O-C bonds in the MOF. This proposal is coherent with the BE shifts expected when comparing the parent carbon components described before, in the sense that if the corresponding carbon is more oxidized,

the oxygen must be more reduced. No constraints were imposed during peak decomposition except for assuming the same FWHM for all components. Finally, for the Zr 3d peak, two species were considered. The first was Zr coordinated to an organic group through oxygen, labeled Zr-O-C, the Zr 3d_{5/2} peak = [181.6, 182.5] eV, and the second Zr belonging to inorganic clusters, the Zr 3d_{5/2} peak = [182.0, 183.0], labeled Zr-O. The above BE assignment was also made considering the relative BE shifts expected from the corresponding oxygen and carbon components. The following constraints were imposed during peak decomposition: a) the area of the Zr 3d_{3/2} core level is equal to two-thirds of the area of the Zr 3d_{5/2} core level, and, b) a separation of 2.37 eV between both core levels was assumed (Moulder et al., 1995). Besides, four components corresponding to overlapping loss features from the Zr 3d core levels of each assigned species were considered for peak decomposition but not accounted for in quantification; i.e., R.S.F. fixed to 0. Additional insights into the surface chemistry were gained by performing a series of time-of-flight secondary ion mass spectrometry analyses. Spectra were recorded using an IONTOF TOF.SIMS 5 instrument in both positive and negative ion secondary ion polarity applying Bi³⁺ primary ions with 30 keV and a pulsed primary ion beam current of 0.3 pA. The analysis area varied from 66 x 66 μm^2 to 141 x 141 μm^2 over which the Bi³⁺ beam was rastered. The resulting primary ion dose density was below $3.4\text{E}^{12} \text{ cm}^{-2}$ for all measurements so that the corresponding spectra mainly contain chemical information on the sample surface. In order to stabilize the surface potential, charge compensation by low energy (20eV) electron flooding was used.

4.3. Results and Discussion

4.3.1. Influence of the chain length of the modulator on the physicochemical properties of MOF-808

The thermograms for the as-synthesized MOFs ZrBTC-F, ZrBTC-A, and ZrBTC-P MOFs are shown in Figure 35, and one of the things that they tell us is that decreasing the length of the carbon chain of the modulator leads to more developed pore structures with larger surface areas, see Section D-2.1. of the Supplementary Information. Accordingly, an analysis of the recorded argon adsorption-desorption χ -plots of ZrBTC-F, ZrBTC-A, and ZrBTC-P, Figure 36, following IUPAC's classification (Thommes et al., 2015), shows that the porous structure of the synthesized materials comprises micropores and mesopores.

Figure 35

Thermogravimetric analysis (TGA) in an air atmosphere of synthesized MOFs.

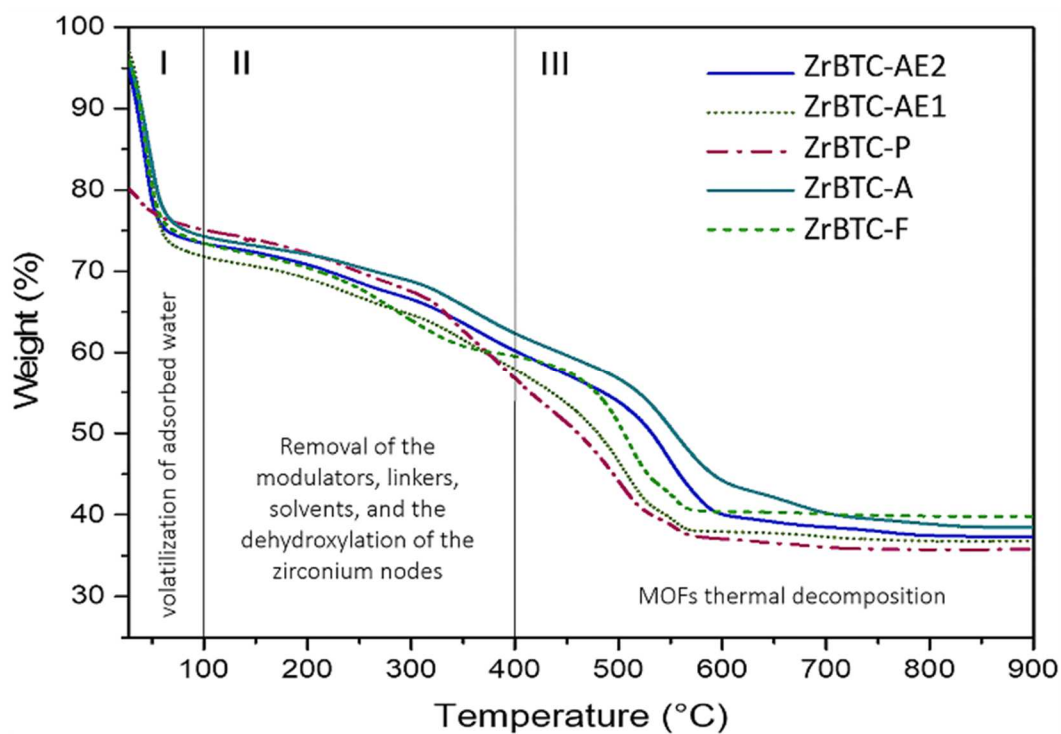
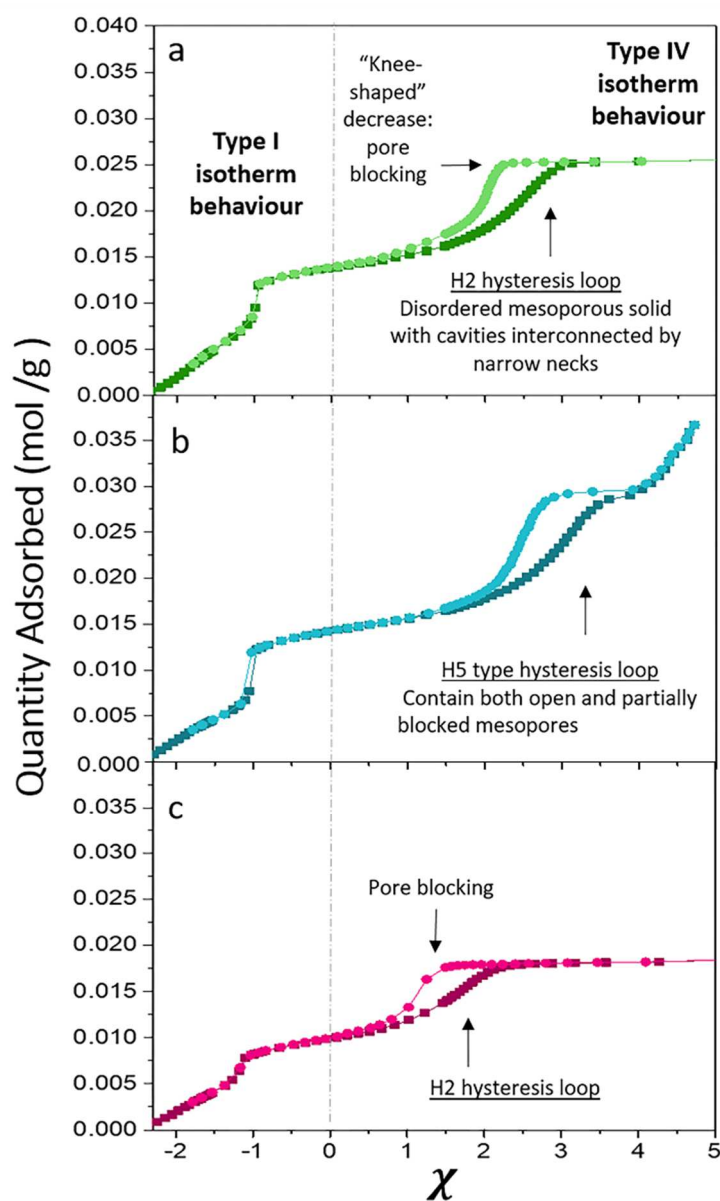


Figure 36

Ar adsorption/desorption isotherms of (a) ZrBTC-F (b) ZrBTC-A and, (c) ZrBTC-P, in all range of the linear P/P_0 . χ -method adsorption/desorption isotherms of the same materials (d) ZrBTC-F, (e) ZrBTC-A, and (f) ZrBTC-P.



The χ -surface areas of the materials decreased with increasing the length of the carbon chain of the modulators, Table 8. Comparatively, the χ -surface areas of the MOF synthesized

with formic acid were ca. 18 and 20% larger than those estimated for the MOFs synthesized with acetic and propionic acid, respectively. According to our calculations, these differences in surface area are due to a more considerable development of the micropore surface of the materials when using formic acid as the modulator, Table 8. It is pertinent to recall that the χ -method for assessing porosity allows differentiating the surface areas related to the different families of pores that the material may possess (James B Condon, 2006).

Table 8

Summary of the textural properties calculated by the χ method of the ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2 materials.

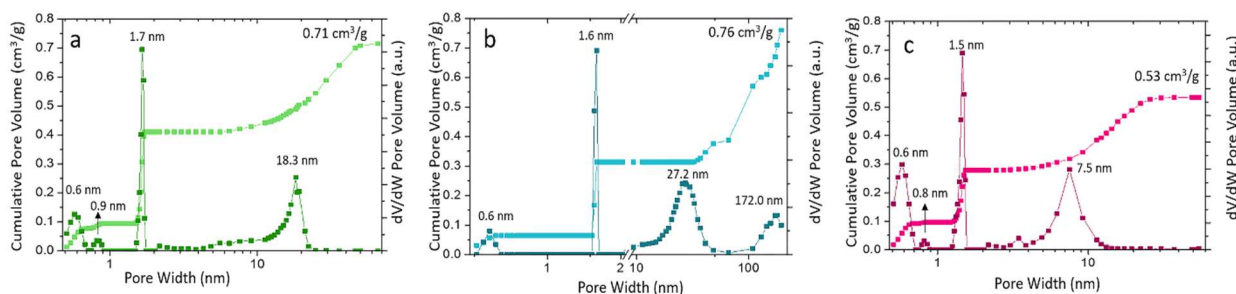
Material	Microporous Range					Non-microporous Range		Total χ surface area m ² /g
	Surface 1		Surface 2		Total			
	χ surface area m ² /g	Rsq	χ surface area m ² /g	Rsq	Microporous χ surface area m ² /g	Non-microporous χ surface area m ² /g	Rsq	
ZrBTC-F	840	0.99	91	0.99	931	227	0.99	1158
ZrBTC-A	727	0.99	19	0.98	746	200	0.99	946
ZrBTC-P	646	0.99	18	0.99	664	254	0.99	918
ZrBTC-AE1	753	1.00	38	0.98	791	214	0.98	1005
ZrBTC-AE2	701	1.00	42	0.98	743	200	0.98	943

Regarding the characteristics of the pore structure of the materials, we performed NLDFT and BJH calculations to derive their pore size distributions, as presented in Figure 37; this figure also shows the corresponding cumulative pore volume plots as a function of the pore diameters. In general, our calculations reflect the existence of at least three families of pores;

two families associated with micropores and one associated with mesopores. The main families of micropores had average diameters of 0.6 and 1.6 nm regardless of the modulator. The presence of these two families of micropores agrees with the characteristics of MOF-808 crystals (Hiroyasu Furukawa et al., 2014), in which its framework is formed through tetrahedral cages with the smallest pore distribution and also, they share vertices forming an adamantane cage with internal pores related to the second microporous size distribution.

Figure 37

Cumulative pore volume and pore-size distribution of (a) ZrBTC-F (b) ZrBTC-A, and (c) ZrBTC-P. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by the BJH desorption method, respectively.



The pore size distributions for the mesopores did not follow a straightforward relationship with the chain length of the modulator. Indeed, while propionic acid led to the narrowest distribution of mesopore diameters with the lowest average pore diameter, 7.5 nm, formic acid produced mesopores with the second lower average pore diameter, 18.3 nm, and acetic acid produced the broadest distribution of mesopores centered at 27.2 nm plus pores in the size range for macroporous materials. For mesopores, the features of the hysteresis loop of

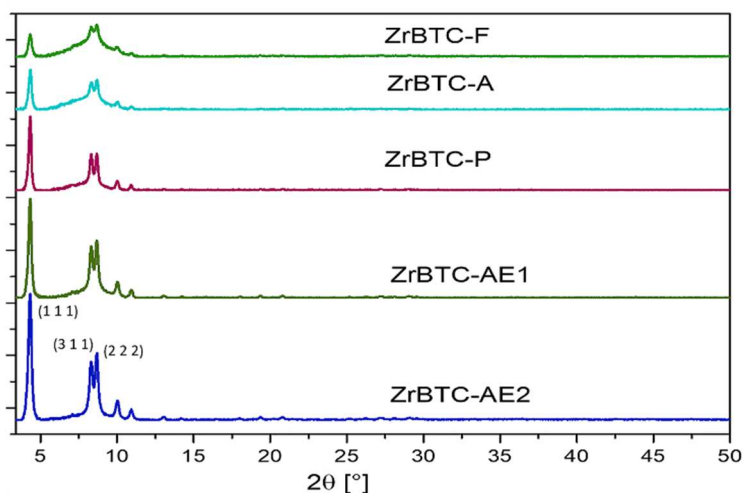
the isotherms reflect the tortuosity of the network of pores (Enniful et al., 2019; Schneider & Valiullin, 2019; Xu & Prodanović, 2018). Notably, our results suggest that using formic and propionic acid produces Zr-MOFs with a disordered and tortuous mesopore network that has cavities interconnected by narrow necks (Thommes et al., 2015). Conversely, the use of acetic acid as the modulator produced a relatively more ordered mesopore network combining opener pores with partially blocked mesopores (Cychosz et al., 2017).

To summarize, the length of the carbon chain of the modulator has a specific impact on the mesoporous structure of MOF-808 type materials without compromising their microporosity. Remarkably, the total surface area follows a straightforward positive correlation with the length of the carbon chain, which is specifically associated with an increase in the surface area associated with the microporous structure of MOF-808. Such a trend may be associated with a modification of the crystallization stage of the synthesis.

X-Ray diffractograms recorded for samples of ZrBTC-F, ZrBTC-A, and ZrBTC-P are shown in Figure 38. The featured patterns match those reported for MOF-808 (Hiroyasu Furukawa et al., 2014) and, at first sight, do not differ from what has already been reported in the literature. However, structure treatment calculations (Section D-2.3. of the Supporting Information) indicated a positive correlation between the length of the carbon chain of the modulator, the cell parameters, and the volume of the crystallites of the synthesized MOFs. Therefore, the use of a modulator with a larger carbon chain length produces larger MOF-808 crystallites that, in turn, will reduce the total microporous surface area, Table 8.

Figure 38

Experimental PXRD data of synthesized MOFs.

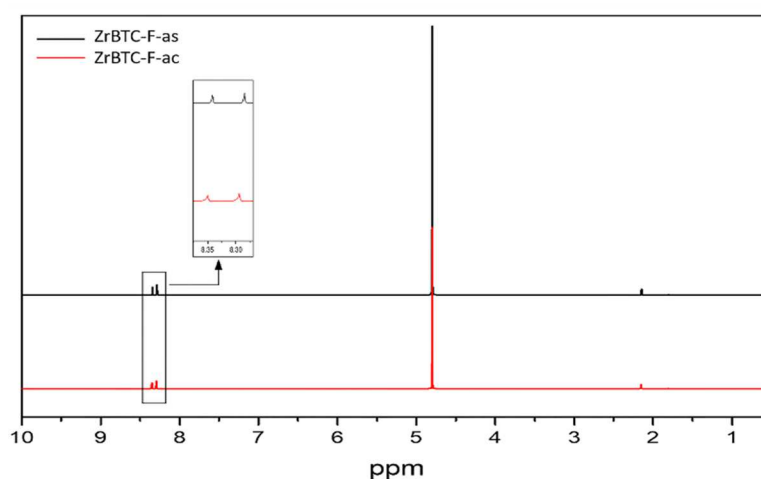


On the other hand, we find worth mentioning that the mesoporosity of the synthesized materials is related to the presence of an amorphous phase whose mechanism of formation is still to be established. In a previous work, we have proposed that the monocarboxylic acid used as modulator coordinates to the metal cluster and contributed to the formation of missing linker defects. The pore size, as well as the order of the mesoporous distributions, depends on the concentration of the modulator (Ardila Suárez, Díaz, et al., 2019). Regardless of the mechanism of the formation of the amorphous phase, it seems clear that it is a product of missing linker defects. In our case, the results of the dissolution- ^1H -NMR experiments. Figures 39, D-3, and D-4 evidenced that monocarboxylates remained coordinated to the zirconium nodes before and after the activation stage of the synthesis process. Besides, we found evidence of the presence of formate groups typically produced by the hydrolysis of DMF solvent under the conditions of the synthesis of MOFs (Wißmann et al., 2012). We estimated the relative concentration of modulator coordinated to the zirconium nodes, R_m/Zr , before and after activation (Section D-2.2. of the Supporting Information). Besides finding a

positive correlation between this parameter and the length of the carbon chain of the modulator, we also determined that acetic acid led to a slightly larger relative concentration of modulator coordinated to the zirconium nodes. In principle, such a difference may be considered to be insignificant, $R_m/Zr = 2.13$ for ZrBTC-A as compared to 2.03 for ZrBTC-P, but we found that the ZrBTC-A lost the largest quantity of mass in TGA experiments, (Section D-2.1. of the Supporting Information), and also that ZrBTC-A had the largest mesopores of all of the materials. Therefore, we think that such evidences might be correlated. We do not know the reason for such a trend, but we speculate that some of the acetates formed during the synthesis of the ZrBTC-A MOF did not bind to the zirconium nodes and instead formed organic clusters.

Figure 39

Dissolution/¹H NMR spectra obtained on the MOF synthesized using formic acid as modulator before (ZrBTC-F-as) and after (ZrBTC-F-ac) the activation process.



The chemical analysis of the surface of the MOFs synthesized with the different modulators gives further insight into their defective nature. In this sense, the relative

concentration of the elements and the components found on the surface of the synthesized materials are displayed in Table 9. Besides carbon, oxygen, and zirconium, traces of nitrogen and chlorine were detected and quantified. The presence of nitrogen gives further support to our hypothesis on the deposition of residua from the hydrolysis of the DMF solvent (Wißmann et al., 2012), while residual chlorine is due to the counter-ion of the zirconium precursor.

Table 9

C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks contributions concentration for ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTC-AE1, and ZrBTC-AE2 MOFs. The species are coded as C-Ar: Carbon belonging to an aromatic ring, Ar-(C-O)-Zr, C-NH₃: Carbon from the carboxylic acid group linked to the Zr cluster, Ar-Carboxy: carbon belonging to the carboxylic acid group of H₃BTC, Aliph-Carboxy: Carbon from the carboxylic acid group linked to an aliphatic chain. Zr-O: oxygen linked to Zr in the organic cluster, R-(C=O)-OH: oxygen belonging to a carboxylic acid functional group, C-O-Zr: oxygen belonging to the C-O-Zr bonds. Zr-O: zirconium belonging to the inorganic cluster and, Zr-O-C: zirconium coordinated to an organic group through oxygen.

Sample					
Relative Molar %	ZrBTC-F	ZrBTC-A	ZrBTC-P	ZrBTC-AE1	ZrBTC-AE2
C 1s					
C-Ar	22.51	21.29	21.12	22.38	19.96
Ar-(C-O)-Zr, C-NH ₃	2.77	3.36	3.72	4.54	3.16
Ar-Carboxy	11.29	8.06	7.21	7.41	8.95
Aliph-Carboxy	12.5	12.22	12.96	11.95	13.87
Total	49.07	44.93	45.01	46.28	45.94
O 1s					
Zr-O	7.34	9.12	8.00	6.82	7.29

R-(C=O)-OH	28.23	28.91	30.9	30.88	32.53
C-O-Zr	5.8	6.97	6.15	6.77	4.1
Total	41.37	45.00	45.05	44.47	43.92
Zr 3d					
Zr-O	24	2.	7.05	2.12	7.02
			2.42		7.65
Zr-O-C	6.71		7.03	2.18	1.97
Total	8.95	9.47	9.15	9.20	9.62
N 1s					
N 1s	0.07	0.19	0.18	0.06	0.13
Cl 2s					
Cl 2s	0.55	0.43	0.61	0	0.39

By calculating empirical formulas for the surface of the synthesized MOFs, Table 9, one finds that the surface of the MOFs synthesized herein is deficient in both oxygen and zirconium as compared to the crystalline core composition of MOF-808 (Hiroyasu Furukawa et al., 2014). In other words, the surface of our MOFs is enriched by carbonaceous species. To complement the chemical analysis of the synthesized MOFs, we performed a decomposition of the high-resolution spectra of the C 1s, O 1s, Zr 3d, N 1s, and Cl 2s core levels of ZrBTC-F, ZrBTC-A, and ZrBTC-P following the methodology that we developed in previous works (Ardila Suárez, Díaz, et al., 2019; Ardila Suárez, Rodríguez Pereira, et al., 2019). The chemical species considered for this procedure are illustrated in Figure 40, and the results of quantifying these chemical species are shown in Table 10. According to results, the surface of the materials synthesized using acetic and propionic acid as modulators is enriched by uncoordinated carboxylates. Meanwhile, the molar ratios that refer to the proportion between the carbon atoms of the aromatic ring of H₃BTC and those of the

carboxylate functional groups in H₃BTC and the inorganic bonds of the zirconium oxo-clusters of the materials were very close to those expected for crystalline MOF-808.

Figure 40

C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks decomposition recorded in XPS analysis of (a,b,c,d,e) ZrBTC-F, (f,g,h,i,j) ZrBTC-A, and (k,l,m,n,o) ZrBTC-P, respectively. The C-(C,H) component at 284.8 eV was taken as a reference for the binding energy.

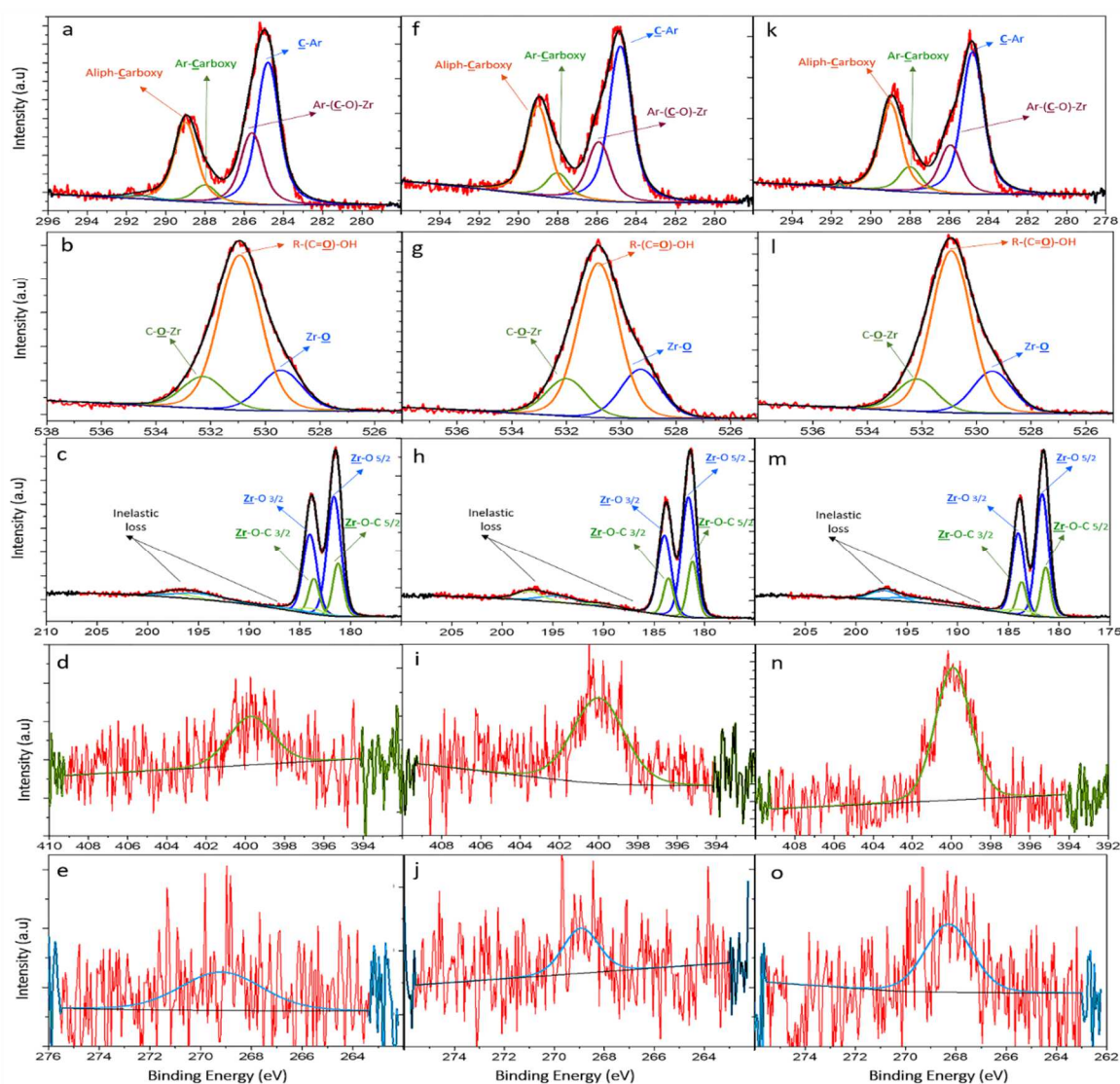


Table 10

Species molar ratios of ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2 materials.

Species molar ratios	Sample				
	ZrBTC-F	ZrBTC-A	ZrBTC-P	ZrBTC-AE1	ZrBTC-AE2
C-Ar/Ar-Carboxy	1.60	1.87	1.93	1.65	1.86
"Free"-[Carboxy/CarbOxy]	0.84	0.63	0.65	0.70	0.70
Coordinated					
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]	0.52	0.93	0.90	0.47	0.91
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr, C-NH ₃]	0.60	0.96	1.03	0.88	0.92
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]	1.16	1.04	1.14	1.87	1.01
Inorganic					
Zr-O/Zr-O	0.31	0.32	0.27	0.27	0.27

In summary, our investigation indicates that, regardless of the length of the carbon chain of the modulator, defective MOF-808 is synthesized under the conditions employed in this work. More defective MOF-808 materials are formed when using acetic acid as a modulator. This modulator promotes the formation of larger MOF-808 crystallites compared to missing linker moieties of uncoordinated formates and propionates. Yang et al. (P. Yang, Mao, Li, Zhuang, & Gu, 2018) also studied the effect on the mesoporosity of the three mentioned modulators on the synthesis of micro/mesoporous UiO-66 materials. They found that the trend in the decrease of acidity formic acid > acetic acid > propionic acid is related to the progressive decrease of the mesopore size distributions of the synthesized materials. This same trend is followed by the materials synthesized herein using formic and propionic acid, but this is not the case for acetic acid modulation.

To continue our research, we chose ZrBTC-A as a model for investigating how the addition of a surfactant during the synthesis of the material may modify its physicochemical properties. The reason for choosing this material was that it exhibited the most ordered and largest mesopores. We present our results below.

4.3.2. Influence of the addition of a surfactant on the physicochemical properties of MOF-808

In the second part of this work, we added cetyltrimethylammonium bromide as the surfactant during the synthesis of ZrBTC-A. In general, the addition of this surfactant modified the porous structure of the material. On the one hand, the surface area increased when adding 3.34 mmol of cetyltrimethylammonium bromide, ZrBTC-AE1, see Table 8. The increase in surface area was also evidenced in the thermogram of ZrBTC-AE1. Doubling the concentration of cetyltrimethylammonium bromide to 6.67 mmol, ZrBTC-AE2 did not increase the surface area further, and instead, the synthesized material showed the same surface area of ZrBTC-A. It can be noticed that the microporous surface of ZrBTC-AE2 was the one that mainly increased by ca. 6%.

On the other hand, the addition of the surfactant modified the hysteresis loop of the MOF, Figure 41. Namely, the type H5 hysteresis loop of the parent ZrBTC-A material evolved into a type H1 hysteresis loop with a sharp rise in the adsorption branch near saturation. This type of hysteresis loop is ascribed to materials with an ordered mesoporous structure consisting of uniform cylindrical inter-crystalline voids (Cychosz et al., 2017; Z. Liu et al., 2017; L. Yang et al., 2017). The calculated pore size distributions for ZrBTC-AE1 and ZrBTC-AE2 are shown in Figure 42. These calculations showed that the addition of CTAB did not alter the microporous structure of the materials, but instead, it expanded the mesopores of ZrBTC-

A, turning them into macropores, i.e., pores whose average diameter is larger than 50 nm (Thommes et al., 2015). Particularly, ZrBTC-AE1, whose concentration of CTAB was lower, showed larger macropores than ZrBTC-AE2.

Figure 41

χ -method adsorption/desorption isotherms of the materials (a) ZrBTC-AE1 and (b) ZrBTC-AE2.

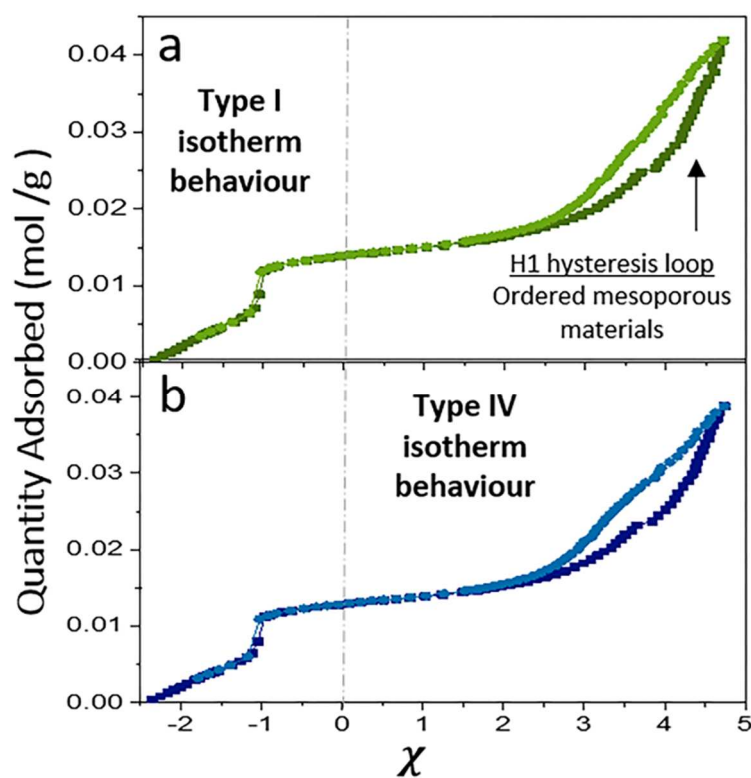
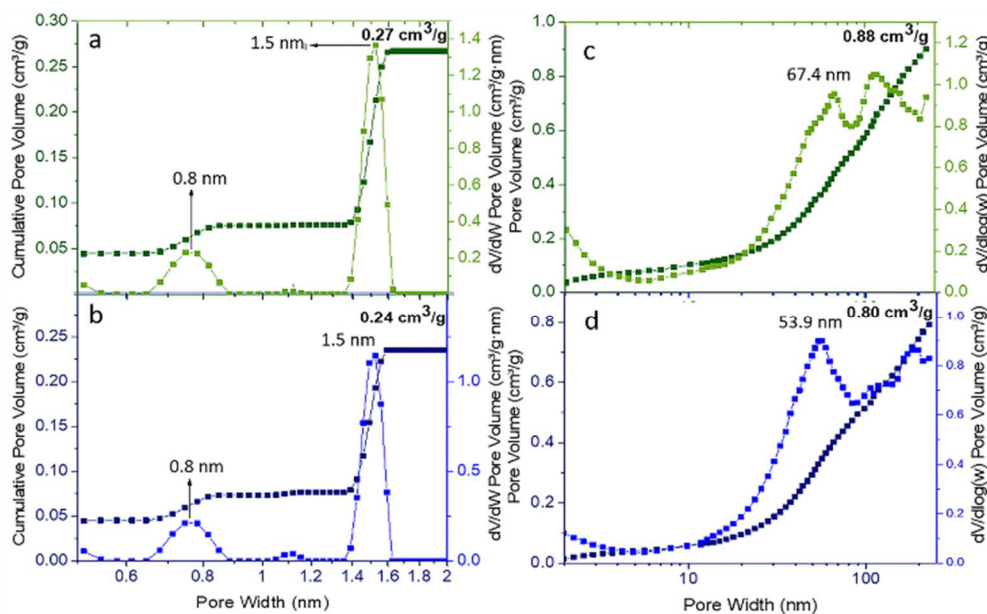


Figure 42

Cumulative pore volume and pore-size distribution of (a,c) ZrBTC-AE1, and (b,d) ZrBTC-AE2. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous-macroporous range by BJH desorption method, respectively.

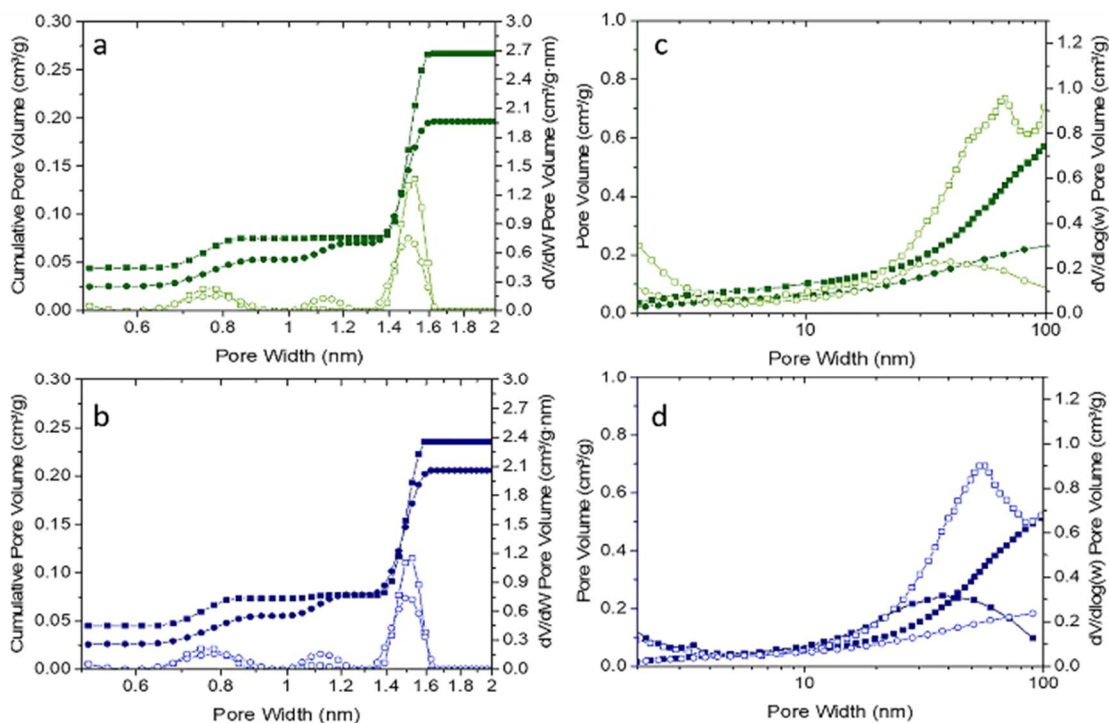


In general, though we plotted the curves for the cumulative pore volume of ZrBTC-AE1 and ZrBTC-AE2, we will refrain from analyzing these results since a saturation of their porous network was not reached during the analyzes as it was evidenced by the fact that the recorded isotherms did not reach a plateau in the high relative pressure region. This behavior suggested that ZrBTC-AE1 and ZrBTC-AE2 had an open macroporous structure. We decided to enquire about the connectivity of the porous network of the synthesized MOFs. For this purpose, we performed a post-synthetic modification of ZrBTC-AE1 and ZrBTC-AE2 with sulfuric acid following the procedure reported in our previous work (Ardila Suárez, Díaz, et al., 2019). We may recall that this procedure served to demonstrate that the ultramicropores of defective MOF-808 were disconnected from the rest of their porous

network. According to Figure 43, in the case of ZrBTC-AE1 and ZrBTC-AE2, we found that the treatment with sulfuric acid caused a general decrease in the micro and macropore pore volumes of the materials.

Figure 43

Cumulative pore volume (solid symbols) and pore-size distribution (open symbols) of (a,c) ZrBTC-AE1, and (b,d) ZrBTC-AE2, before (squares), and after (circles) sulfation process. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by the BJH desorption method, respectively.

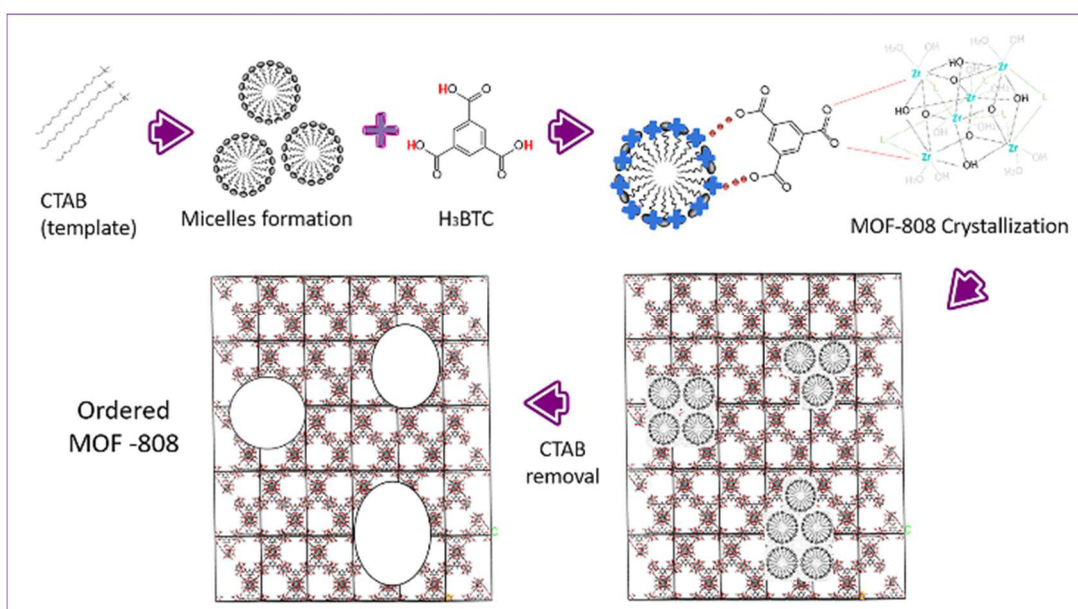


We interpret this trend as a hint of the existence of an interconnectivity pattern between the different pore families of Zr-MOFs synthesized by a surfactant-assisted method. We propose that during this kind of synthesis, the carboxylic acid groups of BTC linker probably act as a counteranion that promotes the assembly between the crystallizing material and the

cationic head group of CTAB. The ionic interaction between oppositely charged groups has been previously reported in the context of the synthesis of zeolites (Y. Zhang et al., 2014). We illustrate our proposal in Figure 44. In it, the carboxylates of BTC interact with the cationic head group of the micelles formed by CTAB. After adding the solution of ZrCl_4 , the formed zirconium oxo-clusters and the BTC^{3-} anions begin to crystallize around the external surface of the CTAB micelles. After removing CTAB, the resulting defective MOF-808 is arrayed around ordered macroporous channels in the inter-crystalline voids. To support the above proposal, we demonstrate, see Sections D-1.2. and D-2.4. of the Supplementary Information, that the concentration of CTAB in the DMF/acetic acid mixture used during the synthesis of the materials is higher than the critical micelle concentration of the system. Under such conditions, it is predicted that surfactants form spherical aggregates that end up making worm-like structures (Dreiss, 2007; Lin, Cai, Scriven, & Davis, 1994).

Figure 44

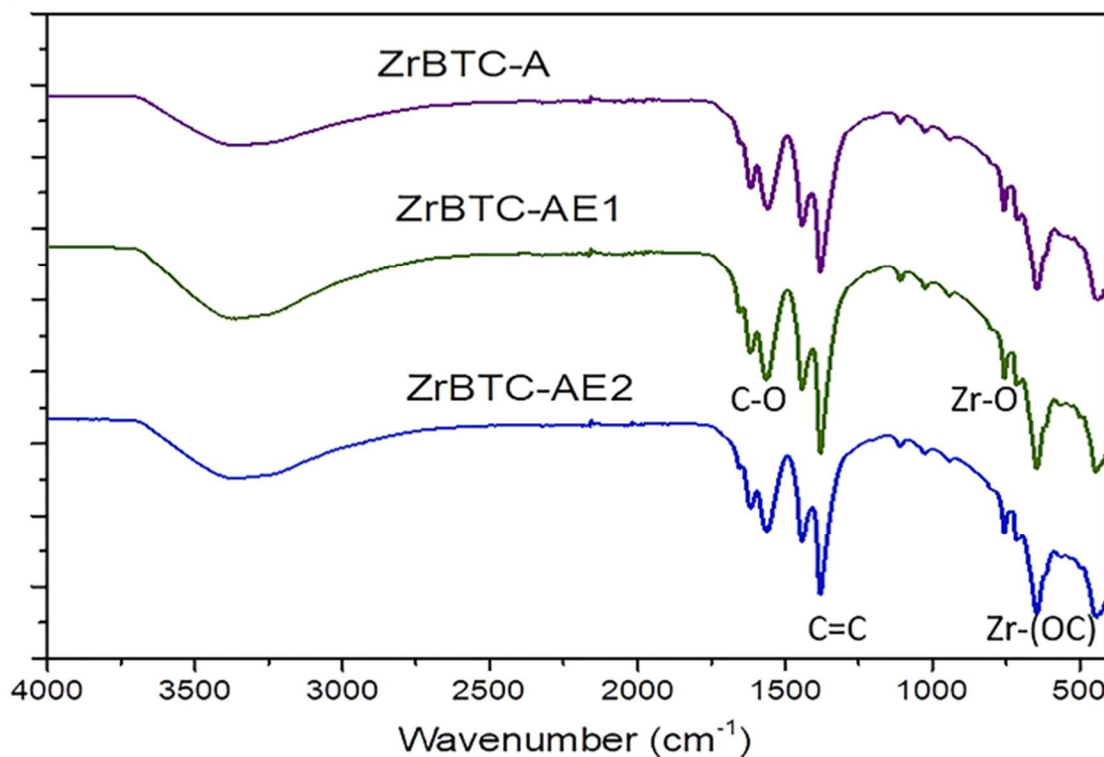
Representation of the possible mechanism of CTAB template synthesis of hierarchical MOF-808.



Furthermore, it has been shown that CTAB can self-assemble into aggregates of different morphologies above a threshold concentration and depending on the particularities of a given system (Khatory et al., 1993). Also, results from FTIR analyses for ZrBTC-AE1 and ZrBTC-AE2, Figure 45, showed that CTAB reacted neither with the organic ligand nor with the zirconium-oxo clusters to form other crystals. Instead, the FTIR spectra for ZrBTC-AE1 and ZrBTC-AE2 exhibited the usual bands ascribed to carboxylate MOFs, see Section D-2.5. of the Supplementary Information, and were similar to the spectrum of ZrBTC-A.

Figure 45

Infrared spectra of synthesized ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2.

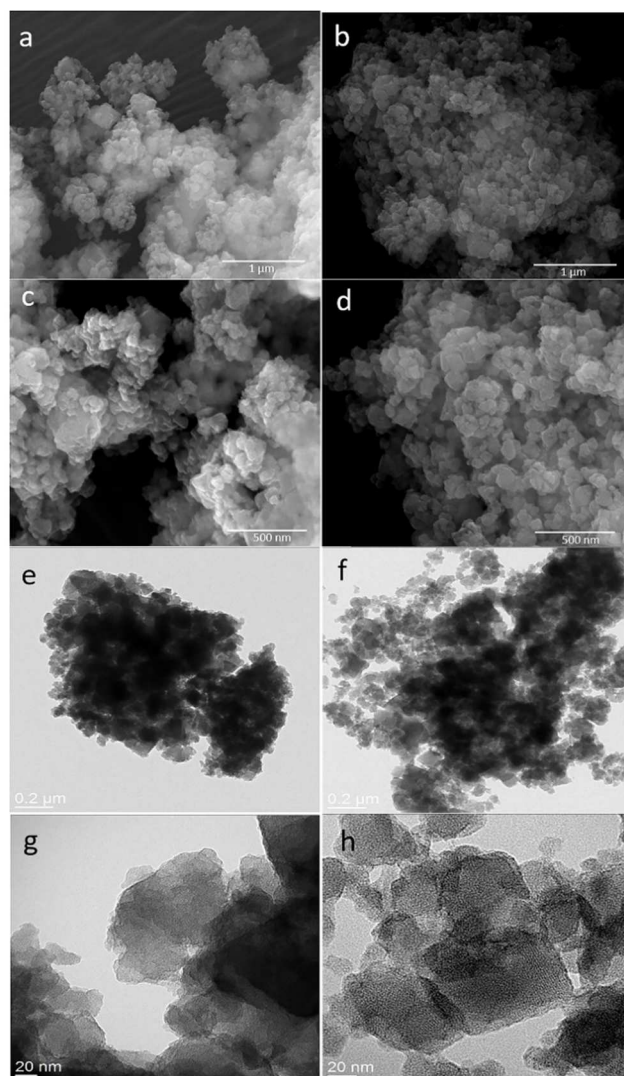


As commented earlier, CTAB promoted the uniformity of the structure of defective MOF-808. In this sense, the SEM images for ZrBTC-A, Figures 46a and 46c, showed larger ill-defined particles as compared to the well-defined particles of ZrBTC-AE2 (Figures 46b and 46d). Furthermore, TEM images offered insight into the local structure of the crystalline phase; Figures 46e, 46g, and 46f, 46h, for ZrBTC-A and ZrBTC-AE2, respectively. For the latter, the images show a structure formed by dense nanoparticles randomly stacked together with inter-crystalline voids (Duan et al., 2017; Huo, Brightwell, El Hankari, Garai, & Bradshaw, 2013). Diffractograms recorded for samples of ZrBTC-AE1 and ZrBTC-AE2 are displayed in Figure 38. The recorded patterns show that using CTAB as a surfactant enhanced the crystallinity of the parent ZrBTC-A.

Moreover, the increase in the concentration of the surfactant further increased crystallinity. The interested reader can consult the Supplementary Information, Section D-2.3, for details. Our results differ from what has been presented in previous works. Indeed, other research groups (K. Li et al., 2018; Y. Li et al., 2011; Seoane et al., 2015) found that adding a surfactant during the synthesis of MOFs leads either to partial amorphization or to the collapse of their structure. We hypothesize that the crystallinity enhancement in our work can be due to the separate preparation of the modulator and the zirconium precursor and the organic ligand and the surfactant solutions. Under such conditions, both the zirconium-oxo clusters and the self-assembled CTAB micelles form before mixing, leading to the formation of ordered structures.

Figure 46

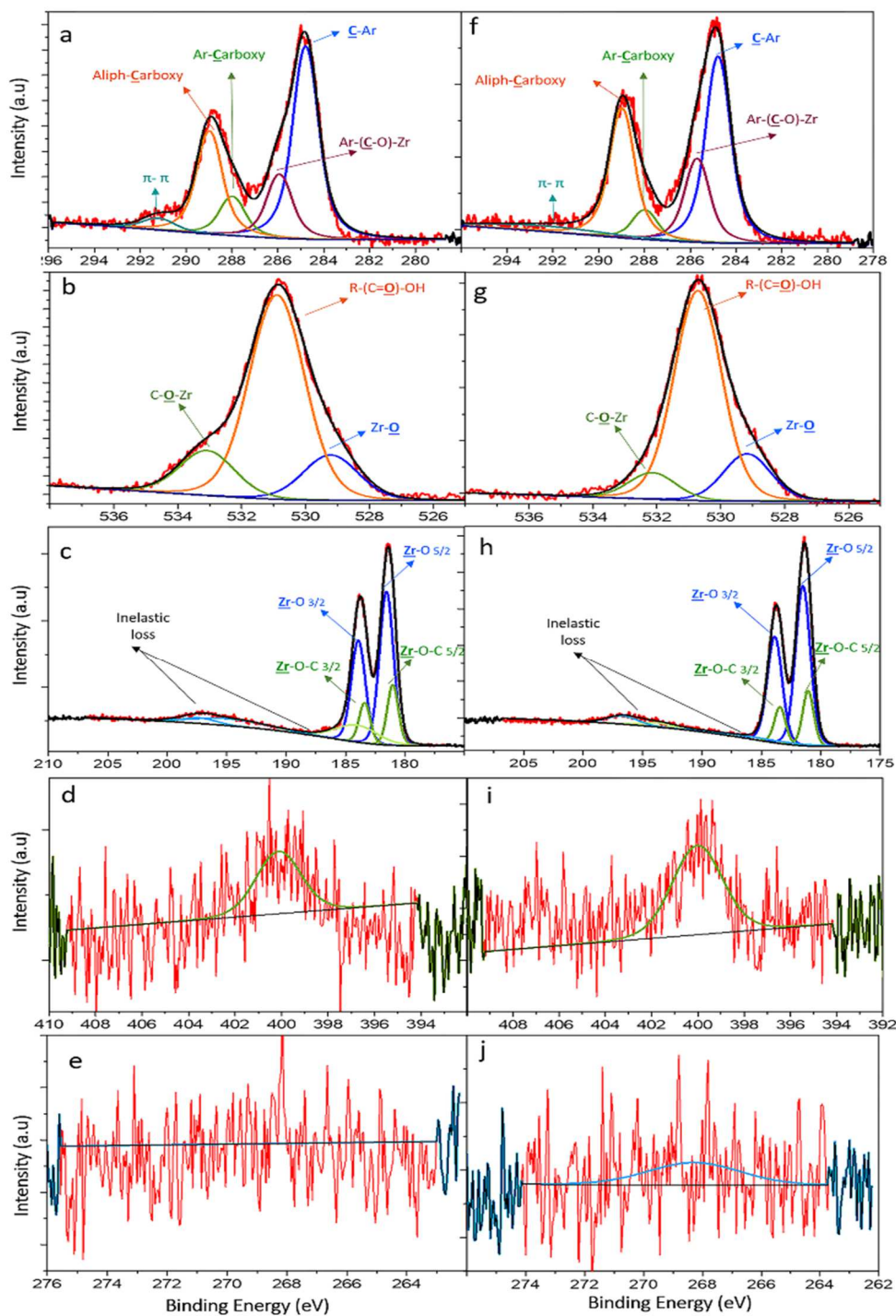
SEM and TEM images of the ordered porous (a,c,e,g) ZrBTC-A, and (b,d,f,h) ZrBTC-AE2



Finally, we found that the addition of CTAB did not have a marked impact on the surface chemistry of the materials. The decomposition of the C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks of ZrBTC-AE1, and ZrBTC-AE2 recorded in XPS are shown in Figure 47, and the results for the quantification of the identified surface chemical species is shown in Table 10. We did not find marked differences between the results for ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2.

Figure 47

C 1s, O 1s, Zr 3d, N 1s, and Cl 2s peaks decomposition recorded in XPS analysis of (a,b,c,d,e) ZrBTC-AE1, and (f,g,h,i,j) ZrBTC-AE2, respectively. The C-(C,H) component at 284.8 eV was taken as reference for the binding energy calibration.

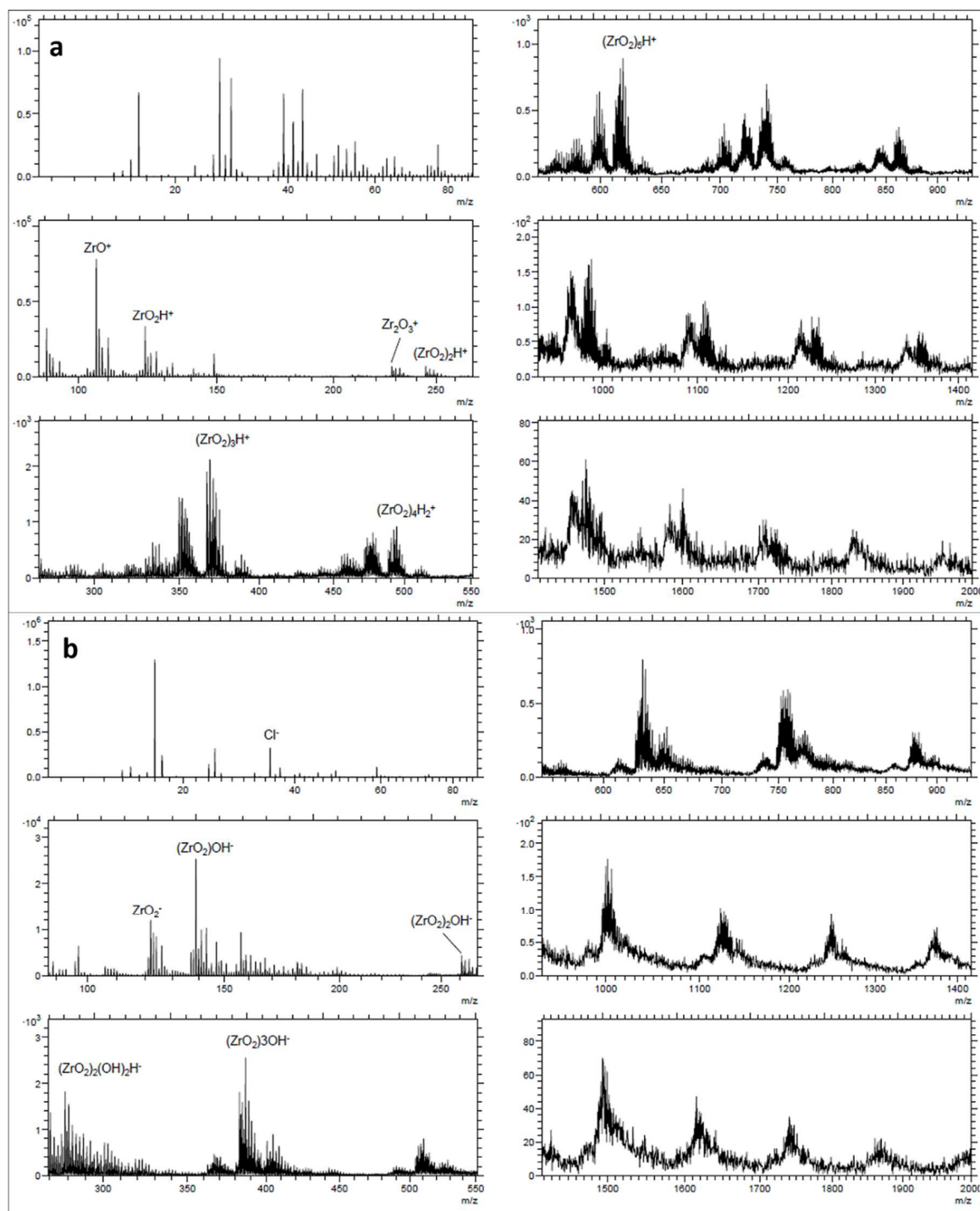


Further evidence showing that the addition of the CTAB surfactant during the synthesis of defective MOF-808 does not modify its surface chemistry was found by ToF-SIMS, Figures 48 and D-12. Indeed, the data collected from both the positive and negative ion spectra for both ZrBTC-A and ZrBTC-AE2 were very similar and consisted on strong, ZrO^+ , $(\text{ZrO}_2)_3\text{H}^+$, $(\text{ZrO}_2)_5\text{H}^+$, $(\text{ZrO}_2)\text{OH}^-$, $(\text{ZrO}_2)_2(\text{OH})_2\text{H}^-$ and $(\text{ZrO}_2)_3\text{OH}$ signals along with weaker signals due to ZrO_2H^+ , Zr_2O^{3+} , $(\text{ZrO}_2)_2\text{H}^+$, ZrO_2^- , and $(\text{ZrO}_2)_2\text{OH}^-$ and similar signals of high m/z ratios coming from the fragmentation of the metal-organic clusters. The sole difference found between ZrBTC-A and ZrBTC-AE2 was that the latter contains some residual bromine; Figure D-13 compares the negative ion spectra recorded in the range from 78.7 to 79 m/z for these two samples. The concentration of this residue was below the limit of detection of the XPS technique mentioned earlier. Therefore, we conclude that the surface chemistry of the defective MOF-808 remains unaltered after adding a surfactant during the synthesis.

In summary, the addition of CTAB during the synthesis of the acetic acid modulated MOF-808 enhanced both its porosity and crystallinity without significantly altering its molecular structure and surface chemistry.

Figure 48

Spectra of the surface (a) Positive (b) Negative Secondary Ion Polarity of ZrBTC-A MOF.



4.4. Conclusions

This work elucidates the effect of defect engineering through the modulator and surfactant approaches on the physicochemical and surface properties of the defective microporous/macroporous MOF-808 series. Results showed that the use of different modulators during synthesis led to the formation of materials with different amounts of missing linker defects and pore size distributions. Notably, the acetic acid attached to the zirconium oxo-cluster was found to be inferior compared to the materials synthesized with formic and propionic acid as modulators. This is consistent with the formation of a microporous/mesoporous material with a larger mesopore size distribution compared to the others. On the other hand, the addition of surfactant allowed the synthesis of ordered and crystalline microporous/macroporous materials. The addition of CTAB did not seem to alter the surface chemical composition compared to the material synthesized with no surfactant. Thus, the MOF-808 series exhibited a defective structure at the surface with adjustable pore size distribution by the application of the defect engineering approach for a wide range of applications.

5. Ordered Multi-modal Porous MOF-808 with Enhanced Catalytic Activity for the Glycerol Esterification with Acetic Acid

5.1. Overview

Ordered and interconnected microporous/macroporous MOFs structures can significantly improve the diffusion-related issues for catalytic applications in which large molecules are involved. In this work, interconnected MOFs with the multi-modal porous structure were evaluated before and after a post-synthetic sulfation process in the liquid-phase esterification reaction of glycerol with acetic acid. This reaction allows the glycerol valorization through the obtainment of di- and triacetin products. The synthesis of ordered and multi-modal porous materials did not affect the acid properties of the inherently defective MOF-808, and the sulfation process led to the formation of strong acid sites into the structure with no affectation of the interconnection of the porous structure. Catalytic activity in terms of the turnover frequency shows that glycerol conversion and selectivity to products of interest are higher for the sulfated material compared to the as-synthesized MOFs in which the effect of the interconnectivity is also evaluated. We show that the activity of MOF-808 is related to both acid strength and the formation of ordered and interconnected structures.

5.2. Experimental Section

Materials

MOFs were synthesized with the following reagents: Zirconium precursor: zirconium chloride, ZrCl_4 (98%), from Merck. The organic ligand, Benzene-1,3,5-tricarboxylic acid (H_3BTC , 95%), and the surfactant Hexadecyltrimethylammonium bromide, CTAB (>98%) were obtained from Sigma-Aldrich. The solvent N, N-dimethylformamide (99.8%), the modulators: formic acid (98 -100%), acetic acid (99.8%) and propionic acid (99%) and the washing solvents; acetone (99.8%) and methanol (99.9%); sulfuric acid (95-97%), chloroform (100%) used for the post-synthetic modification, were all purchased from Merck. The catalytic evaluation was performed with the additional reagents: Ethanol (100%) and acetic acid (100%) were obtained from Merck, p-dioxane ($\geq 99\%$) from J.T. Baker, and commercial glycerol was purchased from a local provider (Laboratorios León Colombia). Reactants were used as received with the glycerol exception, which was rotoevaporated for water removal.

Synthesis of the materials

The synthesis of the materials was performed following the methodology presented in CHAPTER 4. Briefly, 9.99 mmol of zirconium chloride was put in a 250 mL screw-capped glass jar reactor. After that, 98 equivalents (related to the zirconium precursor) of modulator agent (formic, acetic or propionic acid) and 80 mL of DMF were added to the reactor, and the solution was stirred. After 20 min, 3.34 mmol of H_3BTC and the required amount of CTAB (0, 3.34 or 6.67 mmol) (S. Hu et al., 2017) were dissolved in 120 mL of DMF and added dropwise to the solution of the zirconium precursor. The mixture was stirred for an additional 15 min and later sonicated for 30 min. The resulting mixture was portioned among

twenty 50 mL screw-capped glass jar reactors and remained at 25 °C for 24 h and after that at 120 °C for an additional 24 h. After cooling down to room temperature, the contents of the reactors were combined, and the as-synthesized MOFs were recovered by filtration and washed twice with DMF, twice with water and twice with acetone. The resulting powder was dried at 120 °C for 12 h. An activation procedure was performed overnight at 120°C under a vacuum pressure of 0.06 mbar. The materials synthesized using formic, acetic, and propionic acid as modulators were named as ZrBTC-F, ZrBTC-A, and ZrBTC-P, respectively.

Furthermore, the materials synthesized using CTAB as the surfactant were named as ZrBTC-AER (*R* denoted as the CTAB: H₃BTC molar ratio 1 or 2). The sulfation process was performed using the protocol established in our previous work (Ardila Suárez, Díaz, et al., 2019). Thus, 50 mg of the synthesized material was treated with 50 mL of 0.05 M sulfuric acid (2.5 mmol) for 24 h. After that, the solution was solvent exchanged with 50 mL of water for three days, with the water being changed once a day, quickly exchanged with 50 mL of acetone, and immersed in 50 mL of chloroform for three days. During this time, chloroform was exchanged once per day. Finally, all the synthesized materials were activated overnight at 120 °C under a vacuum pressure of 0.05 mbar. The sulfated samples were coded using the S letter at the end of each name. For example, the sulfated sample of ZrBTC-F initial material was named as ZrBTC-FS.

Assessment of physicochemical properties of ZrBTC MOFs

The assessment of the synthesized materials was: the thermal stability, porous structure, morphology, crystallinity, molecular structure, and surface chemistry state (See Section E-1 of the Supplementary Information for the detailed followed methodologies).

Assessment of the acid properties of ZrBTC MOFs

Infrared spectroscopy study of the CO adsorption. Samples of ZrBTC MOFs were pressed (~1.5 Ton) into self-supported disks. The disks were placed in a ten positions sample holder into a glass cell connected to a vacuum line for evacuation and placed into a furnace. Samples were evacuated (10^{-6} mbar) at 120 °C for 60 h. Subsequently, the glass cell was placed in a glovebox, and then, the disks were placed individually in another glass cell equipped with ZnSe windows connected to the vacuum line for evacuation and for the introduction of CO. A movable glass sample holder allowed the adjustment of sample disk. IR spectra were recorded in the 400-4000 cm^{-1} range, on a Thermo Scientific Nicolet iS50 FTIR spectrometer. During the CO adsorption experiment, the sample disk was decreased using liquid N_2 . Spectra were normalized 20 mg of catalyst. The spectra are shown in the difference mode (MOF blank subtracted).

Potentiometric acid-base titrations. Potentiometric titrations were completed with a Metrohm 867 pH module with an 801 stirred equipped with Dosino 800 5 mL dosing units. Calibration was performed using commercial pH buffers, 4.00, 7.00, and 9.00 (Metrohm). The acid-base titrations were performed with slight variations of the protocol reported by Klet et al. (Klet et al., 2016b). Prior measurements, the MOFs were grounded, and then, approximately 50 mg of the sample was dispersed in 60 mL of 0.01 M NaNO_3 solution. The pH was adjusted to 3 using 0.05 M HNO_3 and then titrated with 0.05 M NaOH to a pH of 10.5 using injection volumes of 0.050 mL and an injection rate of 0.02 mL/min. The equivalence points were calculated from the first derivative of the resulting titration curve of pH as a function of the NaOH volume added in which the maximum point of the derivative curve corresponds to the equivalence points.

The Gran method was selected for the data analysis. Accordingly, the sigmoidal potentiometric titration curve is transformed into a linear form with the Gran function allowing the calculation of the equivalence volume by a standard linear regression method. The intersection of the straight line with the added volume axis gives the V_{eq} (the equivalence volume corresponding to each acid site), and then, this value is used for the calculation of the concentration of each acid site. The protonation constants of these acid sites can simultaneously be obtained from the slope of each straight line (Shcherban et al., 2017; Yu et al., 2016).

Catalytic test. Tested catalysts were grounded and sieved to a particle size of 25- 72 μm . The liquid-phase esterification reaction of glycerol with acetic acid was carried out in a 100 mL two-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer bar. The temperature was fixed to 100 $^{\circ}\text{C}$ and maintained using an oil bath and under 1000 rpm of magnetic stirring. In a typical run, the composition of the reaction mixture was acetic acid to glycerol molar ratio 9:1 and catalyst loading of 1 % weight related to glycerol. The acetic acid was charged into the reactor, and after reaching the reaction temperature, the amount of glycerol and the catalyst were added into the reactor. The timing of the experimental run was started after glycerol addition. Samples were taken periodically after filtration through a syringe filter. Reaction products were analyzed using a GC Agilent 6890 equipment with a flame ionization detector. An HP-1 column (100 m x 0.25 mm x 0.5 μm , J&W Scientific) was used for molecules separation. Helium (99.99%, Linde Colombia S.A.) was employed as the carrier gas. 10 μL of the sample aliquots of the reaction tests were diluted in 1000 μL of ethanol (99.9%, Merck) and 10 μL of 1,4-dioxane (99%, Baker), this last used as the internal standard. The GC temperature program started at 90 $^{\circ}\text{C}$ for 1 min, then

increased to 230 °C at a rate of 5 °C/min and held for 1 min, as previously reported (Caballero, Guerrero-Amaya, & Baldovino-Medrano, 2019).

Catalysts reusability and leaching tests. After the catalytic run, the determined catalyst was recovered by filtration, washed with water and acetone, and dried at 60 °C overnight to reuse it in another run, as previously reported (Leus et al., 2014). To evaluate the sulfated MOFs leaching, the reaction product of the esterification reactions was filtered after 2 h reaction, and the run continued with no solid catalyst. Moreover, approximately 50 mg of sulfated material was stirred with distilled water (5 mL). After 24 h, each suspension was filtered and treated with a 0.01 M $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ to test for leached sulfates, as previously reported (Garcia, Teixeira, Marciniuk, & Schuchardt, 2008).

5.3. Results and Discussion

FTIR analyses for the sulfated materials (Figures E-1 and E-2) showed that the spectra for the modified materials exhibited the usual bands ascribed to carboxylate MOFs. Furthermore, the evidence of the metal-bound sulfate groups is observed through the appearance of new bands in the range from 1500 to 800 cm^{-1} , ascribed to sulfate ligands (Adeeva et al., 1995; Juncong Jiang et al., 2014).

The thermograms of the sulfated MOFs synthesized by using different modulators, ZrBTC-FS, ZrBTC-AS, and ZrBTC-FS and those of sulfated samples prepared through the addition of surfactant, ZrBTC-AE1S, and ZrBTCA-AE2S are presented in Figure E-3. The thermal behavior of MOFs displayed the same trend that the pristine samples, see CHAPTER 4. The more significant weight loss on the region I of ZrBTC-FS, ZrBTC-AE1S, and ZrBTC-AE2S materials could indicate their larger surface area compared to the other tested materials.

Therefore, the recorded argon adsorption-desorption χ -plots (James B Condon, 2006) of ZrBTC-FS, ZrBTC-AS, and ZrBTC-PS displayed in Figure 49, show that the sulfated materials exhibited microporous/mesoporous structures, according to IUPAC's classification (Thommes et al., 2015). After sulfation, the materials maintain the trend on the decrease of the χ -surface area with the increasing of the carbon chain length of modulators, see Table 11. In this sense, the χ -surface areas of the ZrBTC-FS material were ca. 38 and 41% larger than those calculated for ZrBTC-AS and ZrBTC-PS, respectively. However, compared to the as-synthesized materials (CHAPTER 4), the ZrBT-F, ZrBTC-A, and ZrBTC-P materials lost a 54% in average of their surface area after sulfation, whereas that loss is less drastic in materials synthesized with the use of surfactant since ZrBTC-AE1 and ZrBTC-AE2 lost a 15 % in average of their initial surface area after the modification, which is also related to the crystallinity of sulfated materials as will be shown later.

Since the χ -method allows the differentiation of surface areas related to the diverse families of pores of the analyzed materials (James B. Condon, 2002), it is possible to compare those different surface areas of pristine materials to the sulfated MOFs. In general, the sulfated materials exhibited an increase in the percentage of their microporous surface and a decrease in the percentage of their mesoporous surface. Accordingly, Figure 50 displayed the pore size distributions from NLDFT and BJH calculations and also, the pore volume as a function of the pore diameters of sulfated samples. The ZrBTC-FS, ZrBTC-AS, and ZrBTC-PS materials presented at least four families of pores; three families related to micropores and very broad distribution in the mesoporous range.

Figure 49

χ -method adsorption/desorption isotherms of the same materials (a) ZrBTC-FS, (b) ZrBTC-AS, (c) ZrBTC-P, (d) ZrBTC-AE1S, and (e) ZrBTC-AE2S.

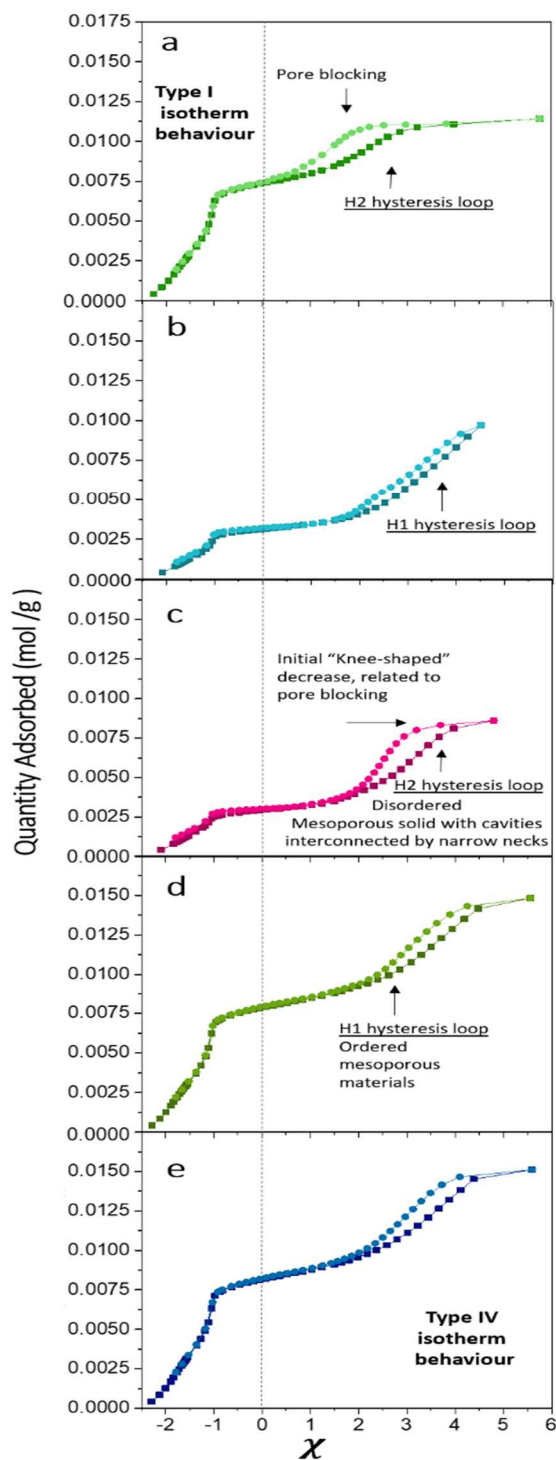


Table 11

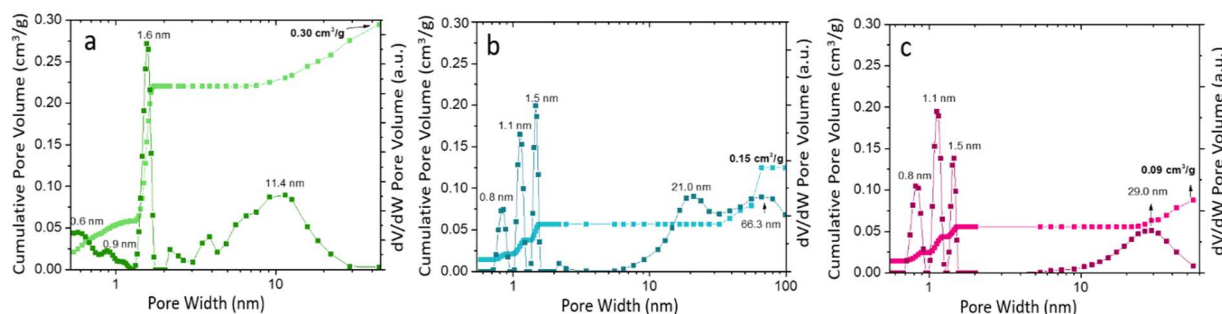
Summary of the textural properties calculated by the χ method of the ZrBTC-FS, ZrBTC-AS, ZrBTC-P, ZrBTC-AE1S, and ZrBTC-AE2S.

Material	Microporous Range					Mesoporous Range		Total χ surface area m^2/g
	Surface 1		Surface 2		Total			
	χ surface area m^2/g	Rsq	χ surface area m^2/g	Rsq	Microporous χ surface area m^2/g	Mesoporous χ surface area m^2/g	Rsq	
ZrBTC-FS	480	0.99	130	0.99	610	89	1.00	699
ZrBTC-AS	240	1.00	141	0.98	381	50	0.98	431
ZrBTC-PS	237	1.00	127	0.98	364	50	0.99	414
ZrBTC-AE1S	581	1.00	139	0.98	720	98	0.99	818
ZrBTC-AE2S	563	0.99	157	0.99	720	100	0.99	820

The three families of micropores are not well defined for ZrBTC-FS compared to ZrBTC-AS and ZrBTC-PS. Besides the two families of micropores centered around 0.8 and 1.5 nm that agrees with the characteristic crystal structure of MOF-808 (Hiroyasu Furukawa et al., 2014), there is a third distribution in between the other two mentioned distributions. The third distribution is not observed in the as-synthesized materials (CHAPTER 4). It seems that there is a correlation between the formation of this third distribution and the decrease in surface area and crystallinity after sulfation. Additionally, the new microporous distribution is not reflected in a new microporous χ surface, see Table 11. It seems that this new distribution exhibit a very similar surface energy than surface 2 (James B Condon, 2006).

Figure 50

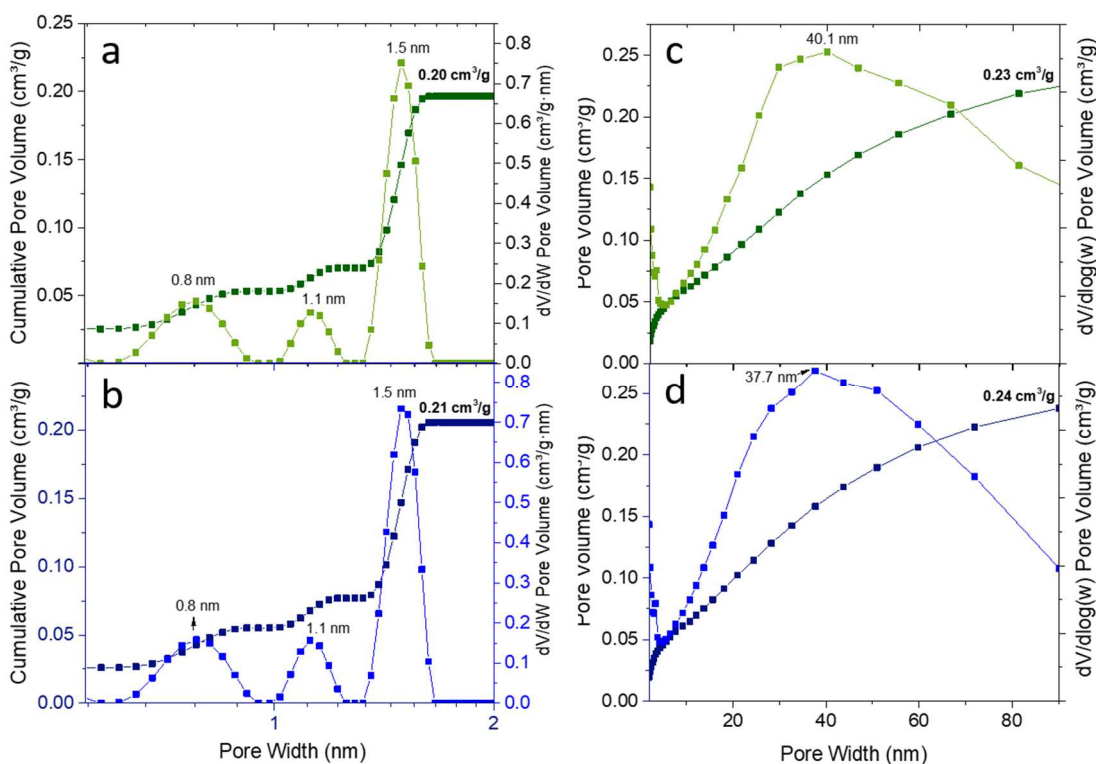
Cumulative pore volume and pore-size distribution of (a) ZrBTC-FS (b) ZrBTC-AS, and (c) ZrBTC-PS. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous range by the BJH desorption method, respectively.



After sulfation, the mesoporous size distributions of the three materials become very broad. In this case, the ZrBTC-PS MOF led to the narrowest distribution of mesopores diameters with the larger pore diameter, centered around 29.0 nm. The tortuosity of the network of pores (Enniful et al., 2019; Schneider & Valiullin, 2019; Xu & Prodanović, 2018) of pristine of ZrBTC-F and ZrBTC-P, and conversely, the more ordered mesopore network of ZrBTC-A remain after sulfation (CHAPTER 4).

Figure 51

Cumulative pore volume and pore-size distribution of (a,c) ZrBTC-AE1S, and (b,d) ZrBTC-AE2S. The microporous range is determined using a pore adsorption NLDFT cylindrical model (Ar on oxides at 87 K) and the mesoporous-macroporous range by BJH desorption method, respectively.



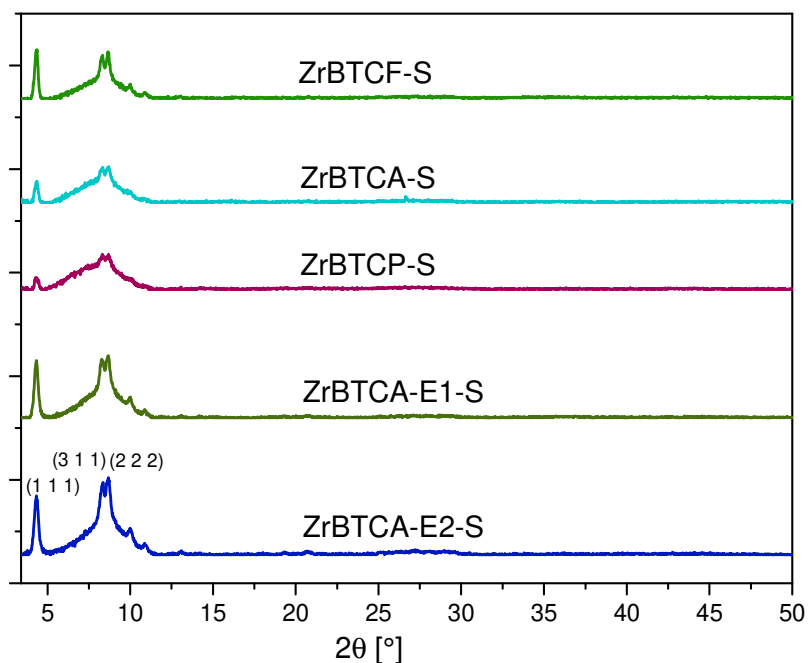
After sulfation, the ZrBTC-AE1 and ZrBTC-AE2 conserved the same microporous structure than the pristine materials with a decrease in the centered of the initially macroporous distributions that after the modification decrease to almost the upper limit of the mesoporous range. According to Figure 51, the ZrBTC-AE1S and ZrBTC-AE2S maintain their ordered and interconnected porous structure after de modification.

X-Ray diffractograms recorded for samples of ZrBTC-FS, ZrBTC-AS, and ZrBTC-PS, ZrBTC-AE1S, and ZrBTC-AE2S are shown in Figure 52. The presented patterns match those

of pristine materials (CHAPTER 4), which are in accordance, in turn, with the reported for MOF-808 (Hiroyasu Furukawa et al., 2014). It seems that after sulfation, the structures lost crystallinity. After sulfation, the materials ZrBTC-F, ZrBTC-A, and ZrBTC-F exhibited an approximately 30% of crystallinity lost; whereas the MOFs synthesized in the presence of surfactants decreased their crystallinity in around 20%. The structure treatment calculations (Section E-2.3. of the Supplementary Information) indicated that after sulfation, the ZrBTC-AE1 and ZrBTC-AE2 MOFs practically conserved the initial cell parameters and volume. Their resulting crystal structure after sulfation is in agreement with the conservation of their higher surface area and ordered porous structure.

Figure 52

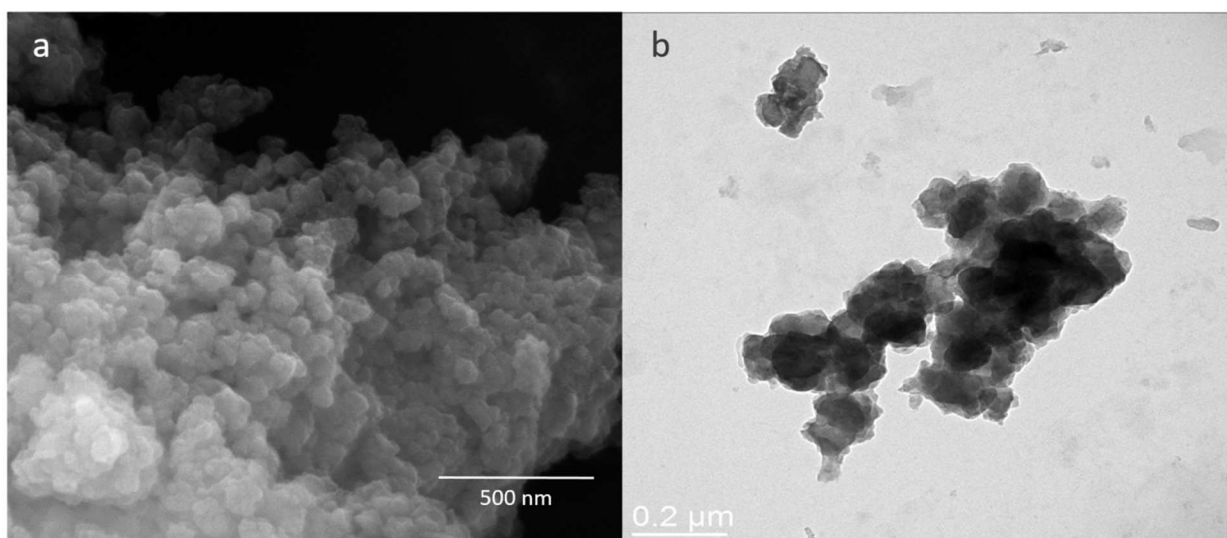
Experimental PXRD data of sulfated MOFs.



The uniformity, promoted by the CTAB surfactant on the defective material ZrBTC-AE2 (CHAPTER 4), seems to almost completely conserve after sulfation, as shown in the SEM image (Figure 53a). On the other hand, the TEM image offered insight into the local structure of the crystalline phase, see Figure 53b.

Figure 53

(a) SEM and (b) TEM images of the ZrBTC-AE2S MOF.



The study of the surface of sulfated MOFs gives further insights into the chemical components at the surface after the modification. As a result, the relative concentration of elements and the components found at the surface of sulfated ZrBTC-A, ZrBTC-AE1S, and ZrBTC-AE2S is showed in Table 12. Carbon, oxygen, zirconium, nitrogen, and sulfur elements were detected and quantified. The presence of nitrogen traces is expected to take into account the possible hydrolysis of residual DMF solvent (Wißmann et al., 2012). Through the calculation of the empirical formulas of the sulfated MOFs surface, it seems that

the surface of these materials exhibits a deficiency of oxygen and zirconium compared to the core components of MOF-808 (Hiroyasu Furukawa et al., 2014). Related to sulfur content, the sulfated materials synthesized through the CTAB-self assembly strategy showed a decrease compared to the previously reported sulfated MOF-808 (Juncong Jiang et al., 2014), see Section E-2.4.1. of the Supplementary Information. Furthermore, we carried out the decomposition of the high-resolution spectra of the C 1s, O 1s, Zr 3d, N 1s, and S 2p core levels of the ZrBTC-AS, ZrBTC-AE1S, and ZrBTC-AE2S as we reported in our previous works (Ardila Suárez, Díaz, et al., 2019; Ardila Suárez, Rodríguez Pereira, et al., 2019). The chemical species considered are presented in Figure 54, and their quantification results are shown in Table 13.

Table 12

C 1s, O 1s, Zr 3d, N 1s, and S 2p peaks contributions concentration for ZrBTC-A, ZrBTC-AE1S, and ZrBTC-AE2S MOFs. The species are coded according to Section E-1 of the Supplementary Information.

Relative Molar %	Sample		
	ZrBTC-AS	ZrBTC-AE1S	ZrBTC-AE2S
C 1s			
C-Ar	16.18	16.81	17.76
Ar-(C-O)-Zr, C-NH ₃	0.29	1.54	0.85
Ar-Carboxy	8.35	8.49	8.48
Aliph-Carboxy	8.23	7.92	8.0
C-S-O/C-O-H	1.43	3.57	1.55
Total	34.48	38.33	36.64
O 1s			
Zr-O/ S-O	12.72	6.59	9.25

R-(C=O)-OH	34.35	32.88	34.48
C-O-Zr	3.55	7.86	4.55
Total	50.62	47.33	48.28
Zr 3d			
Zr-O	6.34	6.60	7.3
Zr-O-C	1.78	1.77	1.57
Zr-O-S	2.1	1.52	1.18
Total	10.22	9.89	10.05
N 1s			
N 1s	0.07	0.12	0.10
S 2p			
S-O-Zr	4.62	4.35	4.93
Total	4.62	4.35	4.93

According to the results, and compared to our previous work (Ardila Suárez, Díaz, et al., 2019), there is a contribution in the C 1s peak probably related to sulfonation of the organic ligand or impurities, C-S-O/C-O-H. However, since there is just one doublet resolved at the sulfur peak, related to the coordinated sulfur, S-O-Zr, the sulfonation, or the trimesic acid remains ambiguous. Furthermore, at the surface of the sulfated materials, the molar ratio related to the proportion between the carbon atoms of the aromatic ring of trimesic acid and those of the carboxylate functional groups of the organic ligand, and the inorganic bonds of the zirconium oxo- clusters. On the other hand, it seems that at the surface, the molar ratio associated with the chelating mode of coordination of sulfate to the zirconium cluster is close to half of the theoretical value (Trickett et al., 2018), probably indicating free sulfur species at the surface.

Figure 54

C 1s, O 1s, Zr 3d, N 1s, and S 2p peaks decomposition recorded in XPS analysis of (a,b,c,d,e) ZrBTC-AS, (f,g,h,i,j) ZrBTC-AE1S, and (k,l,m,n,o) ZrBTC-E2S, respectively. The C-(C,H) component at 284.8 eV was taken as a reference for the binding energy calibration.

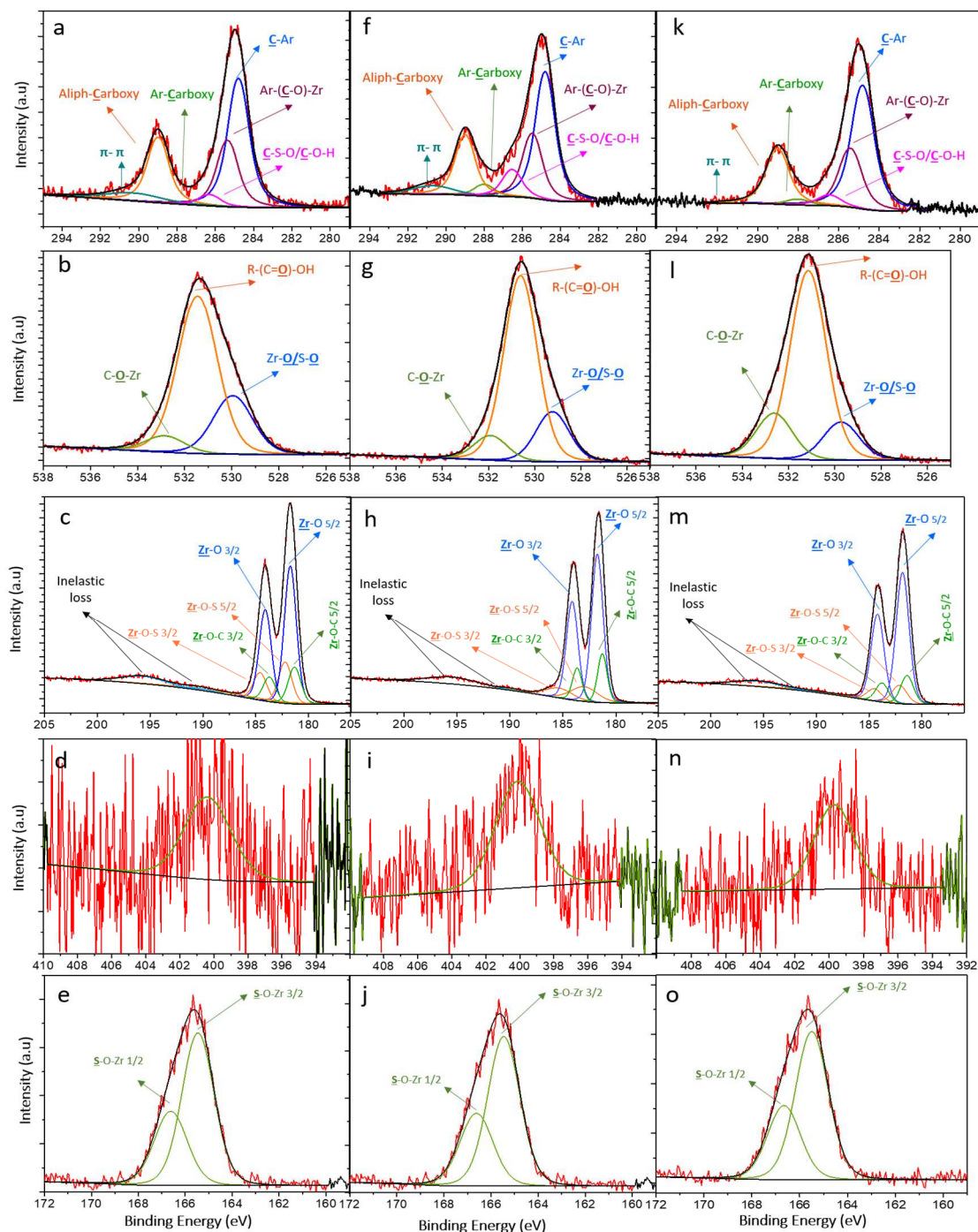


Table 13*Species molar ratios of ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2 materials*

Species molar ratios	Sample		
	ZrBTC-AS	ZrBTC-AE1S	ZrBTC-AE2S
C-Ar/Ar-Carboxy	1.87	1.68	1.90
"Free"-[Carboxy/CarbOxy]	0.48	0.50	0.48
Coordinated			
[Ar-(C-O)-Zr]/{[Ar-(C-O)-Zr]-[2×C-NH]}	0.43	0.95	0.55
[Ar-(C-O)-Zr]/{[Ar-(C-O)-Zr]-[2×C-NH]}	0.22	0.21	0.19
[Ar-(C-O)-Zr]/[Ar-(C-O)-Zr]	0.50	0.23	0.35
Inorganic			
Zr-O/Zr-O	0.50	1.0	0.79
Coordinated sulfur			
Zr-O-S/Zr-O-S	0.45	0.35	0.24

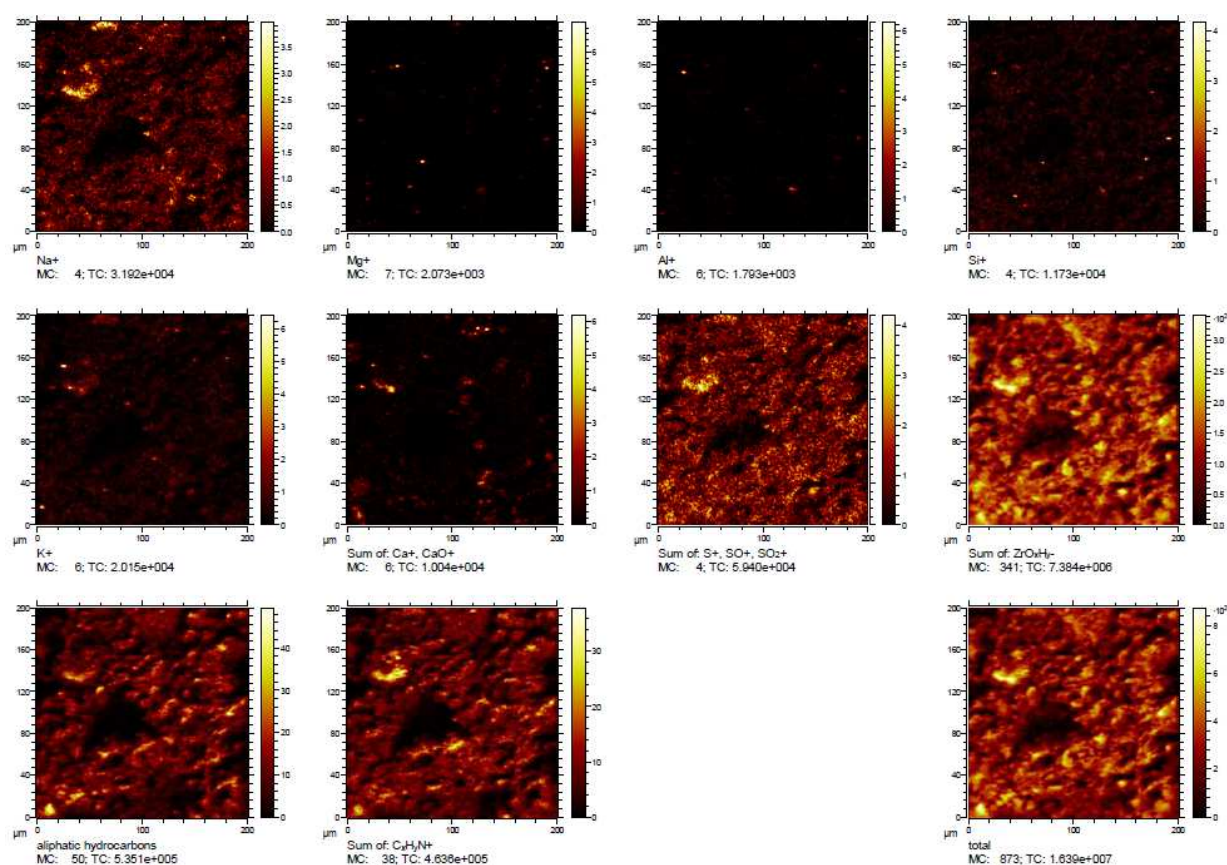
The presence of sulfur species at the surface of ZrBTC-AE2S material is further evidenced through ToF-SIMS. The data collected from both the positive and negative ion spectra are shown in Figures E-9a and E-9b. Concerning the positive ion spectra, it seems that the ZrBTC-AE2S material exhibited very similar signals compared to the unmodified ZrBTC-AE2 (CHAPTER 4), consisted on strong, ZrO^+ , $(\text{ZrO}_2)_3\text{H}^+$, $(\text{ZrO}_2)_5\text{H}^+$ along with weaker signals due to ZrO_2H^+ , Zr_2O^{3+} , and $(\text{ZrO}_2)_2\text{H}^+$ signals. However, the data collected from the negative ion spectra besides the similar species compared to ZrBTC-AE2 spectra, i.e., strong $(\text{ZrO}_2)\text{OH}^-$, $(\text{ZrO}_2)_2(\text{OH})_2\text{H}^-$ and $(\text{ZrO}_2)_3\text{OH}^-$ along with weaker signals due to ZrO_2^- , and

$(\text{ZrO}_2)_2\text{OH}^-$ signals, it is also observed sulfur related signals: S^- , SO_2^- , $\text{ZrO}_2\text{SO}_4\text{H}^-$, and $(\text{ZrO}_2)_2\text{SO}_4\text{H}^-$, which confirms the presence of free sulfur species at the surface. Furthermore, ZrBTC-AE2S material further exhibited the signals of high m/z ratios related to the fragmentation of the metal-organic clusters. Figures E-10 and E-11 defined more precisely in different m/z range of the negative and positive secondary ion polarity, respectively. They show that ZrBTC-AE2S MOF contains some residual bromine and silicon species.

The images of the surface positive and negativity secondary ion polarity of the sulfated ZrBTC-AE2 MOF are given in Figures 55 and 56, respectively. These images allow mapping the chemical surface composition of the topographic MOF powder. Concerning the images of the surface positive secondary ion polarity, Figure 55, it is observed that the sample exhibited a significant distribution of ZrO_xH_y^- species on the surface, compared to aliphatic hydrocarbons and $\text{C}_x\text{N}_y\text{N}^+$ species, which agrees with XPS findings in the previous section. According to Figure 56 which presents the images of the surface negative secondary ion polarity, the material surface-displayed high concentrations of $(\text{ZrO}_2)_x(\text{OH})_y\text{H}_z^-$, and sulfur related species: S^- , SO^- , SO_2^- , SO_3^- compared to C_xH_y^- and $(\text{ZrO}_2)_x(\text{SO}_4)\text{H}^-$ species.

Figure 55

TOF-SIMS high-resolution images of the surface positive secondary ion polarity of ZrBTC-AE2S.

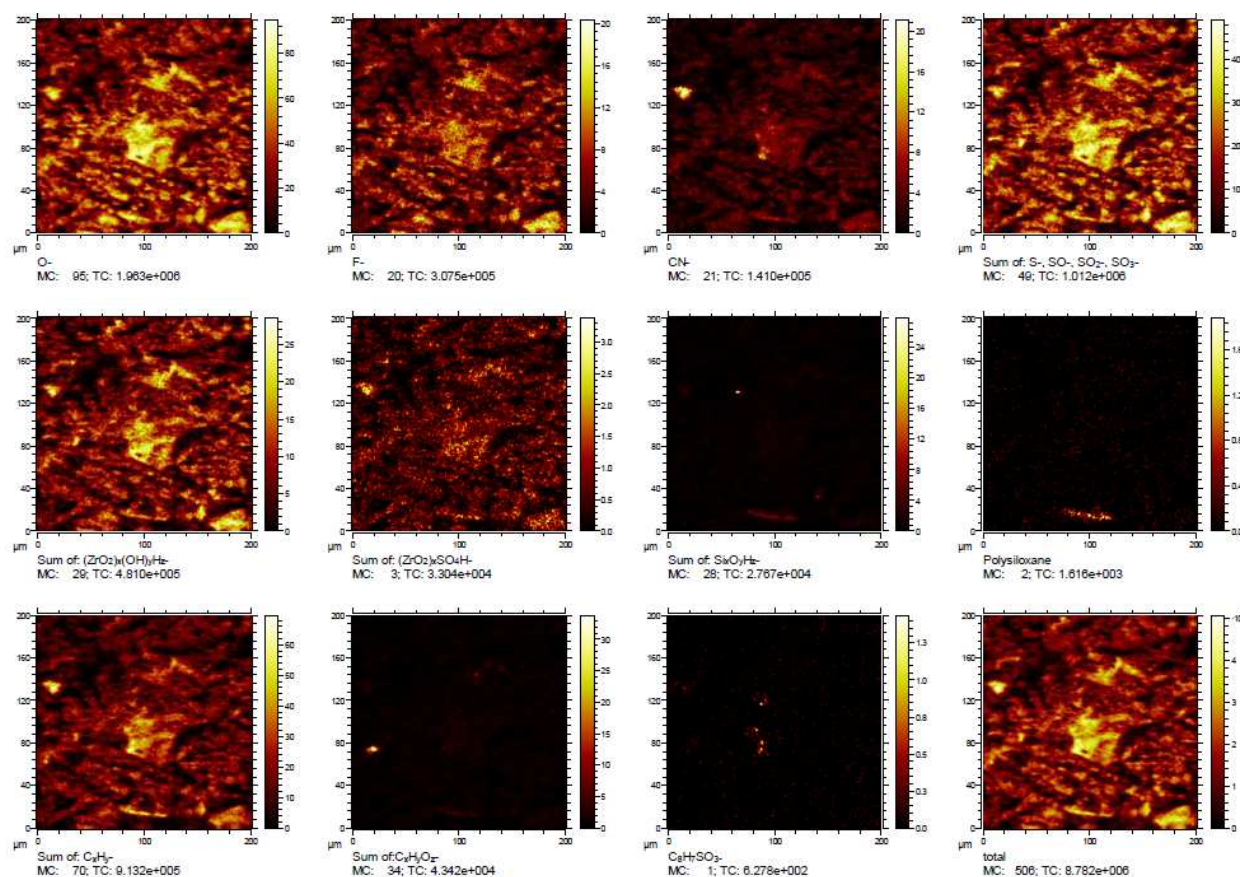


Surface acidity studies

Surface acidity studies were performed to analyze the heterogeneity of acid sites present in the Zr-MOFs synthesized herein and also, in order to assess the impact of the sulfation on their acidic properties. Consequently, the FTIR of absorbed CO studies and potentiometric acid-base titration were achieved.

Figure 56

TOF-SIMS high-resolution images of the surface negative secondary ion polarity of ZrBTC-AE2S.

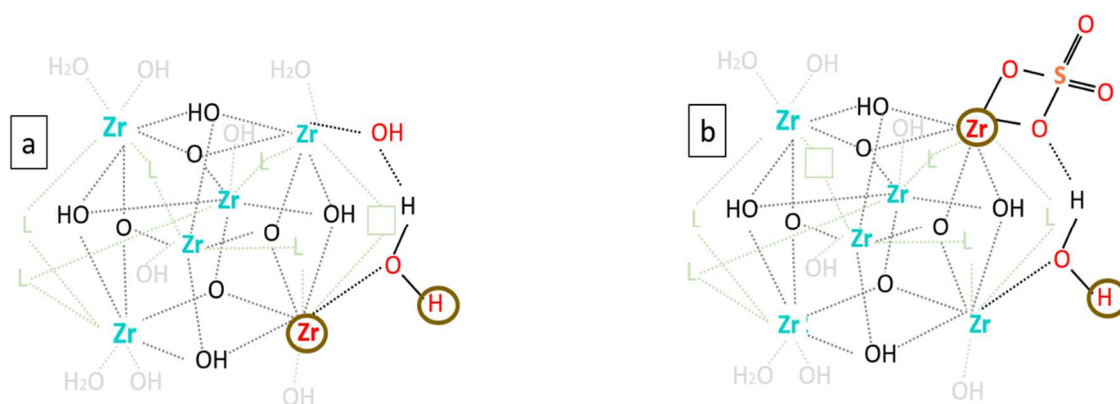


In our previous report, we demonstrated how the activation process increases the strength of Brønsted and Lewis acid sites in MOF-808 (Ardila-Suarez et al., 2018). Consequently, activated MOF-808 exhibits acid sites with moderate strength, as shown in Figure 57-a. Also, after sulfation, additional sites with enhanced acidity are formed, as shown in Figure 57-b. For sulfated zirconia, it is reported that the Lewis acid strength of Zr^{4+} becomes more significant due to the inductive effect of the $\text{S}=\text{O}$ in the formed complex (Spielbauer, Mekhemer, Zaki, & Knözinger, 1996). Moreover, according to Trickett et al. (Trickett et al., 2018), the strength

of the Brønsted acid site lies from the hydrogen-bonding interaction between the coordinated water and a chelating sulfate group. In this study, we used CO, a weak basic molecule, in order to discriminate acid sites with different strengths.

Figure 57

Schematic representation of (a) Moderate Brønsted and Lewis acid sites on activated MOF-808 and (b) additional strong Brønsted and Lewis acid sites after their sulfation.



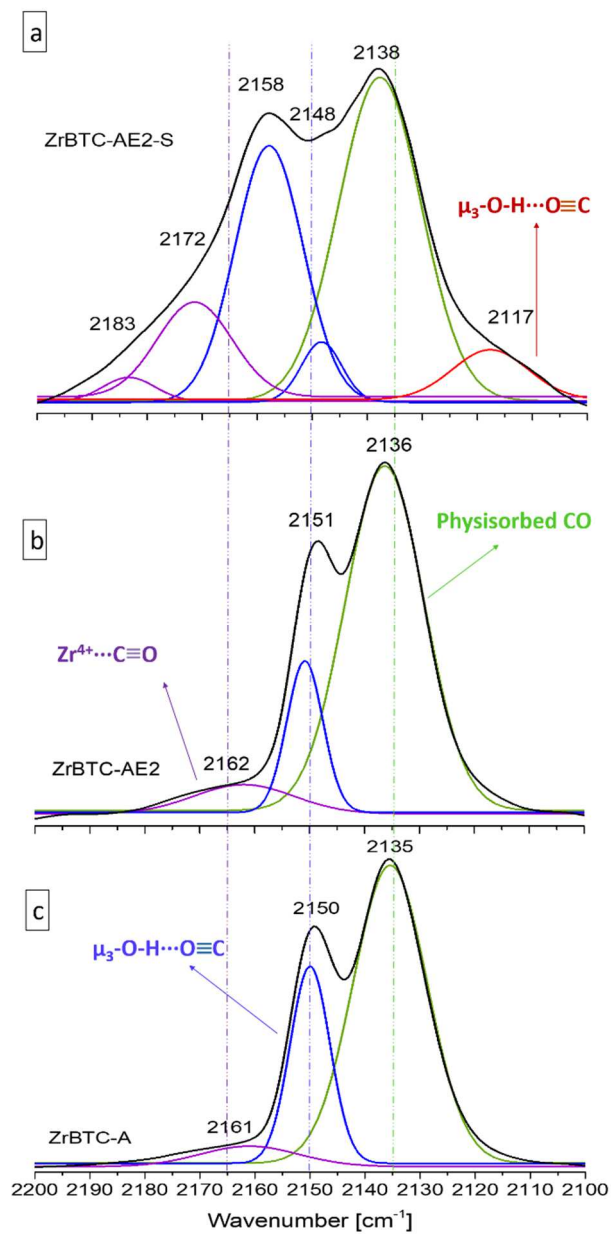
The recorded spectra in the carbonyl stretching region of (2100 – 2200 cm^{-1}) after CO adsorption of ZrBTC-A, ZrBTC-AE2, and ZrBTC-AE2S materials are shown in Figure 58. At low temperature, CO can coordinate on Lewis acid sites, LAS, and also form H bond with acidic OH groups, Brønsted acid sites (BAS). The wavenumbers of $\nu(\text{CO})$ bands are associated with the acidic strength of those Lewis acid sites or hydroxyl groups. Concerning LAS, the vibration frequency of their interaction with CO can reach 2230 cm^{-1} for very strong LAS and shifts down to 2157 cm^{-1} for very weak LAS (Crépeau et al., 2006; Volkringer et al., 2012). Accordingly, the ZrBTC-A and ZrBTC-AE2 showed Zr^{4+} open metal sites of moderate strength at 2161 and 2162 cm^{-1} , respectively. As expected (see Figure 57), after

sulfation, the ZrBTC-AE2 MOF exhibited two different types of LAS with greater strength compared to the unmodified material at 2183 and 2172 cm^{-1} . Related to the CO interaction with acidic OH groups, the $\nu(\text{CO})$ frequency range is located around 2150 cm^{-1} (Mautschke et al., 2018; Volkringer et al., 2012). ZrBTC-A and ZrBTC-AE2 showed a band at 2150 and 2151 cm^{-1} , respectively, associated with the formation of H-bonded species. It is observed two contributions related to Brønsted acidity on the ZrBTC-AE2S material at 2148 and 2158 cm^{-1} . The CO adsorption bands around 2138 cm^{-1} are associated with CO physisorbed inside de MOFs pore structure (Volkringer et al., 2012), and the band located at 2117 cm^{-1} in the sulfated sample could be related to CO interacting with acid hydroxyl groups through the oxygen atom (Driscoll et al., 2019; Ravon et al., 2010). Furthermore, the Brønsted to Lewis (B/L) ratio was measured using the peak intensities of the carbonyl stretching region. Consequently, The ZrBTC-AE2S contained a high B/L ratio of 9.66 compared to the other two catalysts: ZrBTC-A and ZrBTC-AE2 which exhibit B/L ratios of 3.89 and 2.17, respectively. See Section E-2.5.1. of the Supplementary Information for complementary FTIR CO results.

The results of the CO adsorption of the MOFs of interest show us the sites available for either proton transfer or coordinative bonding. According to previous works, the liquid-phase esterification of glycerol with acetic acid does not proceed on solid catalysts with exclusively Lewis sites (W. Hu et al., 2015) and to achieve large conversions and selectivity of products of interest, high Brønsted acidity is required (Kale et al., 2016). The Lewis acid sites in the solid catalysts could act as active catalytic sites involved. Consequently, the knowledge of the surface density of the Brønsted sites is needed for the obtainment of quantitative information on the Brønsted acidity in the MOFs studied herein.

Figure 58

Peak decomposition of Infrared $\nu(\text{CO})$ region recorded at liquid nitrogen temperature of (a) ZrBTC-AE2S, (b) ZrBTC-AE2, and (c) ZrBTC-A after activation at 120 °C for 60 h.

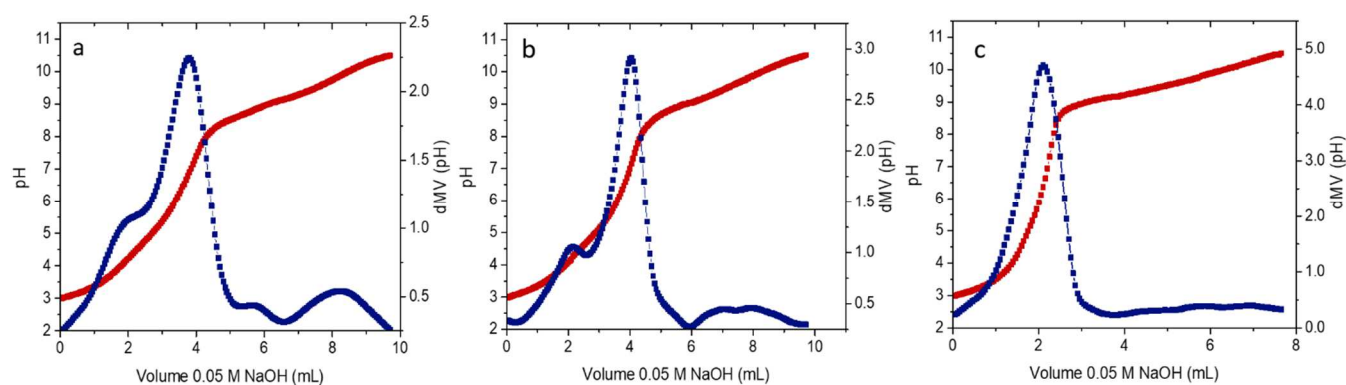


The potentiometric acid-base titration technique allows the determination of Brønsted acid sites of water-stable MOFs. Klet et al. (Klet et al., 2016b) pointed out that the pK_a values found for MOF-808 can be assigned to the μ_3 -OH, -OH₂, -OH protons and an undetermined fourth type of proton. Accordingly, the acid-base titration curves of the MOFs ZrBTC-A, ZrBTC-AE2, and ZrBTC-AE2S are shown in Figure 59, which reveals that the potentiometric acid-base titration curves of ZrBTC-A and ZrBTC-AE2 agree with the ones reported by the mentioned study (Contescu, Popa, Miller, Ko, & Schwarz, 1995; Mora-Vergara, Hernández Moscoso, Gaigneaux, Giraldo, & Baldovino-Medrano, 2018). It is worth mentioning that the addition of surfactant during the synthesis of MOF-808 that leads to ordered materials with interconnected porosity (CHAPTER 4), do not affect the acid sites of the initial material. Related to the ZrBTC-AE2S MOF, see Figure 59-c and d, the inflection points of the first derivative curve are not well-defined.

Consequently, a peak decomposition was performed (See Figure E-13), resulting in the presence of five types of protons, of which the first emerges at lower pH values indicating greater acid strength compared to the initial protons and could be related to the inclusion of the sulfate group (Trickett et al., 2018). To the best of our knowledge, no studies had been conducted related to the quantification of protons using the Gran method on Zr-MOFs. Therefore, the ZrBTC-A and ZrBTC-AE2 curves were decomposed and quantified into four distributions. In contrast, the sulfated material exhibited an additional contribution, which is more acidic compared to the acid protons of the unmodified MOFs, see Table 14.

Figure 59

Acid-base titration curves (red) and first derivative curve (blue) of (a) ZrBTC-A and (b) ZrBTC-AE2, and (c) ZrBTC-AE2S materials.

**Table 14**

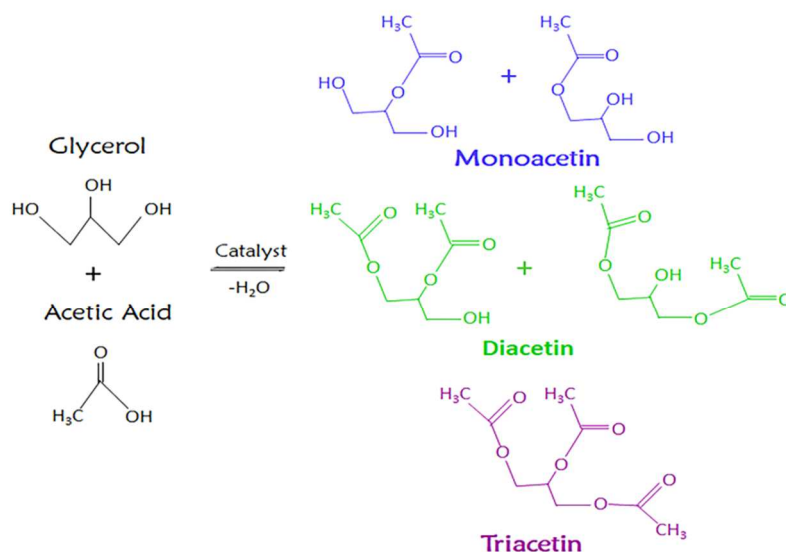
Quantification of acid sites for studied materials.

Acid sites	ZrBTC-A		ZrBTC-AE2		ZrBTC-AE2S	
	Quantification		Quantification		Quantification	
	P _{K_a}	[mmol H ⁺ /g catalyst]	P _{K_a}	[mmol H ⁺ /g catalyst]	P _{K_a}	[mmol H ⁺ /g catalyst]
Type I					3.2	1.6
Type II	3.5	2.7	3.4	2.0	4.1	0.4
Type III	4.7	1.3	4.7	2.5	5	1.0
Type IV	8.1	3.5	8.2	2.2	9.0	3.7
Type V	8.7	2.5	9.0	3.3	9.5	1.3

Catalytic reactions are a measure of the acidic activity of the catalyst. The glycerol (G) esterification with acetic acid (AA) is a sequential reaction that involves three reversible steps: conversion of glycerol to monoacetin (MA) the consecutive conversion of monoacetin to diacetin (DA) and the final obtainment of triacetin (TA) from DA, with a water (W) production as by-product, according to the Figure 60 (Banu et al., 2019; Kong et al., 2016):

Figure 60

Schematic representation of the sequential reaction of the glycerol esterification with acetic acid.

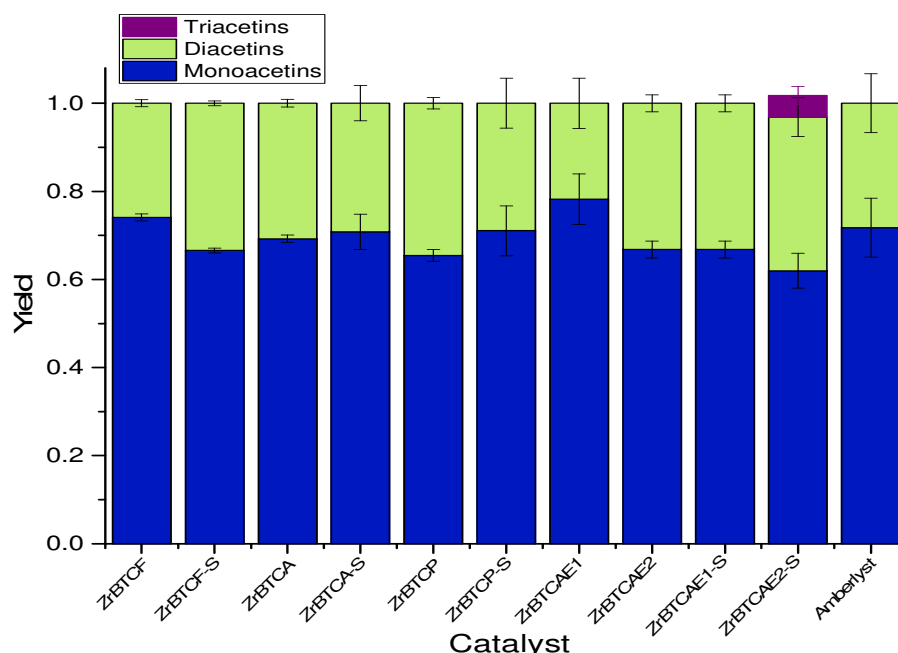


All the studied catalysts were used as fine powders after ground and sieved to sizes between 25 and 75 μm , thus eliminating the intraparticle mass transfer limitations. Furthermore, according to preliminary tests (see Section E-2.6.1. of the Supplementary Information), at stirring speed of 1000 rpm, the influence of external mass transfer was negligible, and consequently, this rotation rate was used in all experiments. The products

yield of glycerol esterification at iso-conversion (c.a. 65%) is shown in Figure 61, and the glycerol conversion after 4h reaction at 100 °C on the evaluated catalyst is shown in Figure E-15.

Figure 61

Products yield at glycerol iso-conversion (c.a. 65%) of studied MOFs and amberlyst catalyst.



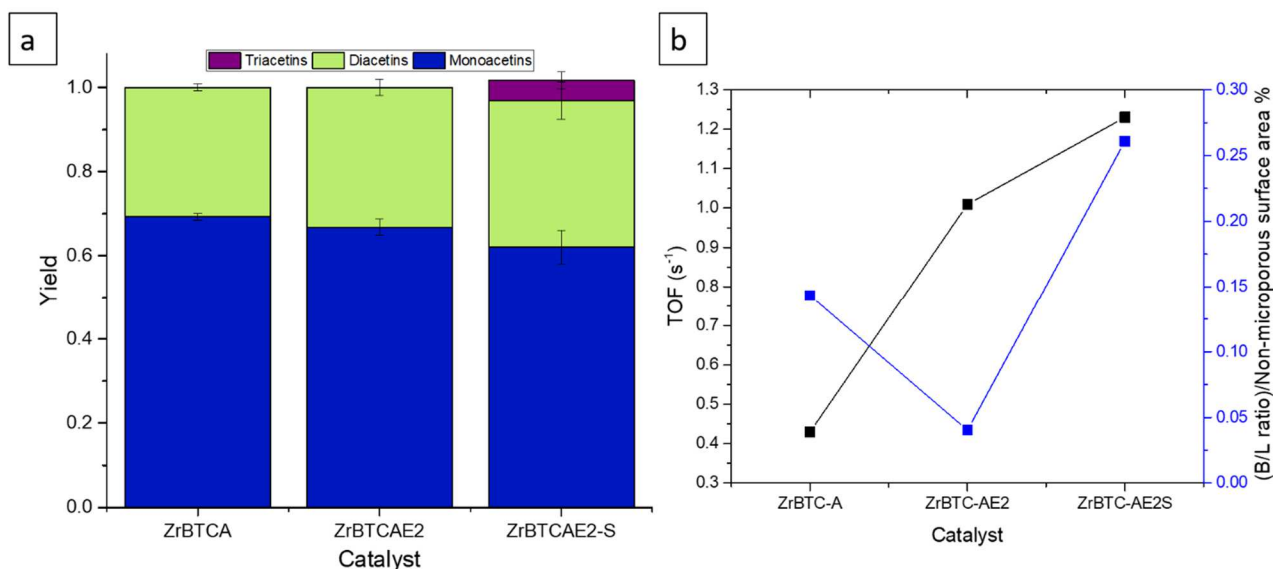
The high monoacetin selectivity at this stage of the reaction for the tested catalyst could be related to its easier formation compared to its consequent acetylation into di- and triacetin. Regardless the thermodynamic features of the reactions calculated through DFT calculations, Gibb's free energy of 1-monoacetin formation was reported as 19.2 KJ/mol, which significantly lower than those of 1,3-diacetin and triacetin, 37.0 KJ/mol and 92.5 KJ/mol, respectively (Liao, Zhu, Wang, Chen, & Li, 2010). As a result, at iso-conversion conditions, the sulfated materials showed an increase in the diacetin selectivity compared to the

unmodified materials, these results could be associated with the presence of stronger acid sites in sulfated MOFs. Moreover, only the ZrBTC-A2S catalyst exhibited selectivity to triacetin at the established conditions. As previously reported (Konwar et al., 2015; Sandesh, Manjunathan, Halgeri, & Shanbhag, 2015), stronger Brønsted sites in the solid catalysts led to higher conversions to di- and triacetin in the glycerol esterification with acetic acid.

Moreover, the Turnover frequency, TOF, for ZrBTC-A, ZrBTC-AE2, and ZrBTC-AE2S catalysts was calculated according to Section E-5.6.3. of the Supplementary Information. According to Figure 62, the TOF for the synthesized materials followed trend $\text{ZrBTC-A} < \text{ZrBTC-AE2} < \text{ZrBTC-AE2S}$. It seems that the activity increase of ZrBTC-AE2 compared to ZrBTC-A is related to the increase of the non-microporous surface area percentage. Also, the ZrBTC-AE2 exhibited an ordered porous structure with macropores centered around 54 nm. Thus, the interconnected porosity of the ZrBTC-AE2 catalyst almost does not affect the acidic properties of the ZrBTC-A materials but favors the diffusion of reactants to the acid sites and consequently, its activity. The surface characterization showed that after the modification process, sulfate and sulfur related species are present and well distributed on the surface of the ZrBTC-AE2S catalyst, see Figures 55 and 56. This sulfation led to the enhancement of the material acid strength (according to the study of its acid properties analysis), which is reflected in its high activity despite the decrease in its non-microporous surface area, see Figure 62-b. Despite the decrease in the non-microporous pore size distribution after sulfation, the permanence of the interconnected and ordered structure and the improved acid strength allowed to ZrBTC-AE2S catalyst higher glycerol conversions and selectivity towards triacetin compared to the unmodified materials.

Figure 62

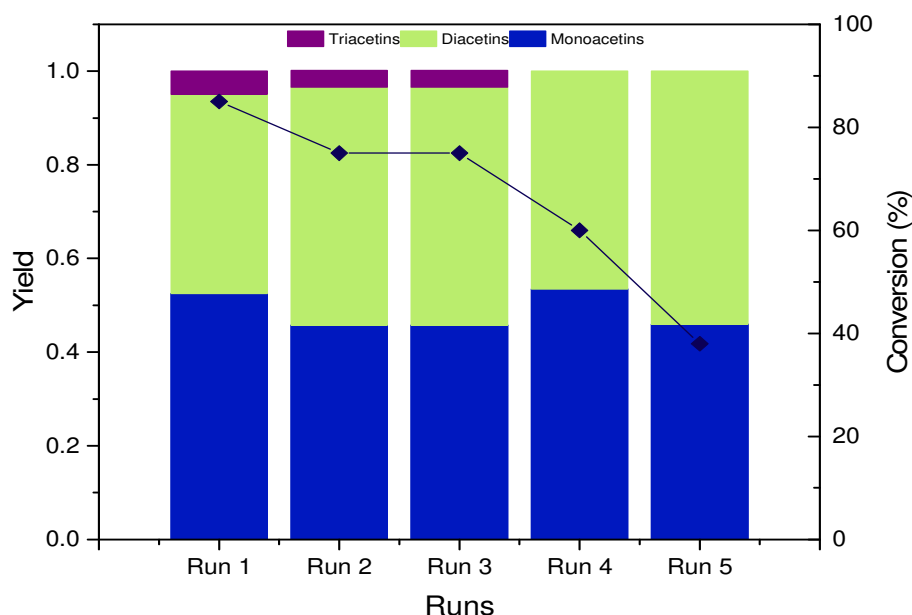
Correlation between textural and acidic properties and selectivity at iso-conversion conditions (c.a. 65%) of ZrBTC-A, ZrBTC-AE2, and ZrBTC-AE2S



In order to evaluate the activity of the ZrBTC-AE2S catalyst after several runs, after 4 h of reaction, the reactant solution was centrifuged, and the catalyst was separated from it. The recovered catalyst was washed according to the experimental section before the next run. Figure 63 displayed the activity of the ZrBTC-AE2S catalyst for 5 consecutive runs. We observed that already in the second run, there is a reduction in the glycerol conversion and triacetin selectivity of 9 and 26.8 %, respectively. Although there are no significant changes after the third run, a drastic fall is already observed from the fourth run. According to Figure A-17, it seems to be no affectation in the catalyst structure. Probably, the reduction of the catalyst activity could be related to leaching issues of the sulfated MOF.

Figure 63

Reusability test of the ZrBTC-AE2S catalyst. Reaction time: 4 hours in a batch reactor at 100 °C; catalyst loading: 1% wt (glycerol reactant basis).

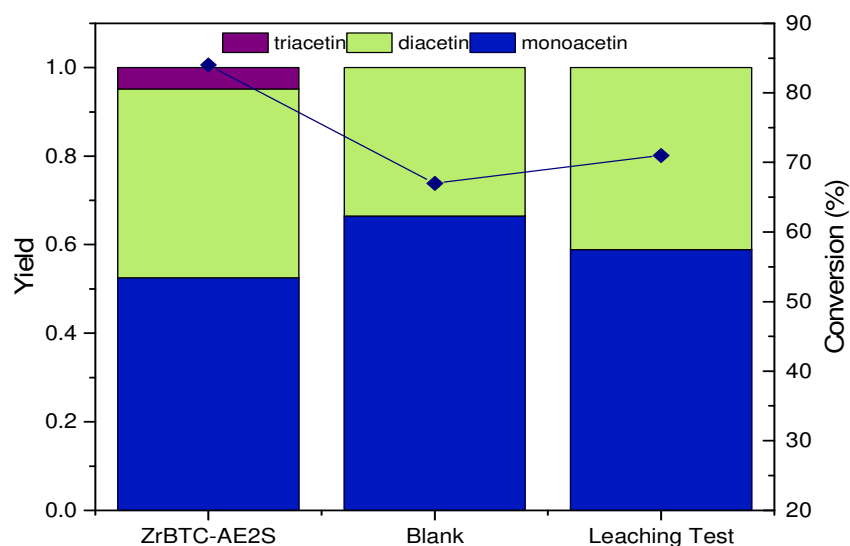


To evaluate the possible leaching of the coordinated sulfates on the zirconium cluster, the reaction products of the glycerol esterification were separated from the ZrBTC-AE2S catalyst after 2 hours of reaction. The reaction continued with no catalyst, and the reaction products were compared to the selectivity and glycerol conversion of the ZrBTC-AE2S and a blank run, as shown in Figure 64. As previously reported (S. Zhu et al., 2013), the glycerol esterification can proceed with no catalyst. Thus, after 4 hours reaction, the conversion of glycerol is around 65 % with a low selectivity to diacetin and with no production of triacetin. However, it seems that after the leaching test, the conversion of glycerol, as well as the diacetin selectivity, increased compared to the blank. This is an indication of a leaching process of the sulfates coordinated to the MOF, which acted as a homogeneous catalyst and continued to the glycerol conversion after solid removal. As reported in the experimental

section, the presence of sulfate ions in solution was verified using BaCl_2 . A white precipitate of BaSO_4 confirmed the presence of sulfate ions in the water. This result confirms that the sulfate leaches into the reaction mixture, as is shown in Figure 64.

Figure 64

Leaching test of the ZrBTC-AE2S catalyst. Reaction time: 4 hours in a batch reactor at 100 °C.



The superior performance of sulfated materials over unmodified MOFs was showed. However, the leaching issues related to the sulfation process encourage the search for new methods for the addition of strong Brønsted sites. The synthesis of ordered and interconnected micro-mesoporous/macroporous MOF-808 with the addition of a small quantity of a secondary organic ligand that leads the post-synthetic addition of sulfonic acid moieties avoiding leaching (Zongcheng Miao, Qi, Wensley, & Luan, 2016).

5.2. Conclusions

The formation of ordered and interconnected microporous/macroporous tricarboxylate zirconium-based MOFs seems not to affect the acid properties of the material synthesized with no surfactants. Moreover, the catalytic tests reflect that the interconnected porosity of the surfactant-assisted synthesized materials favors overcoming diffusion and accessibility of bulky molecules leading to an improvement of the catalytic performance in the liquid-phase esterification of glycerol with acetic acid. Concerning the sulfation of MOFs, this post-synthetic process affects the crystallinity and textural properties in a significantly lower proportion of the materials synthesized using CTAB surfactant compared with materials synthesized with the conventional method. It seems that the sulfation process did not affect the interconnectivity of surfactant-assisted synthesized materials. The surface characterizations showed that the sulfate groups are attached to the structure and well distributed over the catalyst surface. The FTIR of absorbed CO studies and potentiometric acid-base titration showed that sulfation led to the formation of additional Brønsted sites with more strength compared to the unmodified material. The catalytic activity in terms of TOF measurements showed that at iso-conversional conditions, the selectivity to di- and triacetin of sulfated material is related to its Brønsted sites distribution. However, the reusability test shows that sulfated MOF drastically decreases its activity after the third run, a fact that could be related to leaching issues.

6. General Conclusions and Recommendations for Future Work

It was performed the systematic design of multi-modal Zr-based MOF-808 materials through defect engineering strategy and their post-synthetic modification towards the obtainment of suitable solid catalysts materials for liquid-phase esterification reactions application.

It was concluded that the use of different precursors impacts the morphology, crystallinity, and porosity of MOF-808. Conversely, zirconium precursors did not affect the thermal stability and surface chemistry. Furthermore, the synthesized materials exhibited a defective structure at the surface with an abundance of uncoordinated zirconium oxo-clusters compared to the formula reported MOF-808 bulk material.

The activation process for defect-free and defective structures of MOF-808 has been investigated using AIMD and ReaxFF MD methods. The cluster model shows that the formate ion that replaces the organic linker remains only slightly bonded to the zirconium node. ReaxFF MD calculations for the MOF-808 supercell in agreement with the ab initio calculations evidenced the removal of the majority of the formate ions that replaced the organic linkers. Bader charge analysis evidence the decrease of the zirconium atoms coordination environment as well as the charge differences of the different oxygen atoms types after the activation process. The inclusion of defects leads to more localized zirconium d-states, which also appear at lower energy sites where the removed linkers were previously

located. It is shown that the dehydroxylation process does not increase the strength of the Brønsted sites in the cluster with no defects. Conversely, if the dehydroxylation is performed on the defective structure, the energy of ammonia adsorption increases. However, the reported sites only exhibit weak Brønsted acidity.

Regarding the study of the effect of modulator concentration, it was found that all the synthesized materials displayed a certain degree of amorphicity related to the formation of a mesoporous structure. Also, increasing the concentration of the employed modulator promoted the formation of a more crystalline structure without affecting the thermal stability of the material. After the post-synthetic modification process, it was observed that the sulfuric acid chemically attack the surface structure of the defective Zr-MOF. The attack performed by sulfuric acid enhanced the thermal stability of the Zr-MOF, but it degraded its porous and crystalline structure. It seems that after the sulfation process, only the families of mesopores and the larger micropores are interconnected within the material. Finally, the PSM procedure led to the formation and enhancement of both Lewis and Brønsted surface acid sites in the studied Zr-MOFs.

The use of different modulators during synthesis led to the formation of materials with different amounts of missing linker defects and pore size distributions. On the other hand, the addition of surfactant allowed the synthesis of ordered and crystalline microporous/macroporous materials. The addition of CTAB did not seem to alter the surface chemical composition compared to the material synthesized with no surfactant. Thus, the MOF-808 series exhibited a defective structure at the surface with adjustable pore size distribution by the application of the defect engineering approach for a wide range of applications.

The formation of ordered and interconnected microporous/macroporous tricarboxylate zirconium-based MOFs seems not to affect the acid properties of the material synthesized with no surfactants. Moreover, the catalytic tests reflect that the interconnected porosity of the surfactant-assisted synthesized materials favors overcoming diffusion and accessibility of bulky molecules leading to an improvement of the catalytic performance in the liquid-phase esterification of glycerol with acetic acid. Concerning the sulfation of MOFs, this post-synthetic process affects the crystallinity and textural properties in a significantly lower proportion of the materials synthesized using CTAB surfactant compared with materials synthesized with the conventional method. It seems that the sulfation process did not affect the interconnectivity of surfactant-assisted synthesized materials. The catalytic activity in terms of TOF measurements showed that at iso-conversional conditions, the selectivity to di- and triacetin of sulfated material is related to its Brønsted sites distribution.

Accordingly to the presented conclusions, the first recommendations may be focused on synthesis strategies. A second recommendation is addressed to other strategies for the addition of Brønsted acidity. The last recommendation would be the catalytic evaluation of the synthesized and modified materials in other reactions of interest.

Taking this into account, future work is proposed:

- Continue with the synthesis of MOFs with adjustable pore size distributions through the addition of a second organic ligand. The 2-hydroxy terephthalic acid, the biphenyl 4-4' dicarboxylic acid, and the 2-sulfo-terephthalic acid are proposed. These ligands could be added during the synthesis of MOF-808 at different trimesic acid/second ligand ratios. The first mentioned ligands could add new pore size distribution within the framework, and thus, the materials can be evaluated in shape-selectivity gas separation, adsorption and catalysis

applications. The last proposed ligand could also provide a Brønsted site without requiring a post-synthetic modification.

- Another study for the obtainment of materials of the MOF-808 family with adjustable pore size distributions is their synthesis with the use of trimethyl-ammonium bromides cationic surfactants of different chain lengths, namely: octyl-trimethyl-ammonium bromide (OTAB), dodecyl-trimethyl-ammonium bromide (DTAB), and tetradecyl trimethyl ammonium bromide (TTAB) and compared them with the results obtained herein using the cetyl-trimethylammonium bromide (CTAB) and elucidate the effect of the surfactant chain-length in the final textural properties of synthesized materials.
- It is also proposed to theoretically corroborate the adsorption of CO molecule on the synthesized and modified materials and the subsequent study of the effect of these post-synthetic modifications on the adsorption of glycerol, acetic acid and others reagents of interest to study different reaction mechanisms and complement the experimental results of this Dissertation.
- In order to replace fossil fuels with renewable sources, it is proposed the employment of the materials synthesized in this work as solid acid catalysts for the conversion of biomass-derived compounds (glucose, xylose, fructose, among others) into high-added-value platform chemicals with high industrial potentials such as levulinic acid, 5-hydroxymethyl furfural, and furfuryl alcohol.

7. Scientific Disclosure

PUBLICATIONS

Ardila-Suárez, C., Rojas-Avellaneda, D., and Ramirez-Caballero, G.E. "Effect of Temperature and Catalyst Concentration on Polyglycerol during Synthesis" *International Journal of Polymer Science*, vol. 2015, 2015. <https://doi.org/10.1155/2015/910249>.

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AIChE Annual Meeting. Pittsburgh, USA. "Surfactant-Templated MOF – 808: Effect of CTAB Incorporation on Final Properties and Catalytic Activity". Poster Presentation. 2018

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AIChE Annual Meeting. Atlanta, USA. “Synthesis and Characterization of Novel Stimuli-Responsive Hydrogels Based on Polyglycerol.” Oral Presentation. 2014

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Appendices

Appendix A. Supplementary Information Chapter 1⁵

A-1. Experimental Methods

A-1.1. Crystallinity

The indexation of the powder diffraction patterns was performed with the Dicvol06 program, and the Le Bail whole powder pattern of structural information was employed using the FullProf software (Rodríguez-Carvajal, 2001). All parameters were refined according to the least-squares method (Pawley, 1981). The pseudo-Voigt function was employed as the peak profile function (Thompson, Cox, & Hastings, 1987). Also, an estimate of the relative crystallinity between the synthesized materials was performed by the analysis of the integrated intensity areas of the characteristic XRD diffraction peaks of MOF-808 (ZrBTC MOF) ($2\theta = 4.33^\circ, 7.14^\circ, 8.32^\circ, 8.69^\circ, 10^\circ, 10.9^\circ, 13^\circ, 14.2^\circ$ and 19.32°), using the OriginPro software after baseline correction following a procedure reported elsewhere (S. Liu et al., 2013).

⁵ Reprinted with permission from: Ardila-Suárez, C., Rodríguez-Pereira, J., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). An analysis of the effect of zirconium precursors of MOF-808 on its thermal stability, and structural and surface properties. *CrystEngComm*, 21(9), 1407-1415, doi: 10.1039/C8CE01722K.

A-1.2. Porosity Calculations

Microporous pore size distributions were calculated using the Ar recorded isotherms via a Non-Local Density Functional Theory (NLDFT) routine with a model isotherm for oxides with cylindrical pores as in agreement with previous literature proposals (Kaskel, 2016; Moellmer et al., 2010). A regularization factor of 0.0316 was employed. Mesoporous pore size distributions were calculated by the Barret-Joyner-Halenda (BJH) method (Barrett, Joyner, & Halenda, 1951) assuming cylindrical pores. Cumulative pore volumes were calculated from the NLDFT routine. The calculation routines were provided in the *MicroActive* Micromeritics software of the instrument.

A-1.3. Surface Chemistry

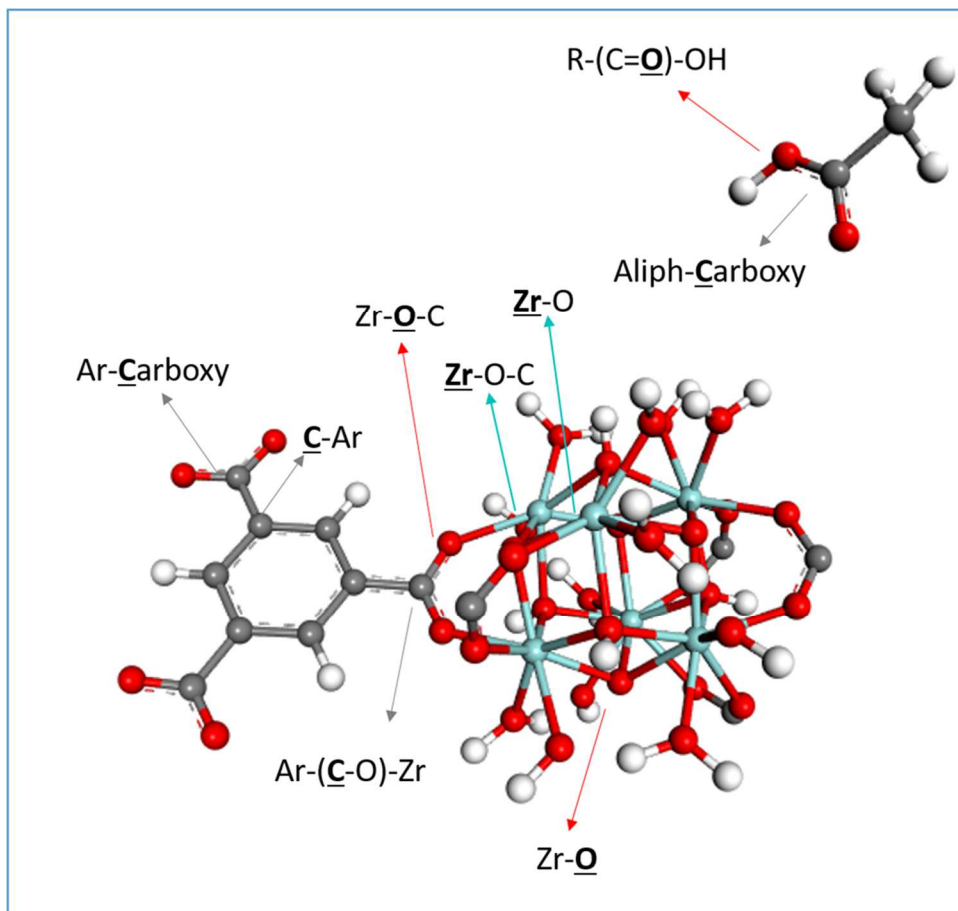
Analyses were performed on the A. Centeno-XPS/ISS/UPS surface characterization platform built by SPECS. The platform is provided with a PHOIBOS 150 2D-DLD energy analyzer package. A monochromatized Al K α X-ray source (Focus 500) operated at 200 W was employed. The pressure in the analysis chamber was approximately 1×10^{-7} Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 54°. Samples were mounted on carbon conductive tape over metallic sample holders for analysis. Surface charge compensation was controlled with a flood gun (FG 15/40-PS FG500 device) operated at 58 μ A and 1.0 eV. Spectra were collected in the Fixed Analyzer Transmission mode. The spot area for analyses was 3.5 $\times$ 1.0 mm². The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and to 60 eV for high-resolution spectra. The energy step for acquisition was set to 0.050 eV. General spectra were recorded first for all samples followed by high-resolution spectra. The C 1s peak was recorded both at the beginning and at the end of the measurements for checking the evolution

of surface charge during the analyses. High resolution spectra were recorded following elements identification in the general spectra and according to samples chemistry and history. Data analysis was performed with the CasaXPS program (Casa Software Ltd) using the SPECS Prodigy library for R.S.F. values. A U 3 Tougaard baseline (J. Walton et al., 2016) was employed for background modeling together with a Lorentzian line shape, LA(1.53,243) in CasaXPS, for peak decomposition. For the C 1s peak, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) Carbon belonging to an aromatic ring, labeled as C-Ar. Under the analysis conditions employed herein, this component is indistinguishable from the peak from the C-(C,H) species from aliphatic hydrocarbons. In consequence, a single component centered at 284.8 eV (Rouxhet & Genet, 2011) was assumed for both species. This component was employed as a reference for correcting the BE scale of the spectra. (ii) Carbon from the carboxylic acid group linked to the Zr cluster, labeled as Ar-(C-O)-Zr. For the analyzed samples, the mean BE for this component was within the 95.0 % confidence interval (t-Student, 2 degrees of freedom) - C.I._{0.05;2}- for the mean = [285.9, 286.3] eV-. (iii) Carbon belonging to the carboxylic acid group of H₃BTC, labeled as Ar-Carboxy. Based on literature references (Genet et al., 2008; Rouxhet & Genet, 2011), the peak for this component was fixed at 288.0 eV. (iv) Carbon from the carboxylic acid group linked to an aliphatic chain, labeled as Aliph-Carboxy and fixed at 289.0 eV (Genet et al., 2008). An additional peak corresponding to the $\pi - \pi^*$ from the aromatic ring was considered for peak decomposition (Briggs & Beamson, 1992). The C.I._{0.05;2} mean BE for this component was within the range: [290.6, 291.4] eV. For this component, the R.S.F. value was set to 0 during chemical species quantification. The same FWHM for set for all carbon species and for the $\pi - \pi^*$ transition peak. For the O 1s peak, three species were considered. The first was oxygen linked to Zr in the inorganic cluster,

labeled O-Zr; C.I._{0.05;2} for the mean = [530.4, 531.0] eV. The second was oxygen belonging to a carboxylic acid functional group; C.I._{0.05;2} for the mean = [531.9, 532.4] eV. In the O 1s peak, this component, labelled as R-(C=O)-OH, cannot be further decomposed into carboxylates linked to an aromatic or aliphatic chain (Rouxhet & Genet, 2011). The third oxygen component; C.I._{0.05;2} for the mean = [533.6, 534.1] eV, was ascribed to oxygen belonging to the Zr-O-C bonds in the MOF. This proposal is coherent with the BE shifts expected when comparing the parent carbon components described before, in the sense that if the corresponding carbon is more oxidized, the oxygen must be more reduced. No constraints were imposed during peak decomposition except for assuming the same FWHM for all components. Finally, for the Zr 3d peak, two species were considered. The first was Zr coordinated to an organic group through oxygen, labeled Zr-O-C; C.I._{0.05;2} for the mean of the Zr 3d_{5/2} peak = [182.0, 182.5] eV, and the second Zr belonging to inorganic clusters; C.I._{0.05;2} for the mean of the Zr 3d_{5/2} peak = [182.7, 183.0], labeled Zr-O. The above BE assignation was also made considering the relative BE shifts expected from the corresponding oxygen and carbon components. The following constraints were imposed during peak decomposition: a) the area of the Zr 3d_{3/2} core level is equal to two thirds of the area of the Zr 3d_{5/2} core level, and, b) a separation of 2.37 eV between both core levels was assumed (Moulder et al., 1995). In addition, four components corresponding to overlapping loss features from the Zr 3d core levels of each assigned species were considered for peak decomposition but not accounted for in quantification; i.e. R.S.F. fixed to 0. The chemical structures used for peak decomposition are illustrated in Figure A-1.

Figure A-1.

Schematic representation of the proposed surface chemical species of C 1s, O 1s and Zr 3d peaks for the synthesized materials.



A-2. Results and Discussion

A-2.1. Thermal Stability

The thermal profiles of all materials were similar. In region I, relative weight losses decreased in the order: ZrBTC1 (~28.1%) > ZrBTC2 (~25.7%) > ZrBTC1 (~23.9%). One may notice that this trend resembles the one obtained for the surface areas. In region II, weight losses followed the trend: ZrBTC3 (~11.7%) > ZrBTC2 (~10.4%) > ZrBTC1 (~10.2%). Finally, in region III, the trend was: ZrBTC3 (~29.4%) > ZrBTC1 (~27.4%) > ZrBTC2 (~26.6%). Finally, under the assumption that there is a complete combustion of the organic components of the material under the air atmosphere at the end of the thermogram, the materials are converted to ZrO₂, the following percentages of ZrO₂ were calculated: ZrBTC2 = 37.3 %, ZrBTC3 = 35.0 %, and ZrBTC1 = 34.3 %. Accordingly, the relative percentages of zirconium of the synthesized materials were: 27.6% for ZrBTC2, 25.9 % for ZrBTC3, and 25.4 % for ZrBTC1.

A-2.2. Crystallinity

Table A-1.

Indexation of the powder diffraction pattern of synthesized materials, using DICVOL06 program at Fullprof Software and resulted Le Bail indexation powder diffraction patterns.

ZrBTC1			ZrBTC2			ZrBTC3		
hkl index	2 theta (indexation)	2 theta (Le Bail)	hkl index	2 theta (indexation)	2 theta (Le Bail)	hkl index	2 theta (indexation)	2 theta (Le Bail)
(1 1 1)	4,3439	4,3437	(1 1 1)	4,3874	4,3874	(1 1 1)	4,4252	4,4252
(2 2 0)	7,0964	7,0961	(2 2 0)	7,1676	7,1676	(2 2 0)	7,2293	7,2294
(3 3 1)	8,3233	8,3229	(3 1 1)	8,4068	8,4067	(3 1 1)	8,4793	8,4793

(2 2 2)	8,6941	8,6937	(2 2 2)	8,7813	8,7813	(2 2 2)	8,857	8,857
(4 0 0)	10,0423	10,0418	(4 0 0)	10,1431	10,1431	(4 0 0)	10,2306	10,2307
(3 3 1)	10,946	10,9454	(3 3 1)	11,0559	11,0559	(3 3 1)	11,1513	11,1514
(4 2 2)	12,3072	12,3066	(4 2 2)	12,4308	12,4309	(4 2 2)	12,5383	12,5383
(3 3 3)	13,0569	13,0562	(5 1 1)	13,1882	13,1882	(3 3 3)	13,3022	13,3022
(4 4 0)	13,0569	13,0562	(3 3 3)	13,1882	13,1882	(5 1 1)	13,3022	13,3022
(5 3 1)	14,2203	14,2195	(4 4 0)	14,3633	14,3634	(4 4 0)	14,4876	14,4877
(4 4 2)	14,8755	14,8748	(5 3 1)	15,0253	15,0253	(5 3 1)	15,1553	15,1554
(6 2 0)	15,0877	15,087	(4 4 2)	15,2397	15,2397	(4 4 2)	15,3716	15,3717
(5 3 3)	15,909	15,9082	(6 2 0)	16,0693	16,0693	(6 2 0)	16,2085	16,2086
(6 2 2)	16,4988	16,498	(5 3 3)	16,6651	16,6652	(5 3 3)	16,8096	16,8097
(4 4 4)	16,6909	16,6901	(6 2 2)	16,8592	16,8592	(6 2 2)	17,0054	17,0055
(7 1 1)	17,4387	17,4379	(4 4 4)	17,6147	17,6148	(4 4 4)	17,7675	17,7675
(6 4 2)	17,9798	17,9789	(7 1 1)	18,1613	18,1614	(5 5 1)	18,319	18,319
(7 3 1)	17,9798	17,9789	(5 5 1)	18,1613	18,1614	(7 1 1)	18,319	18,319
(8 0 0)	18,8482	18,8473	(6 4 2)	19,0387	19,0387	(6 4 2)	19,2041	19,2041
(7 3 3)	19,3513	19,3503	(7 3 1)	19,5469	19,5469	(7 3 1)	19,7168	19,7168
(6 4 4)	19,3513	19,3503	(5 5 3)	19,5469	19,5469	(5 5 3)	19,7168	19,7168
(8 2 2)	20,1628	20,1617	(8 0 0)	20,3668	20,3668	(8 0 0)	20,5439	20,544
(7 5 1)	20,635	20,6339	(7 3 3)	20,8438	20,8439	(7 3 3)	21,0253	21,0253
(6 6 2)	20,7901	20,789	(6 4 4)	21,0006	21,0006	(6 4 4)	21,1834	21,1835
(8 4 0)	21,3998	21,3987	(6 6 0)	21,6166	21,6166	(8 2 2)	21,8049	21,805
(9 1 1)	21,3998	21,3987	(8 2 2)	21,6166	21,6166	(6 6 0)	21,8049	21,805
(8 4 2)	21,8465	21,8454	(5 5 5)	22,0679	22,068	(7 5 1)	22,2603	22,2603
(6 6 4)	21,8465	21,8454	(7 5 1)	22,0679	22,068	(5 5 5)	22,2603	22,2603
(9 3 1)	21,9935	21,9923	(6 6 2)	22,2164	22,2165	(6 6 2)	22,4101	22,4101
(8 4 4)	22,5722	22,571	(8 4 0)	22,8012	22,8012	(8 4 0)	23,0001	23,0001
(7 7 1)	22,9972	22,996	(9 1 1)	23,2306	23,2306	(7 5 3)	23,4334	23,4334
(8 6 2)	22,9972	22,996	(7 5 3)	23,2306	23,2306	(9 1 1)	23,4334	23,4334
(7 7 3)	23,1372	23,136	(8 4 2)	23,3721	23,3721	(8 4 2)	23,5761	23,5762
(9 5 1)	23,6895	23,6883	(6 6 4)	23,9302	23,9302	(6 6 4)	24,1392	24,1392
(6 6 6)	24,0959	24,0946	(9 3 1)	24,3408	24,3408	(9 3 1)	24,5535	24,5535
(10 2 2)	24,7592	24,758	(8 4 4)	25,0111	25,0111	(8 4 4)	25,2299	25,23

Table A-2.

Crystallinity data and structure treatment of the ZrBTC1, ZrBTC2, and ZrBTC3 materials, synthesized from ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ precursors, respectively.

	ZrBTC1	ZrBTC2	ZrBTC3
Crystal system	Cubic	Cubic	Cubic
Space group	$\text{Fd}\bar{3}\text{m}$	$\text{Fd}\bar{3}\text{m}$	$\text{Fd}\bar{3}\text{m}$
Cell parameters	35.2039(48)	34.8548(143)	34.5580(674)
Volume	43628.660(3.99)	42343.605(20.320)	41270.965(49.210)
Chi2	1.73	1.32	1.82

Figure A-2.

Le Bail profile fitting for ZrBTC1 synthesized from ZrCl_4 precursor using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, difference in blue line, and Bragg reflection markers in green.

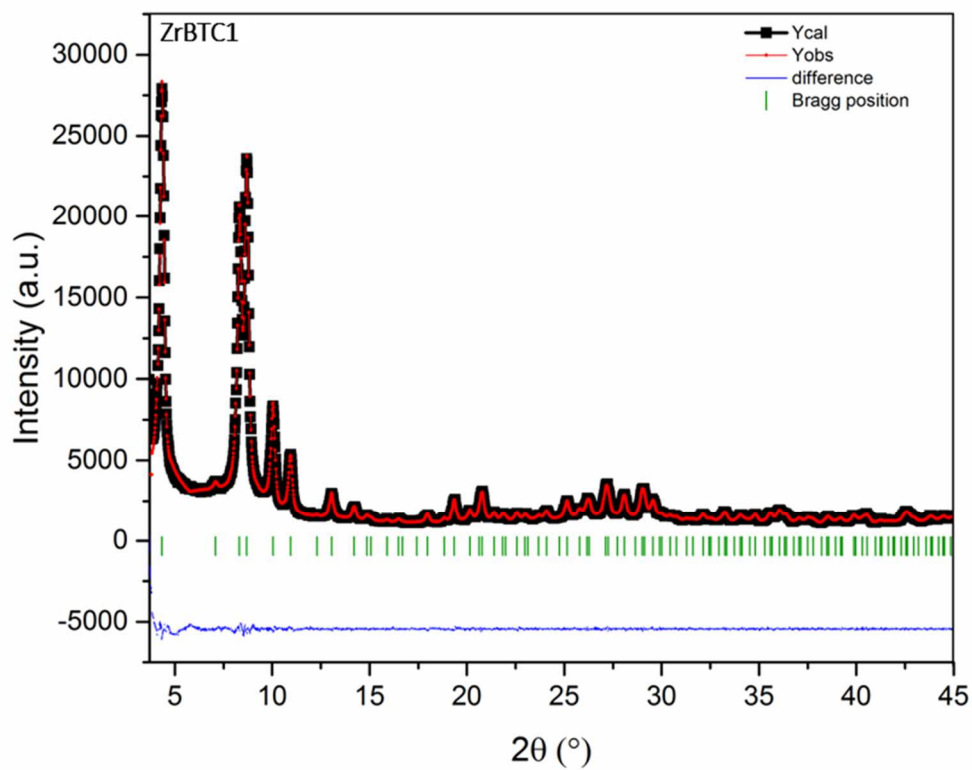


Figure A-3.

Le Bail profile fitting for ZrBTC2 synthesized from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ precursor using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, difference in blue line, and Bragg reflection markers in green.

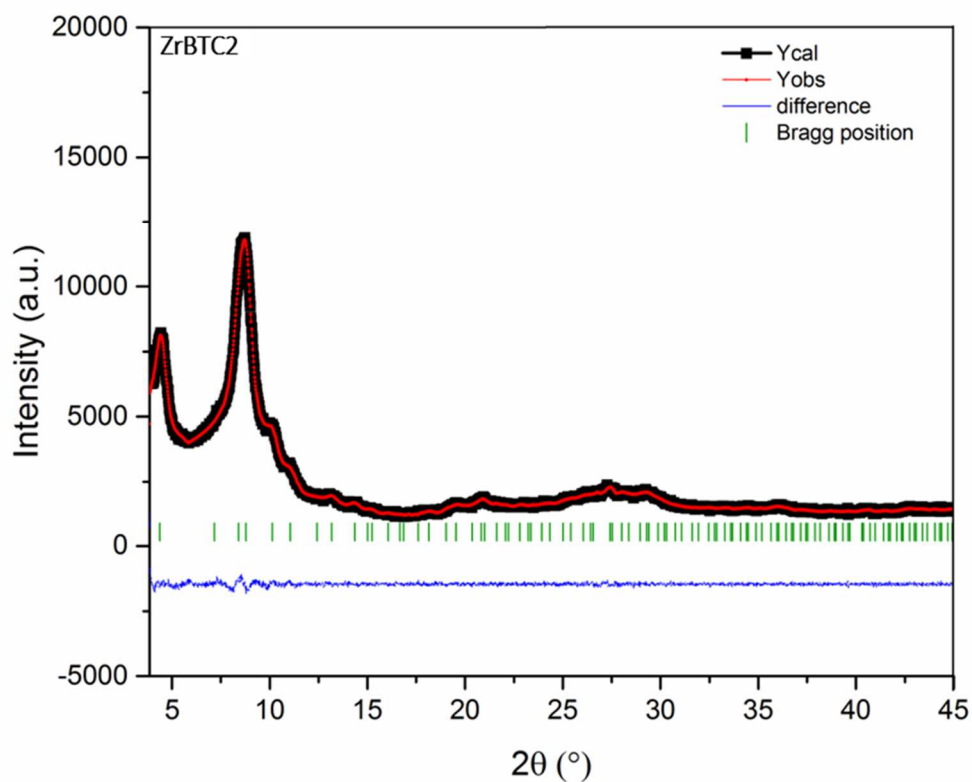
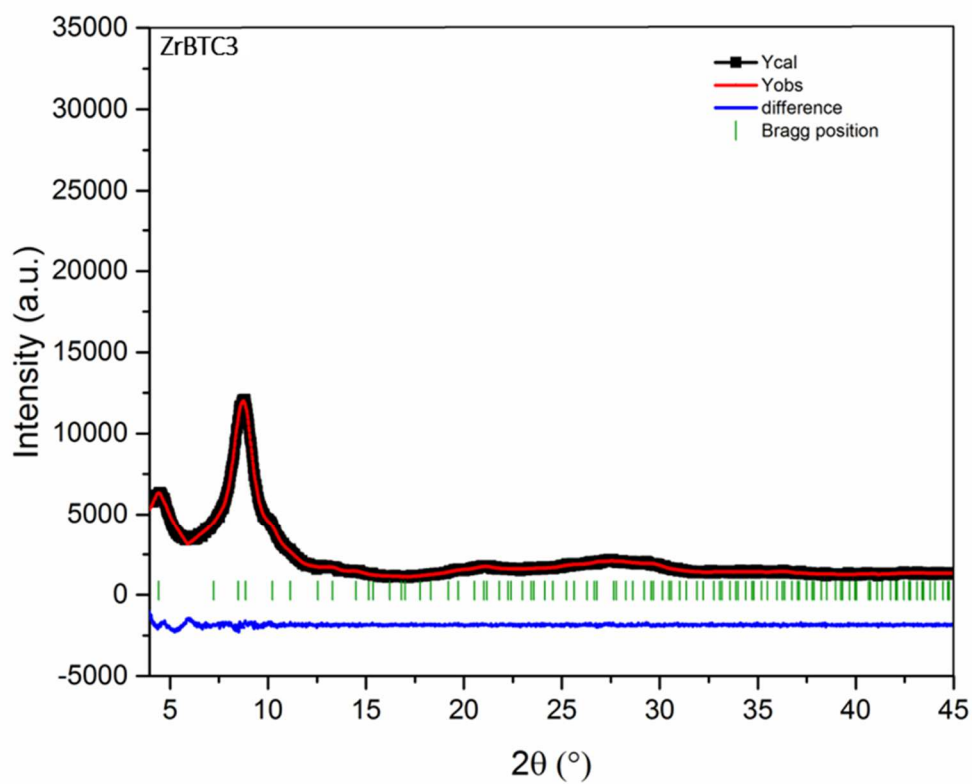


Figure A-4.

Le Bail profile fitting for ZrBTC3 synthesized from $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ precursor using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, difference in blue line, and Bragg reflection markers in green.



A-2.3. Surface Area and Porosity

A-2.3.1. BET- Rouquerol Consistency Criteria

Rouquerol et al (Rouquerol et al., 2007) proposed that the following conditions must be met for choosing an appropriate P/P_0 range for surface area calculation: (1) In a plot of $n(1 - P/P_0)$ vs P/P_0 , one should select only those experimental points where the former increases monotonically. (2) The value of the BET constant C estimated from the linear regression of the BET transform plot should be positive. (3) The amount of the adsorbed gas probe calculated for the BET statistical monolayer; i.e. the BET monolayer capacity (n_m), must be within the range of selected P/P_0 . And, (4) the relative pressure corresponding to the BET monolayer capacity should be approximately equal to $(1/((C)^{1/2}+1))$. They also suggested that the points select for estimating the surface must conform to a linear adjustment. Table S3 shows the calculated SA_{BET} for the synthesized materials and the compliance of the above criteria found for these calculations. According to results, SA_{BET} followed the trend: ZrBTC1 ($SA_{BET} = 1068 \text{ m}^2/\text{g}$) > ZrBTC2 ($SA_{BET} = 764 \text{ m}^2/\text{g}$) > ZrBTC3 ($SA_{BET} = 552 \text{ m}^2/\text{g}$). In general, the four consistency criteria commented above were met except for the linear fitting criterion established by the software. The latter is due to the fact that the isotherms presented changes in their slopes within the P/P_0 region where micropores are found. Such a feature is not encountered on other microporous materials such as the zeolites that Rouquerol et al. (Rouquerol et al., 2007) studied. Therefore, even when the consistency criteria other than the linear fitting criterion were met, the microporous structure of the ZrBTC MOFs synthesized

herein does not allow for a rigorous quantitative assessment of surface area via the BET method; not even if the calculated surface areas are said to be apparent surface areas (Rouquerol et al., 2007). This does not invalidate the qualitative trend found for the effect of the change of Zr precursor on surface area though. In this sense, calculated SA_{BET} values evidenced that the use of $ZrOCl_2 \cdot 8H_2O$ and $ZrO(NO_3)_2 \cdot xH_2O$ produced materials with lower surface areas as compared to $ZrCl_4$.

Table A-3.

Comparison of the apparent surface areas calculated using BET method taking into account the full consistency criteria proposed by Rouquerol of the ZrBTC1, ZrBTC2 and, ZrBTC3 materials, synthesized from $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, and, $ZrO(NO_3)_2 \cdot xH_2O$ precursors, respectively.

BET - Rouquerol Consistency Criteria						
Sample	SA (m ² /g)	C value > 0	n(min) < monolayer < n(max)	P/Po(mono) ~1/(√C+1)	Linear fitting R ²	Rsqr
ZrBTC1	1068	True- 89.08	True	True	False	0.89536
ZrBTC2	764	True- 112.7	True	True	False	0.97406
ZrBTC3	552	True-101.64	True	True	False	0.98441

A-2.3.2. Considerations of the χ - Method (James B Condon, 2006)

The equation for the χ - theory is:

$$\frac{n f A_m}{A_s} = -\ln \left[-\ln \left(\frac{P}{P_s} \right) \right] - \ln \left(-\frac{E_a}{RT} \right)$$

Then, in the transformed equation $y = n_{ad}$ and $x = -\ln \left[-\ln \left(\frac{P}{P_s} \right) \right]$.

Where the slope and the intercept are, respectively: $S_i = \frac{A_s}{fA_m}$ and $I_i = S_i \left[-\ln \left(\frac{E_a}{RT} \right) \right]$

The surface area is calculated using a value of 1.84 for f and determining the value of A_m (the molar area) from

$$A_m = (V_m)^{2/3} (N_A)^{1/3}$$

Where V_m is the molar volume and N_A is the Avogadro's number. The value of A_m for argon is $7.90 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$ at its normal boiling point.

If several segments are observed in the isotherm, the surface areas for each segment, $A_{s,i}$ is given by

$A_{s,i} = 1.84A_m(S_i - S_{i-1})$, where $S_0 = 0$. Also, the Energy of adsorption of each segment is given by:

$$E_{a,i} = -RT \exp \left(-\frac{I_i}{S_i} \right)$$

For the mesoporous range, $S_{hi} = \frac{A_{ex}}{fA_m}$

Also, it necessary to determine the value of $\chi_c = -\frac{I_{lo}}{S_{lo}}$, where I_{lo} is the intercept of the low-pressure linear portion. Then, the pore volume is:

$$V_p = V_m(S_{hi}\chi_c + I_{hi})$$

The theory is characterized by the fact that it is possible to consider several surfaces with different energies of adsorption for the calculation of the total surface area. Surface area assessment by the χ -method follows from a rather simple transformation of the physisorption isotherm; i.e. the χ -plot in Figures 2d to 2f. According to Condon (James B Condon, 2006), regardless of the isotherm type, the section of a χ -plot found at lower relative pressures is associated to the interaction of the probe molecule with the highest surface energy. For MOFs studied herein, such section belongs relative pressures below ca. $P/P_0 = 0.1$ where micropores are accessed by argon. One may observe in Figures 2d to 2f an initial linear section for the constructed χ -plots. Such a section would thus correspond to argon accessing the smallest pores; i.e. micropores, of the materials. Upward bendings of the isotherm may be interpreted as the probe molecules in the gas phase increasing the frequency of their interactions with other adsorbed probe molecules instead of solely adsorbing on the bare surface of the solid. When a further linear section appears in the χ -plot it implies that the probe molecule is now mostly interacting with a surface of the solid that is more open hence with lower surface energy. Every linear portion of the χ -plot is considered to correspond to a surface with a characteristic average surface energy hence resulting in a distribution of surface energies. Such energy distribution is associated to a distribution of surface areas in the χ -theory and related methods using standard plots (James B Condon, 2006; James B. Condon, 2001, 2002; Fuller & Condon, 1989). In general, the total surface area is considered to be a linear summation of the surface areas of each of the surfaces of the solid displaying a similar surface energy. Hence, the application of the χ -method is sensitive to the presence of different distributions of micropores and mesopores in a studied material; which is the case of the MOFs synthesized in this work.

A-2.3.3. Pore Size Distributions and Pore Volume

All Materials displayed multiple families of pores whose presence led to stepped cumulative pore volume curves. In the case of ZrBTC1, a total pore volume of $0.61 \text{ cm}^3/\text{g}$ was estimated. According to calculations, 15.7 % of this volume corresponds to pores with an average size of ca. 0.6 nm, 42.8% corresponds to pores with an average size of ca. 1.5 nm, and 41.5 % corresponds to pores with an average size of ca. 28 nm. The two families of micropores described above displayed relatively narrow ranges of pore sizes. Conversely, the family of mesopores had a wide range of sizes spanning from 10 to 50 nm. For ZrBTC2, the cumulative pore volume amounted to $0.43 \text{ cm}^3/\text{g}$; *ergo*, a 40% decrease in pore volume was obtained by using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as metallic precursors instead of ZrCl_4 . As in the case of ZrBTC1, two families of micropores with average sizes of 0.6 and 1.5 nm were also found for ZrBTC2. Conversely, calculations indicated the existence of one additional family of micropores with an average size around ca. 1.0 nm for ZrBTC2. The relative percentages of pore volumes for these three families of micropores were: 23% for pores of average size equal to 0.6 nm, 4.7% for pores of average size equal to ca. 1.0 nm, and 30% for pores of average size of ca. 1.3 nm. Besides these three families of micropores, ZrBTC2 displayed a family of mesopores with an average size of ca. 6.0 nm. In contrast to what was observed for ZrBTC1, the distribution of sizes of the mesopores was narrower spanning from 2.0 to 10.5 nm. ZrBTC3 presented the lowest cumulative pore volume; namely 0.28 cm^3 , implying that by using $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ as precursor 61% of the pore volume is lost as compared to the use of ZrCl_4 . As in the case of ZrBTC2, four families of pores were found for ZrBTC3. While the three families of micropores found for ZrBTC3 had similar average sizes as those estimated for ZrBTC2, the average size of the mesopores shifted to ca. 3.5 nm as compared to the 6.0 nm calculated for ZrBTC2. In addition, mesopore sizes spanned from 2.0 to 10 nm

for ZrBTC3 hence implying a further reduction in sizes span as compared to ZrBTC1. Concerning the pore volume associated to these families of pores, the family at 0.6 nm contributed 36% to the total pore volume, whereas the families at 1.0, 1.3, and 3.5 nm contributed 7, 39, and 17%, respectively.

A-2.3.4. Surface Chemistry

Table A-4.

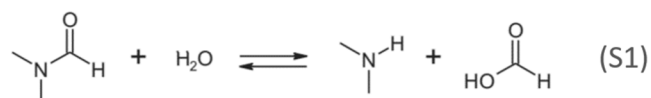
Elemental surface quantification of ZrBTC1, ZrBTC2, and ZrBTC3 materials synthesized from ZrCl_4 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ precursors, respectively.

Relative molar %	Sample		
	ZrBTC1	ZrBTC2	ZrBTC2
carbon	49.46	51.12	49.30
oxygen	41.84	40.27	41.77
zirconium	7.92	6.56	7.19
nitrogen	0.11	0.08	0.13
silicon	0.65	0.63	0.40
aluminum	< D.L.*	1.34	1.22
Empirical formula (surface)**	$\text{CO}_{0.846}\text{Zr}_{0.160}\text{N}_{0.002}\text{Si}_{0.0}$	$\text{CO}_{0.788}\text{Zr}_{0.128}\text{N}_{0.002}\text{Si}_{0.012}\text{Al}_{0.02}$	$\text{CO}_{0.847}\text{Zr}_{0.146}\text{N}_{0.003}\text{Si}_{0.008}\text{Al}_{0.02}$
	13	6	5

*D.L. = Detection Limit; **Measured on a hydrogen free basis.

The nitrogen presence can be associated to the deposition of residual dimethylamine from the hydrolysis of the DMF solvent (Wißmann et al., 2012) (Equation S1). This is corroborated by the fact that the peak corresponding to the N 1s core level measured in XPS, see Figure S6a-c, was found within a C.I._{0.05;2} for the mean = [400.5, 401.5] eV hence being ascribed to C-NH species ("NIST X-ray Photoelectron Spectroscopy Database, NIST Standard

Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 (2000),"). Considering the hydrolysis of DMF (Equation S1) such a species can be more precisely attribute to residual dimethylamine. Given that the corresponding component of this species in the C 1s core level overlaps with the component Ar-(C-O)-Zr, Figure S6d-f, the relative concentration of C-NH was subtracted from the total relative concentration of the corresponding carbon component following the stoichiometry of dimethylamine.



Concerning silicon and aluminum, their presence can be related to the impurities of the precursors salts themselves or, in the case of silicon, to Silicone contamination from sample handling and storage in conventional desiccators. (Aguié-Béghin et al., 2009). The Si 2p and Al 2p peaks recorded in XPS are shown in Figure A-5. The General Spectra of the three synthesized materials is showed in Figure A-6.

Figure A-5.

Si 2p and Al 2p peaks recorded in XPS analysis of ZrBTC MOFs from precursors: (a,d) $\text{ZrCl}_4(\text{ZrBTC1})$, (b,e,) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2) and (c,f) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3). The C-(C,H) component at 284.8 eV was taken as reference for the binding energy calibration.

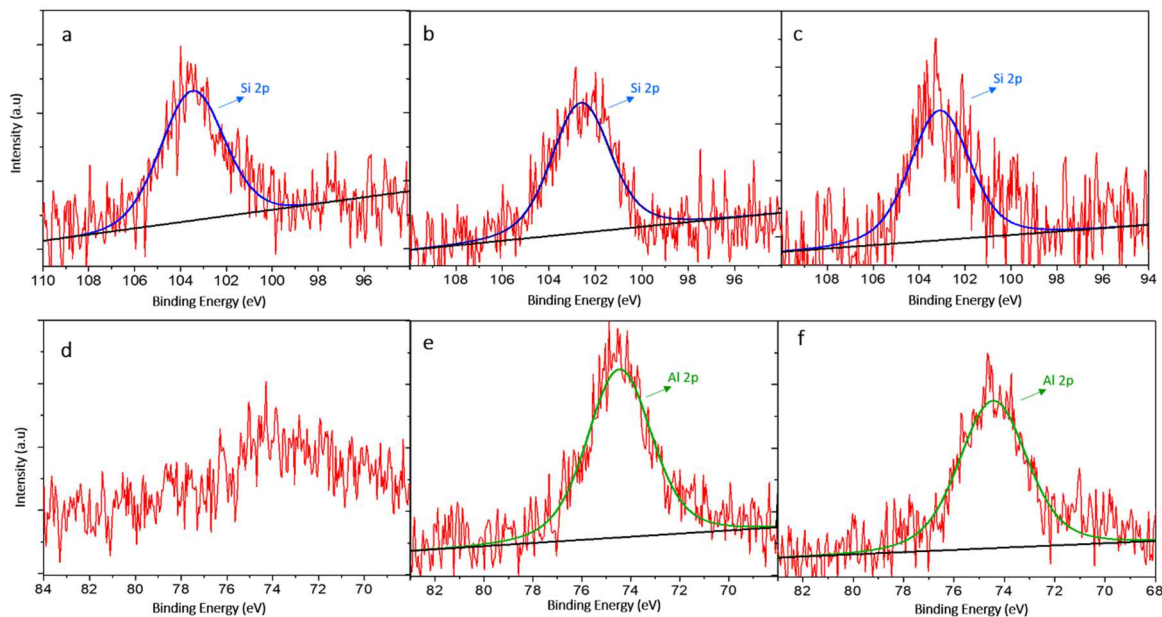
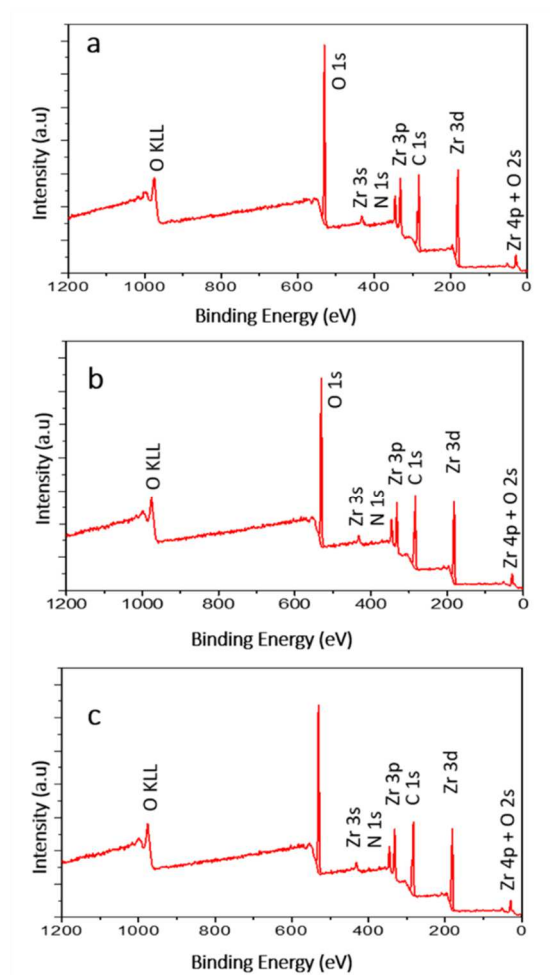


Figure A-6.

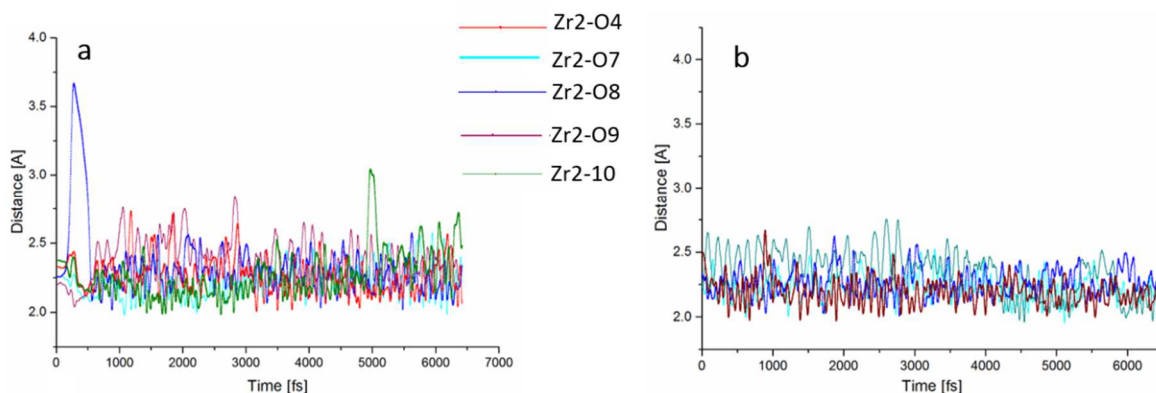
General spectra recorded in XPS analysis of ZrBTC MOFs from precursors: (a) ZrCl_4 (ZrBTC1), (b) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (ZrBTC2) and (c) $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (ZrBTC3). The C-(C,H) component at 284.8 eV was taken as reference for the binding energy calibration.



Appendix B. Supplementary Information Chapter 2⁶

Figure B-1.

Zr2 ...O distance changes in defect-free structure (a) initial steps (b) after removal of surrounding water molecules at 383 K.



⁶ Reprinted with permission from: Ardila-Suarez, C., Perez-Beltran, S., Ramirez-Caballero, G. E., & Balbuena, P. B. (2018). Enhanced acidity of defective MOF-808: effects of the activation process and missing linker defects. *Catalysis Science & Technology*, 8(3), 847-857. doi: 10.1039/C7CY02462B

Figure B-2.

Bader charge of the initial defect-free cluster.

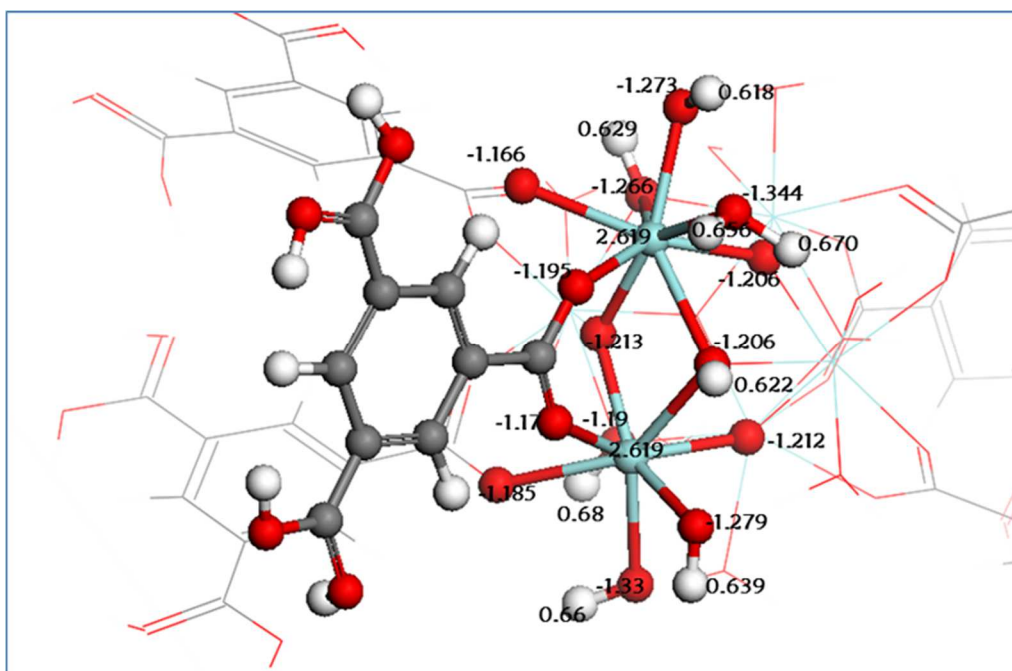


Figure B-3.

*Total DOS of (a) hydroxylated-defect free, (b) dehydroxylated-defect free, and (c) dehydroxylated defect **MOF 808** structures. The defect-free MOF808 exhibits inherently six missing linker defects per cluster.*

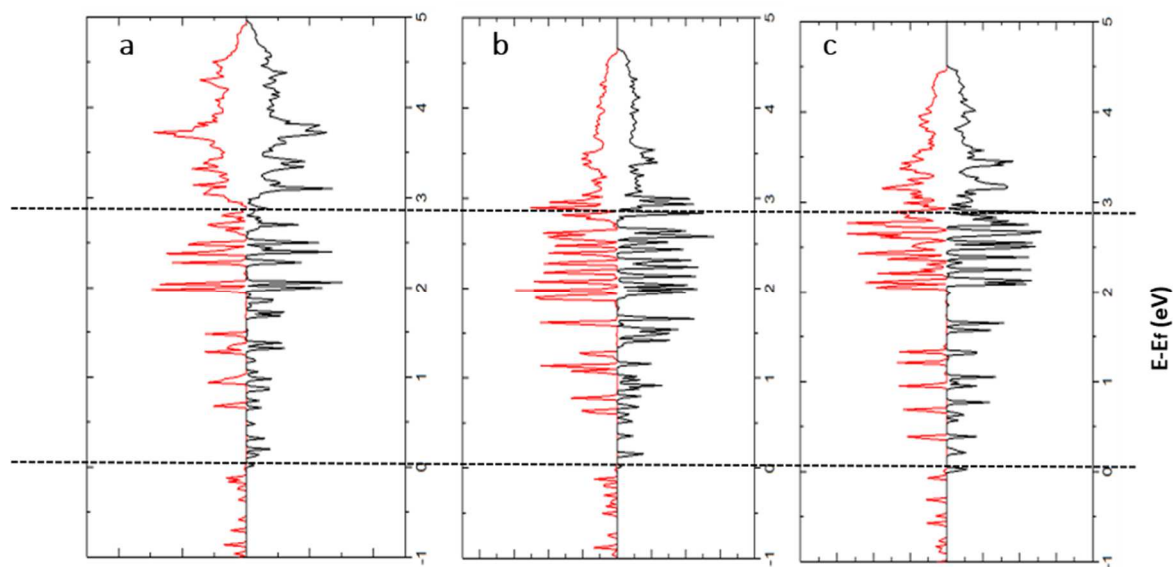


Figure B-4.

Nomenclature used for the studied carbon, oxygen and hydrogen atoms. States overlapping supporting covalent bonding and d-states of zirconium atoms.

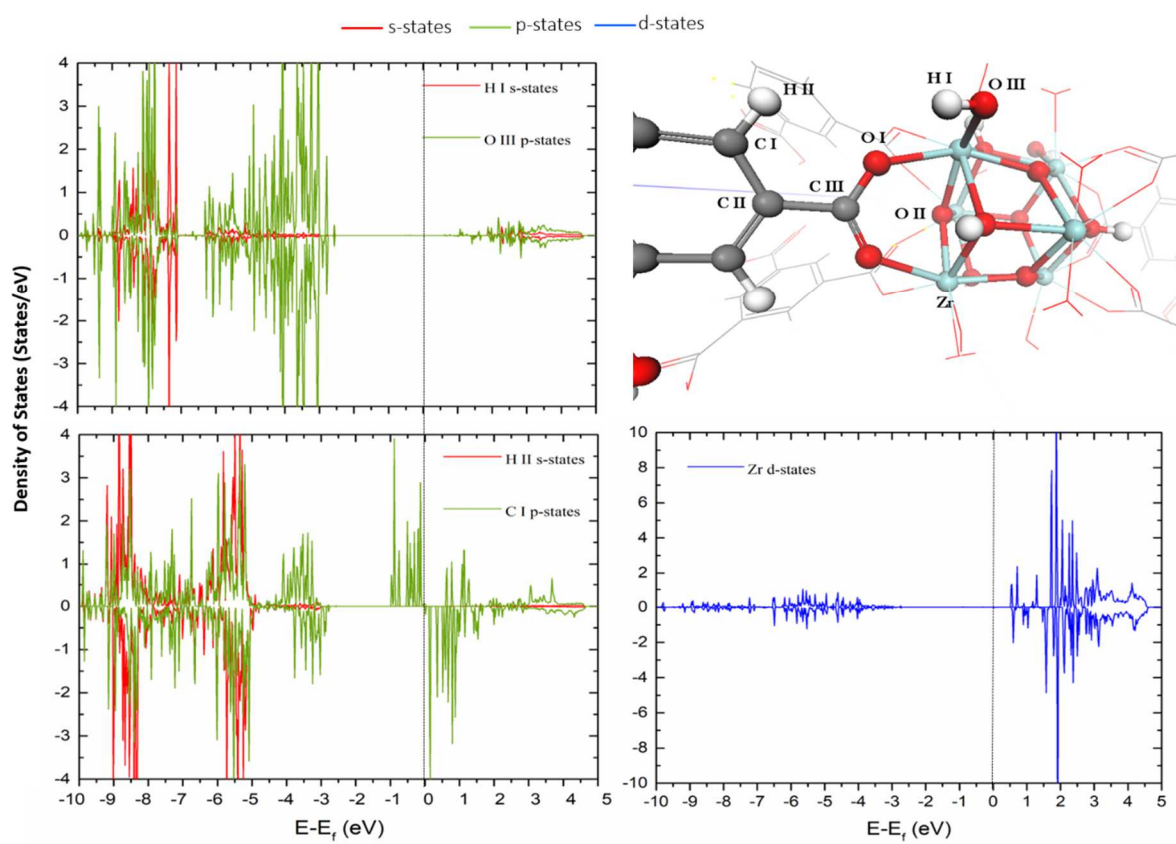
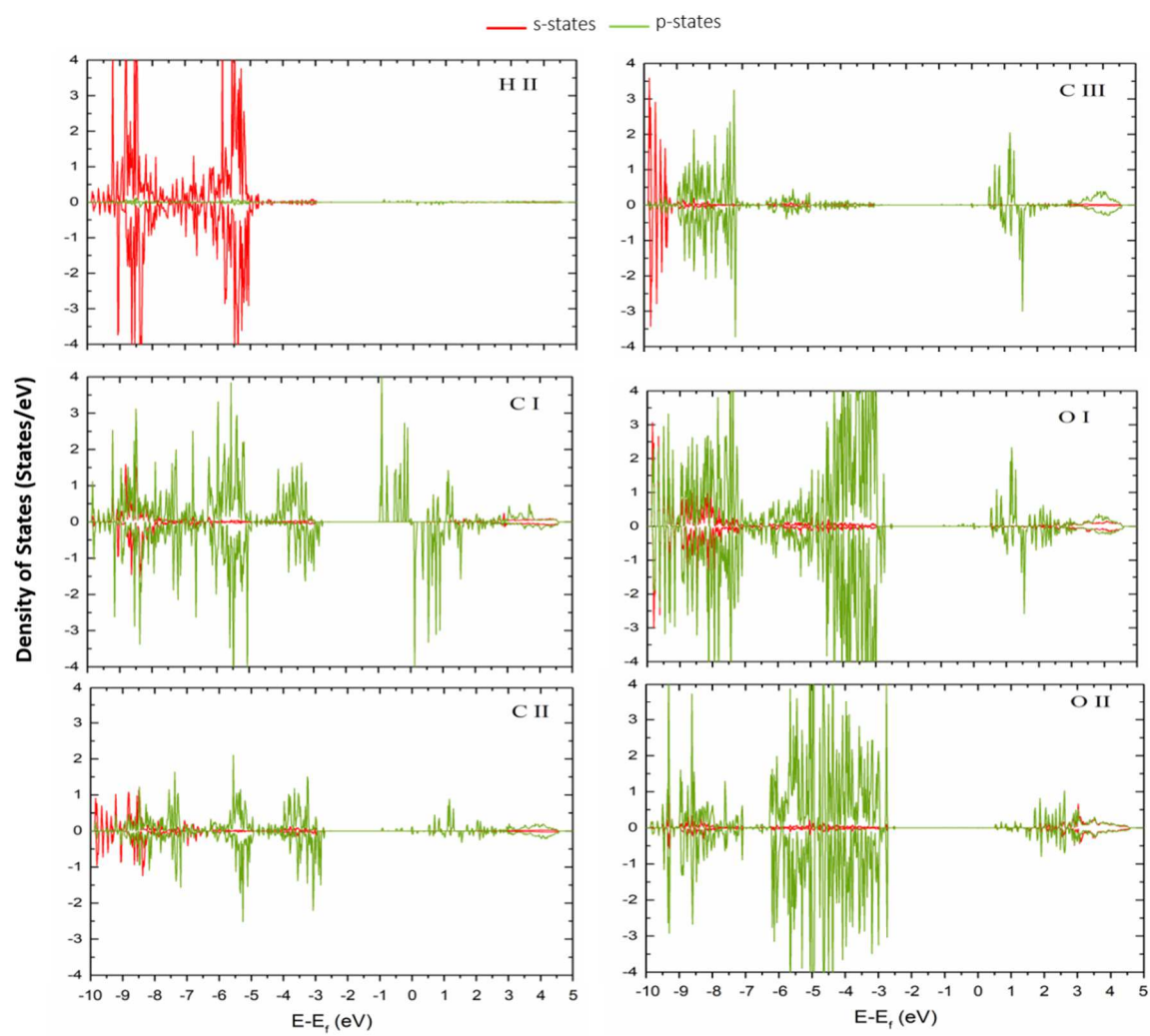


Figure B-5.

Partial density of states of the defect-free structure after activation process.



Appendix C. Supplementary Information Chapter 3⁷

C-1. Results and Discussion

C-1.1. Influence of the concentration of modulator on the properties of zirconium tricarboxylate MOFs

⁷ Reprinted with permission from: Ardila-Suárez, C., Díaz-Lasprilla, A. M., Díaz-Vaca, L. A., Balbuena, P. B., Baldovino-Medrano, V. G., & Ramírez-Caballero, G. E. (2019). Synthesis, characterization, and post-synthetic modification of a micro/mesoporous zirconium–tricarboxylate metal–organic framework: towards the addition of acid active sites. *CrystEngComm*, 21(19), 3014-3030, doi: 10.1039/C9CE00218A

Assessment of surface area and porosity

Figure C-1.

N_2 adsorption/desorption isotherms of (a) ZrBTC-114.6 (b) ZrBTC-83.5 and, (c) ZrBTC-52.4, in the all range of the linear P/P_o . χ -method adsorption/desorption isotherms of the same materials (d) ZrBTC-114.6, (e) ZrBTC-83.5, and (f) ZrBTC-52.4.

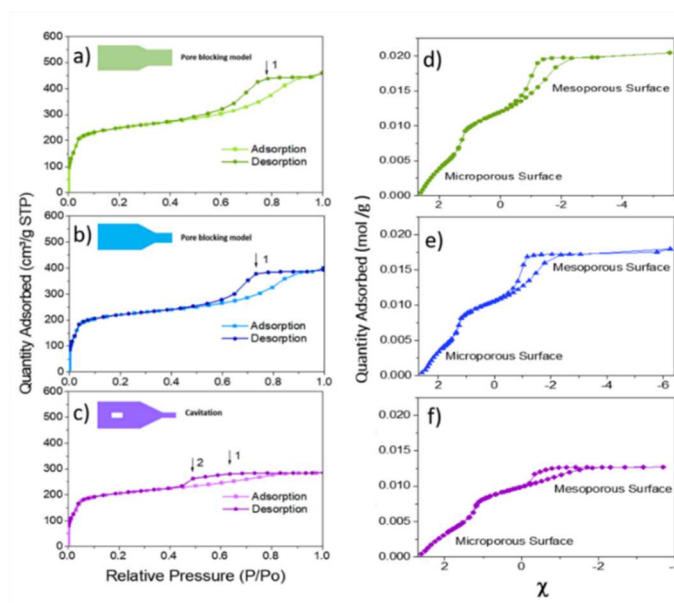


Table C-1.

Comparison of the apparent surface areas calculated using BET method taking into account the full consistency criteria proposed by Rouquerol of the ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 materials and using argon as probe molecule.

BET - Rouquerol Consistency Criteria						
Sample	SA (m ² /g)	C value > 0	n(min) < monolayer < n(max)	P/Po(mono) ~1/(√C+1)	Linear fitting R ²	Rsq
ZrBTC-114.6	804	True- 105.17	True	True	False	0.96590
ZrBTC-83.5	744	True- 106.77	True	True	False	0.95738
ZrBTC-52.4	717	True- 101.04	True	True	False	0.98691

Crystallinity

Table C-2.

Crystal data and structure treatment of the synthesized Zr-MOFs

	ZrBTC-114.6	ZrBTC-83.5	ZrBTC-52.4
Crystal system	Cubic	Cubic	Cubic
Space group	Fd-3m	Fd-3m	Fd-3m
a (Å)	35.14027	35.05387	35.07650
b (Å)	35.14027	35.05387	35.07650
c (Å)	35.14027	35.05387	35.07650
α (°)	90	90	90
β (°)	90	90	90
Ψ (°)	90	90	90
Volume (Å³)	43392.578	43073.266	43156.750
Chi2	1,33	1,38	1,30
% Approximate crystallinity	74.5	62	61

Figure C-2.

Le Bail profile is fitting for ZrBTC-114.6 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

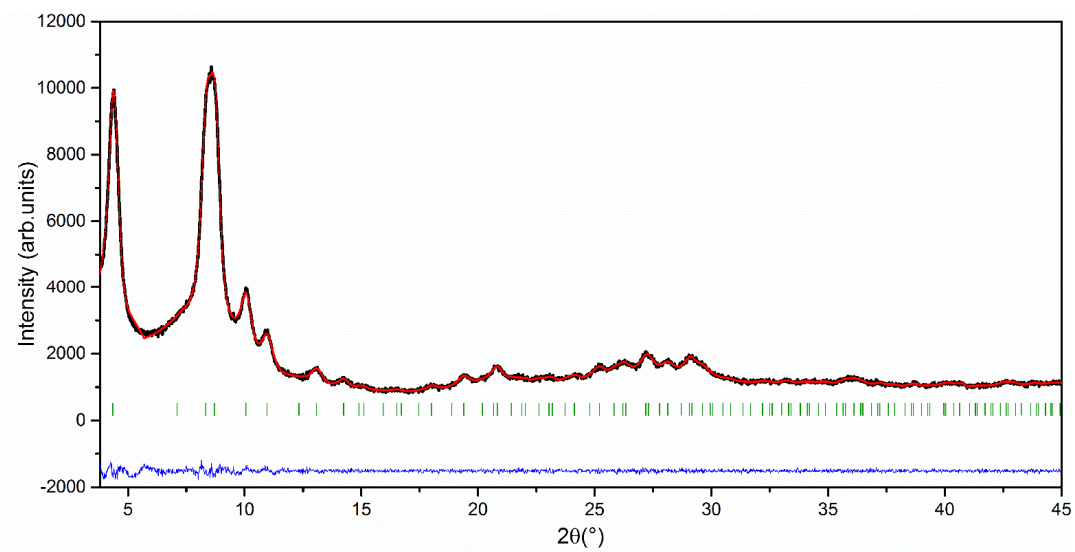


Figure C-3.

Le Bail profile is fitting for ZrBTC-83.5 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

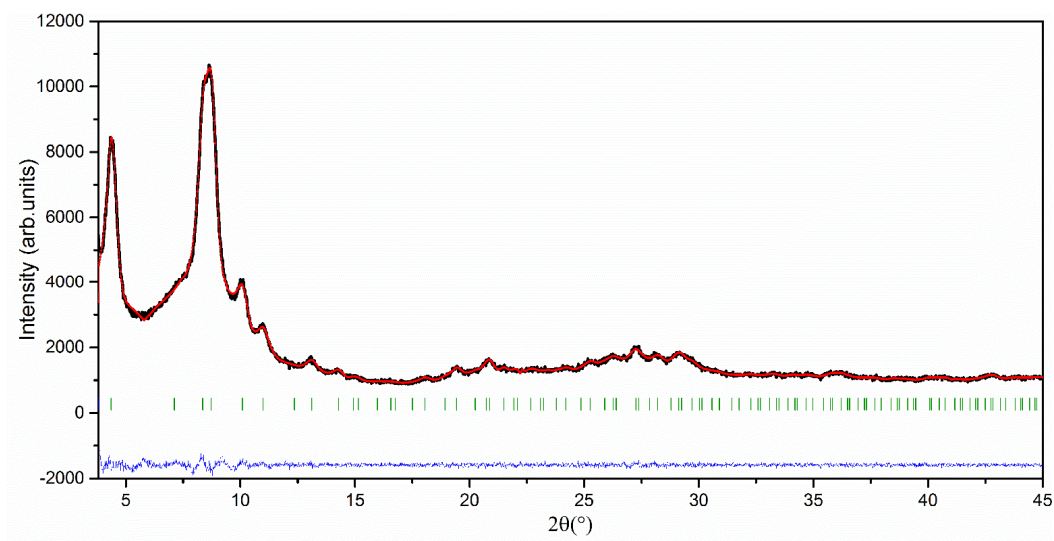
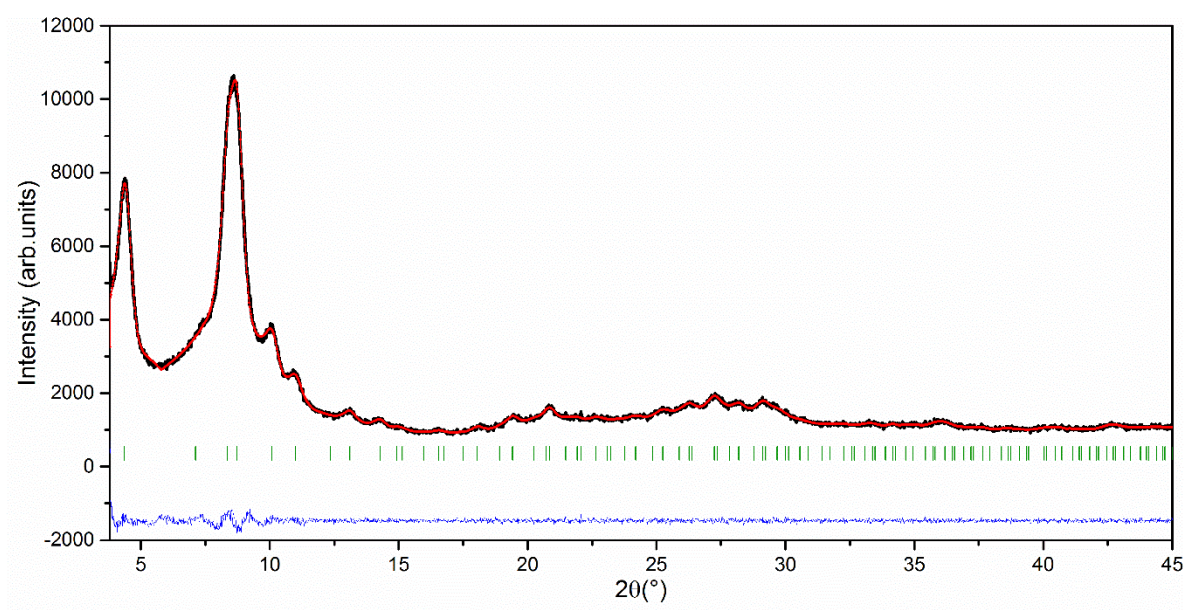


Figure C-4.

Le Bail profile is fitting for ZrBTC-52.4 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

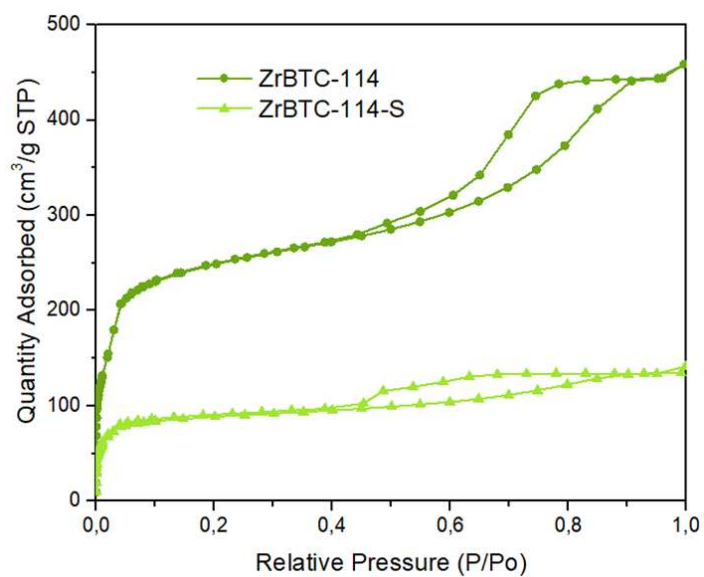


C-1.2. Properties Comparison of Unmodified and Sulfated Samples.

Assessment of the effect of sulfation on surface area and porosity

Figure C-5.

N₂ adsorption-desorption isotherms of MOF ZrBTC-114.6 before and after sulfation process.



Appendix D. Supplementary Information Chapter 4⁸

D-1. Experimental Methods

D-1.1. Dissolution/¹H NMR Spectroscopy

We performed the analysis of as-synthesized and activated MOFs, according to previous work (Shearer et al., 2016). Thus, 600 μ L of NaOH 1M in D₂O were added to 20 mg of each sample. The samples were digested for a period of 24 h. This procedure dissolves just the organic portion of the MOF, i.e., organic ligand, modulator agent, and solvent. The remaining ZrO₂ sinks to the bottom, and it does not interfere with the analysis.

D-1.2. Spectrophotometric Determination of the CMC of CTAB

An Agilent/HP 8453 UV-Visible Spectrophotometer was employed for the calculation of the critical micelle concentration of CTAB, according to previous work (Antoine, Devanathan, & Patonay, 1991). The study was first performed in aqueous solutions with the

⁸ Adapted from: Ardila-Suárez, C., Daniel R. Molina V, Halima Alem, Baldovino-Medrano, V.G., & Ramírez-Caballero, G. E. "Synthesis of Ordered Microporous/Macroporous MOF-808 through Modulator-Induced Defect-Formation, and Surfactant Self-Assembly Strategies." *Physical Chemistry Chemical Physics (PCCP)*, 22 (2020): 12591-12604. doi: <https://doi.org/10.1039/D0CP00287A>, **with permission from The Royal Society of Chemistry.**

aim of corroborating the accuracy of the methodology. Then, 5 CTAB aqueous solutions, i.e., 0.8, 0.60, 0.77, 0.99, 1.98 and 19.92 mM were prepared and 0.001 M of methylene blue was added to each solution. Subsequently, 8 solutions of CTAB in a DMF/Acetic Acid mixture (8:3 v/v), namely, 0.37, 0.56, 0.83, 1.20, 2.29, 4.34, 10.34 and 21.36 mM. The solutions absorbance was measured over a wavelength range of 400-600 nm, and a baseline correction was made using deionized water and the DMF/Acetic Acid mixture, respectively.

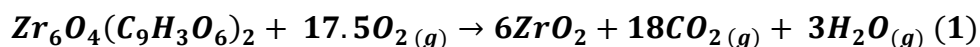
D-2. Results and Discussion

D-2.1. Thermal stability

Three different weight loss regions were identified, according to previous studies (Carolina, Jhonatan, Víctor Gabriel, & Gustavo E, 2018). The use of different modulators during synthesis leads to changes in their resulting thermograms. Thus, according to the literature (Araujo & Jaroniec, 2000; Pan et al., 1996), the more significant weight losses in the region I, are related to larger surface areas. In our case, the weight loss in this region follows the trend ZrBTC-F > ZrBTC-A > ZrBTC-P.

Consequently, the ZrBTC-F MOF, which exhibited the most significant weight loss in the region I, exhibited also the highest surface area. Furthermore, in region II, due to a similar temperature range of weight loss, is not possible to analyze separately two different events: the removal of the monocarboxylate linkers: formate, acetate, and propionate of ZrBTC-F, ZrBTC-A, and ZrBTC-P MOFs, respectively, and the dehydroxylation of the zirconium nodes. Moreover, there are also differences in region III of synthesized MOFs. Shearer et al. (Shearer et al., 2016) studied the correlation between decomposition weight loss with the presence of missing linker defects, and accordingly, we performed a quantitative analysis of

TGA data. The formula of the dehydroxylated MOF-808 is reported as $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2$ (Hiroyasu Furukawa et al., 2014) and, after combustion, the residue in the TGA experiments is assumed to be ZrO_2 , as presented in Equation 1 (James & Lin, 2016). Thus, the expected weight loss for the decomposition, according to the stoichiometry, was calculated and then compared with the corresponding weight loss in the recorded thermograms.



We performed a mass balance of the III region of the TGA thermogram. If we assume a base calculation of 100 g of the initial $\text{Zr}_6\text{O}_4(\text{C}_9\text{H}_3\text{O}_6)_2$ (MW=1025.57 g/mol), the mass of the solid residue 6 moles of ZrO_2 (739.34 g/mol) is consequently, 72.11 g. Then, the expected total weight loss would be ca. 27.89%. Accordingly, the ZrBTC-F, ZrBTC-A, and ZrBTC-P MOFs exhibited a decomposition weight loss magnitude of 19.54%, 23.23%, and 21.00%, respectively. These weight losses are lower than the theoretical defect-free behavior, which can be related to the partial deficiency of organic linkers that were replaced by modulators on the coordination of zirconium nodes. Moreover, the weight loss of the ZrBTC-F and ZrBTC-P materials are similar and lower than the resulting one of the ZrBTC-A MOF.

D-2.2. Dissolution/¹H NMR Spectroscopy

In general, the spectra recorded on the resulting MOFs after the digestion are clean. There are only the signals assigned to the dimethylamine, the BTC³⁻, formate, acetate, and propionate, See Figures S1 and S2. The ¹H NMR spectra recorded from the ZrBTC-F, ZrBTC-A and ZrBTC-P samples after digestion are shown in Figures 5, S3, and S4, respectively. To determine if the monocarboxylates are indeed incorporated into the MOF

-808 framework or just occluded in the pores as free acids, we recorded the spectra for the ZrBTC-A, ZrBTC-F, and ZrBTC-P MOFs before and after the activation process. Therefore, the monocarboxylates detected after the activation process are coordinated to the zirconium nodes. Moreover, all spectra recorded on the synthesized materials contain

As reported previously for the UiO-66 MOF (Shearer et al., 2016), we calculated the molar ratios between the modulator and the BTC linker, $\frac{Modulator}{BTC}m_r$, before and after the activation process with the aim of compare quantitatively the concentration of modulator coordinated to the zirconium nodes. After activation, this ratio decreased 1.39 %, 1.38 %, and 0 % for ZrBTC-A, ZrBTC-F, and ZrBTC-P MOFs, respectively. Then, after activation, the molar ratio between each modulator and the BTC linker were 2.13, 1.43, and 2.03 for the ZrBTC-A, ZrBTC-F, and ZrBTC-P, respectively. Accordingly, the ZrBTC-F and ZrBTC-P materials exhibited similar and higher ratios compared to the ZrBTC-A MOFs. These results could be correlated to the fact that the ZrBTC-F and ZrBTC-P materials exhibited a larger percentage of microporous volume compared to the ZrBTC-A MOF, and this last, by the contrary, showed larger mesoporous volume than the other two materials. Furthermore, TGA results reflect that the weight loss percentage of ZrBTC-A, in the region associated with the decomposition of the organic linker, was more significant compared to the ZrBTC-F and ZrBTC-P MOFs. Probably, a low quantity of acetates was attached to the zirconium nodes, and instead, they formed clusters than favored the formation of large mesopores in ZrBTC-A MOF.

Figure D-1.

Dissolution/ ^1H NMR spectra obtained on the modulators using in this work.

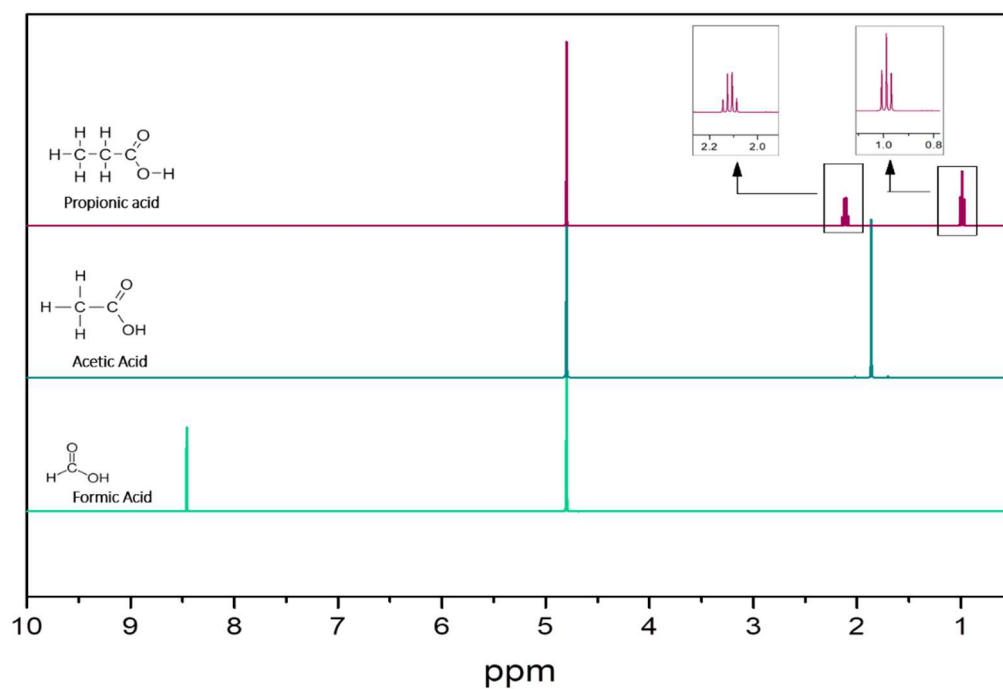


Figure D-2.

Dissolution/ ^1H NMR spectra obtained on dimethylamine (DMF hydrolysis product) and trimesic acid, BTC (organic ligand).

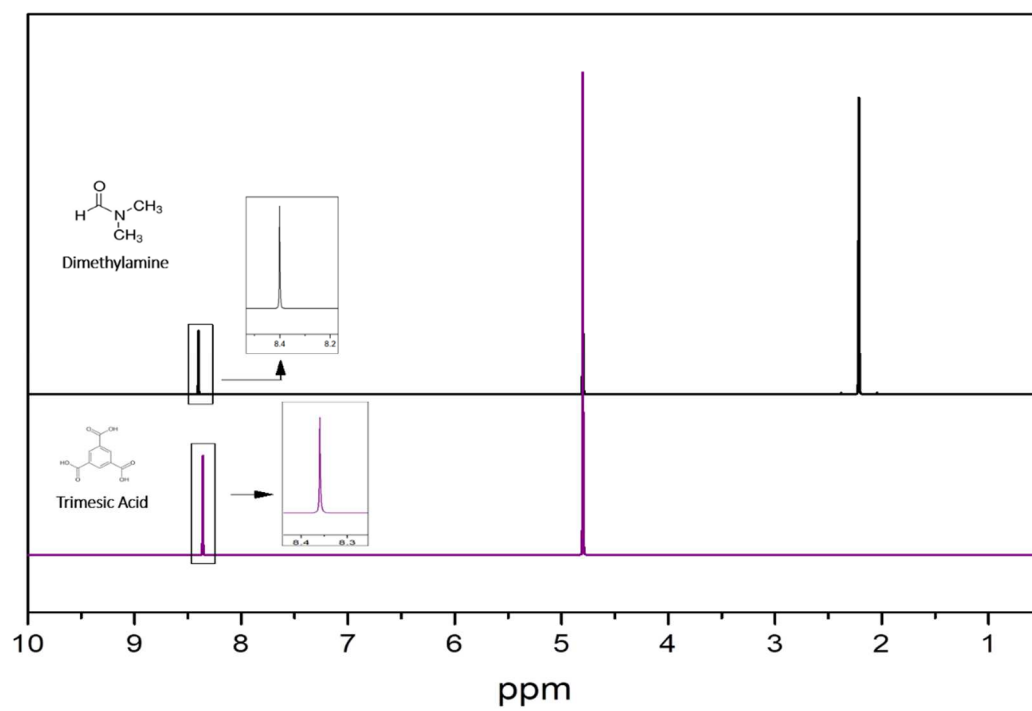


Figure D-3.

Dissolution/ ^1H NMR spectra obtained on the MOF synthesized using acetic acid as modulator before (ZrBTC-A-as) and after (ZrBTC-A-ac) the activation process.

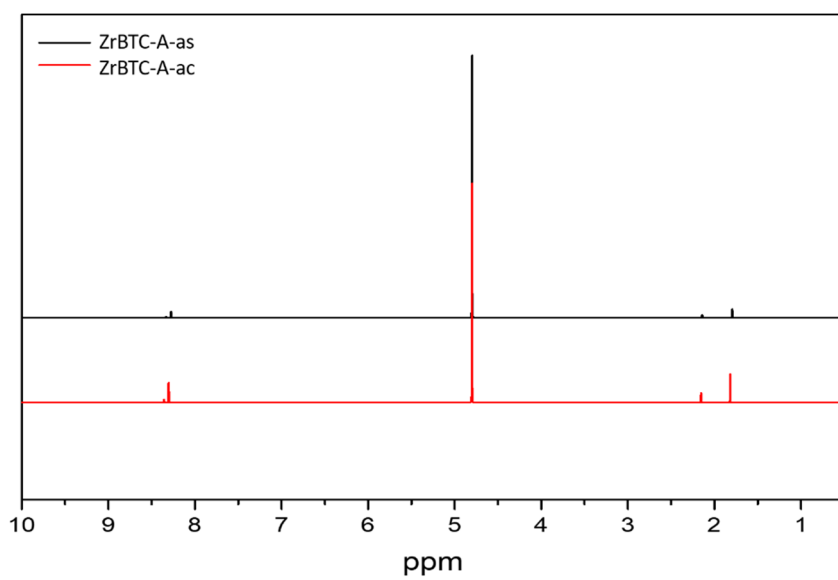
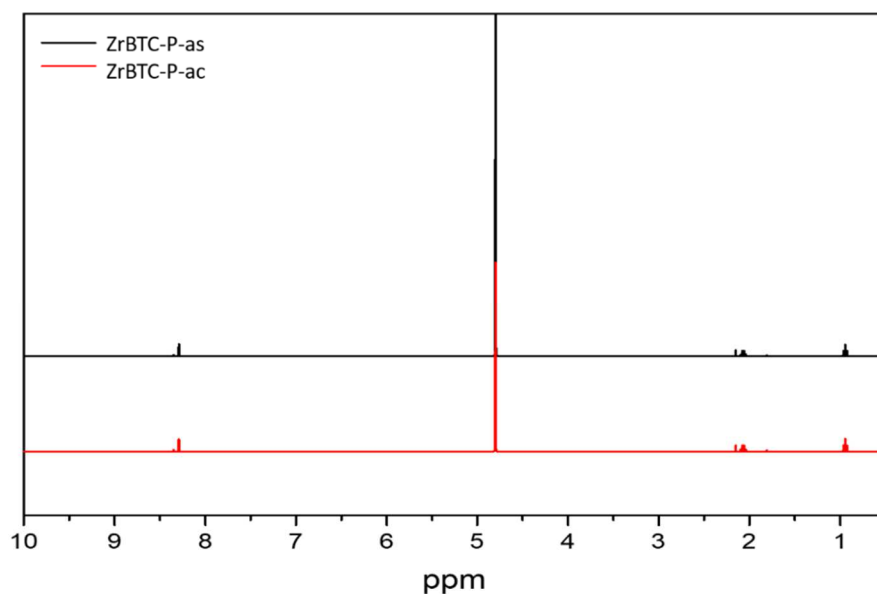


Figure D-4.

Dissolution/ ^1H NMR spectra obtained on the MOF synthesized using propionic acid as modulator before (ZrBTC-P-as) and after (ZrBTC-P-ac) the activation process.



Formic Acid Modulation

ZrBTCF-as

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-\text{BTC}}}{N_{H-\text{FA}}} \right) = \left(\frac{0.72}{1.00} \right) \left(\frac{3}{1} \right) = 2.16$$

ZrBTCF-ac

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-\text{BTC}}}{N_{H-\text{FA}}} \right) = \left(\frac{0.71}{1.00} \right) \left(\frac{3}{1} \right) = 2.13$$

Acetic Acid ModulationZrBTCA-as

$$\frac{\text{Acetic Acid}}{\text{BTC}} m_r = \frac{\text{Acetic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-AA}} \right) = \left(\frac{1.00}{0.69} \right) \left(\frac{3}{3} \right) = \mathbf{1.45}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.11}{0.69} \right) \left(\frac{3}{1} \right) = \mathbf{0.48}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Acetic Acid}}{\text{BTC}} = \mathbf{1.92}$$

ZrBTCA-ac

$$\frac{\text{Acetic Acid}}{\text{BTC}} m_r = \frac{\text{Acetic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-AA}} \right) = \left(\frac{1.00}{0.70} \right) \left(\frac{3}{3} \right) = \mathbf{1.43}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.11}{0.70} \right) \left(\frac{3}{1} \right) = \mathbf{0.48}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Acetic Acid}}{\text{BTC}} = \mathbf{1.91}$$

Propionic Acid Modulation

- Triplet

ZrBTCP-as

$$\frac{\text{Propionic Acid}}{\text{BTC}} m_r = \frac{\text{Propionic Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-PA}} \right) = \left(\frac{3.00}{1.48} \right) \left(\frac{3}{3} \right) = \mathbf{2.03}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.19}{1.48} \right) \left(\frac{3}{1} \right) = \mathbf{0.39}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Propionic Acid}}{\text{BTC}} = \mathbf{2.42}$$

ZrBTCP-ac

$$\frac{\text{Propionic Acid}}{\text{BTC}} m_r = \frac{\text{Propionic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-PA}} \right) = \left(\frac{3.00}{1.48} \right) \left(\frac{3}{3} \right) = \mathbf{2.03}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.18}{1.48} \right) \left(\frac{3}{1} \right) = \mathbf{0.37}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Propionic Acid}}{\text{BTC}} = \mathbf{2.40}$$

- Quadruple

ZrBTCP-as

$$\frac{\text{Propionic Acid}}{\text{BTC}} m_r = \frac{\text{Propionic Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-PA}} \right) = \left(\frac{2.00}{1.48} \right) \left(\frac{3}{2} \right) = \mathbf{2.01}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.19}{1.48} \right) \left(\frac{3}{1} \right) = \mathbf{0.38}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Propionic Acid}}{\text{BTC}} = \mathbf{2.39}$$

ZrBTCP-ac

$$\frac{\text{Propionic Acid}}{\text{BTC}} m_r = \frac{\text{Propionic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-PA}} \right) = \left(\frac{2.00}{1.48} \right) \left(\frac{3}{2} \right) = \mathbf{2.03}$$

$$\frac{\text{Formic Acid}}{\text{BTC}} m_r = \frac{\text{Formic Acid Int.}}{\text{BTC Int.}} \left(\frac{N_{H-BTC}}{N_{H-FA}} \right) = \left(\frac{0.18}{1.48} \right) \left(\frac{3}{1} \right) = \mathbf{0.36}$$

$$\frac{\text{Modulators}}{\text{BTC}} m_r = \frac{\text{Formic Acid}}{\text{BTC}} + \frac{\text{Propionic Acid}}{\text{BTC}} = \mathbf{2.39}$$

D-2.3. Crystallinity

The crystalline structure analysis done by powder X-ray diffraction showed that the materials synthesized have the previously reported set of reflections of MOF-808, i.e., $2\theta = 4.34^\circ$ which was assigned to the (111) plane of MOF-808 and $2\theta = 8.32^\circ$ and 8.69° which were assigned to diffraction from the planes (311) and (222), respectively. Although the ZrBTC-P material exhibited more defined peaks compared to the ZrBTC-F and ZrBTC-A MOFs, the three materials exhibited a certain degree of amorphicity, that could be related to their significant mesoporosity caused by missing linker defects. The synthesized materials crystallized in the cubic space group $Fd\bar{3}m$, Table S1. The lattice parameters of the materials synthesized herein are very similar to the previously reported for MOF-808 and as postulated by Liang et al. (W. Liang et al., 2014). The differences between them, according to the LeBail treatment results, could be related to the differences of solvent molecules that remain occluded inside the structure.

Table D-1.

Crystallinity data and structure treatment of the ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTCAE-1, and ZrBTC-AE-2 material.

	Crystal system	Space group	Cell parameters (Å)	Volume (Å ³)	Chi2
ZrBTC-F	Cubic	Fd3̄m	35.12450(329)	43334.152(70.47)	1.41
ZrBTC-A	Cubic	Fd3̄m	35.24473(210)	43780.695(45.20)	1.24
ZrBTC-P	Cubic	Fd3̄m	35.27621(150)	43887.953(32.44)	1.24
ZrBTCAE-1	Cubic	Fd3̄m	35.18252(106)	43549.270(22.87)	1.26
ZrBTCAE-2	Cubic	Fd3̄m	35.19824(81)	43607.660(17.45)	1.18

Figure D-5.

Le Bail profile fitting for ZrBTC-F, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in blue line, and Bragg reflection markers in green.

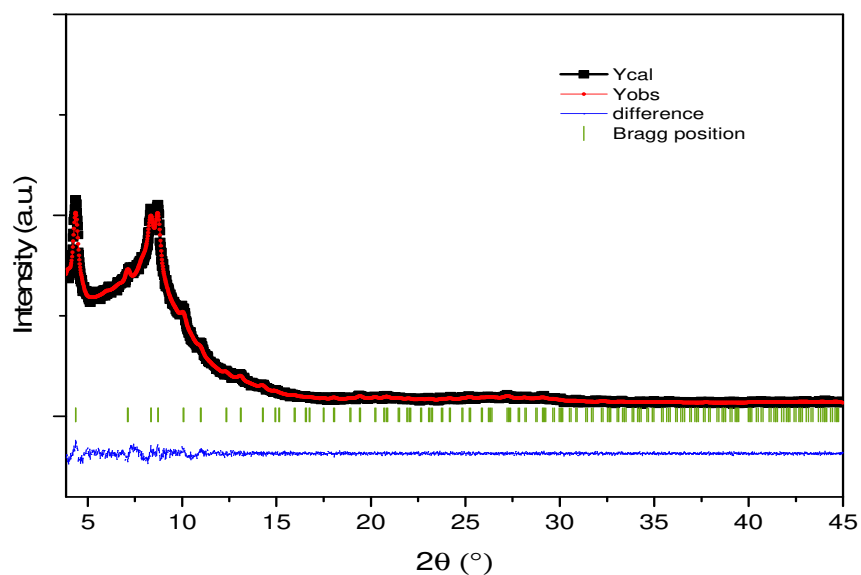


Figure D-6.

Le Bail profile fitting for ZrBTC-A, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in blue line, and Bragg reflection markers in green.

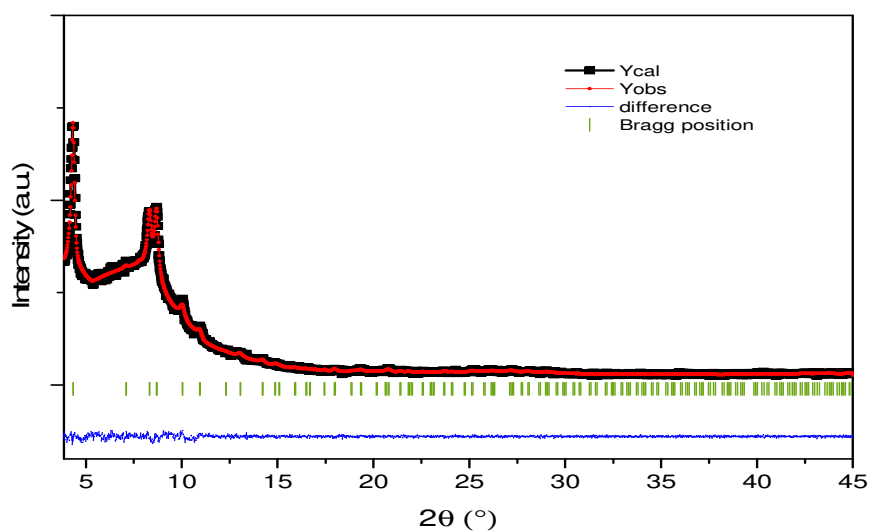


Figure D-7.

Le Bail profile fitting for ZrBTC-P, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in blue line, and Bragg reflection markers in green.

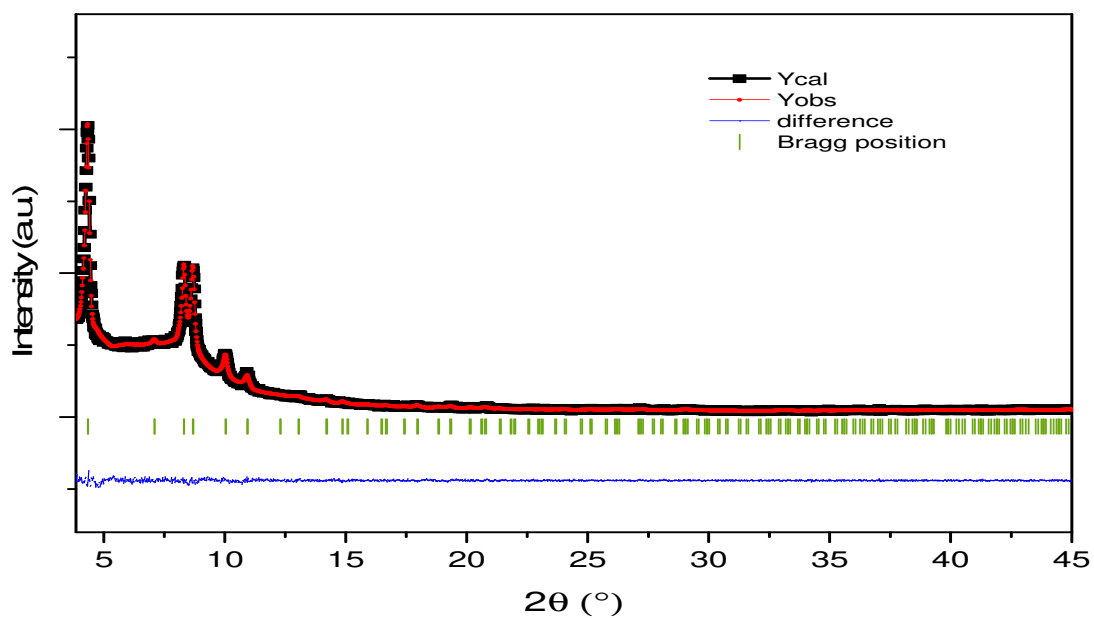


Figure D-8.

Le Bail profile fitting for ZrBTC-AEI, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in blue line, and Bragg reflection markers in green.

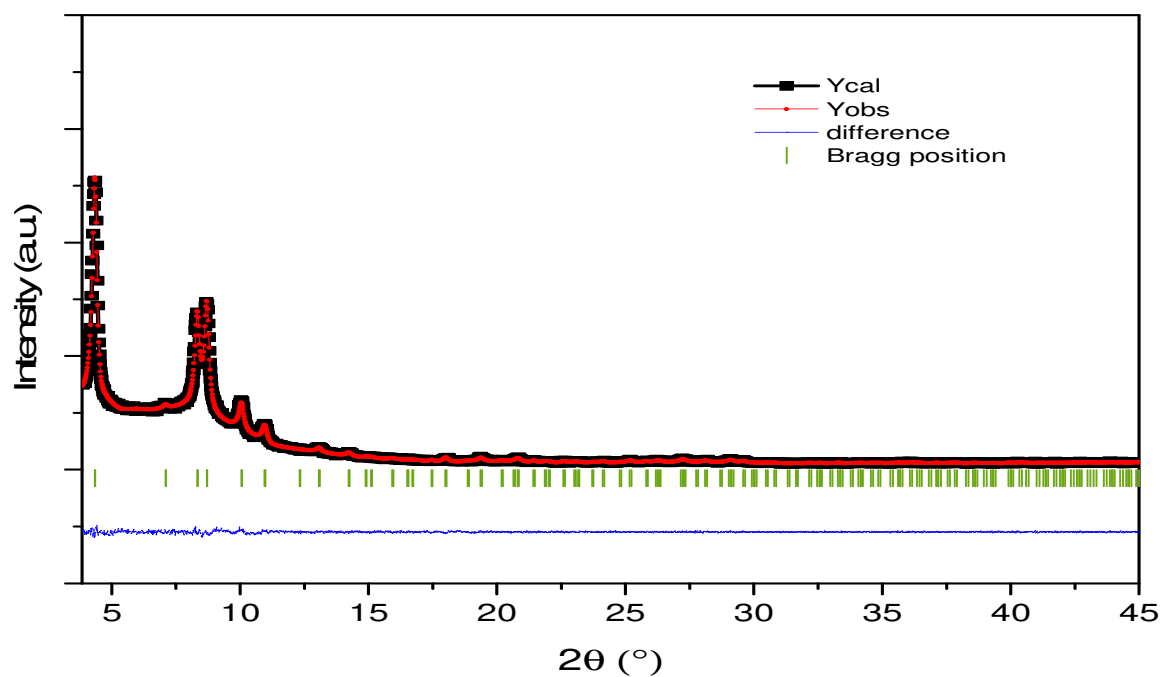
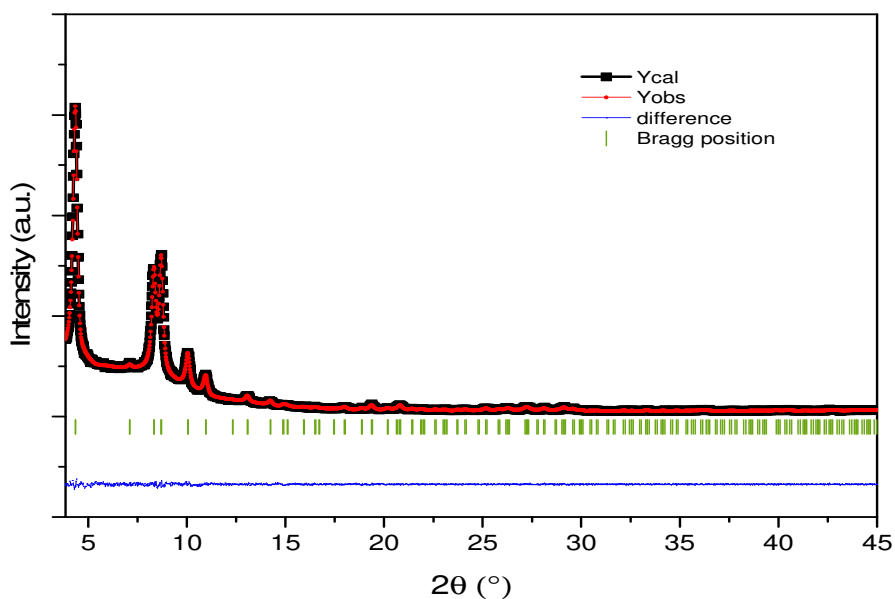


Figure D-9.

Le Bail profile fitting for ZrBTC-AE2, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in blue line, and Bragg reflection markers in green.



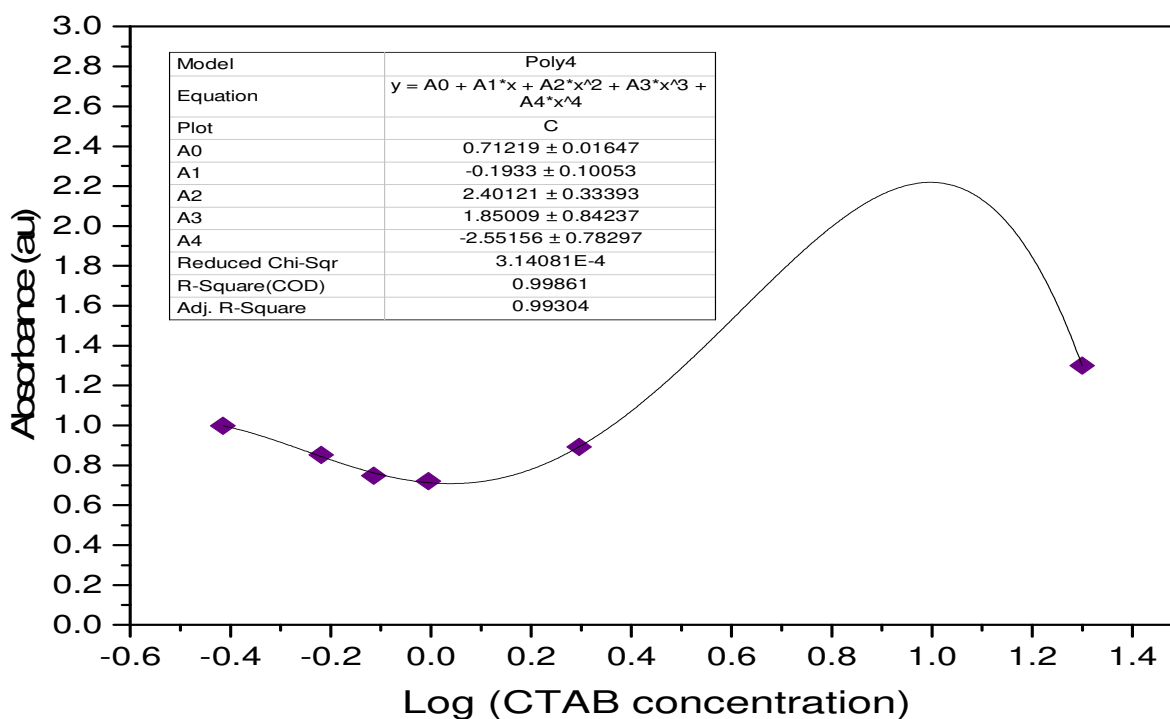
We followed the methodology of our previous work (Ardila Suárez, Rodríguez Pereira, et al., 2019), assuming that the ZrBTC-AE2 material can represent a 100 % crystalline MOF-808. Hence, its XRD pattern was taken as a reference for the calculation of the degree of amorphicity of ZrBTCA-E1 and ZrBTC-A. Accordingly, the relative crystallinity of ZrBTC-AE1 and ZrBTC-A were 86 % and 59 %, respectively. The addition of CTAB during synthesis allows the formation of more ordered crystals of MOF-808.

D-2.4. Spectrophotometric Determination of the CMC of CTAB

The maximum absorbance for each aqueous CTAB solution is observed at $\lambda = 397$ nm. These values were plotted and fitted according to Figure SX. After the calculation of the function minimum, the calculated CMC of CTAB is 1.1 mM, which is very similar to the previously reported CMC of 1 mM for CTAB in aqueous solutions (Mukerjee & Mysels, 1971).

Figure D-10.

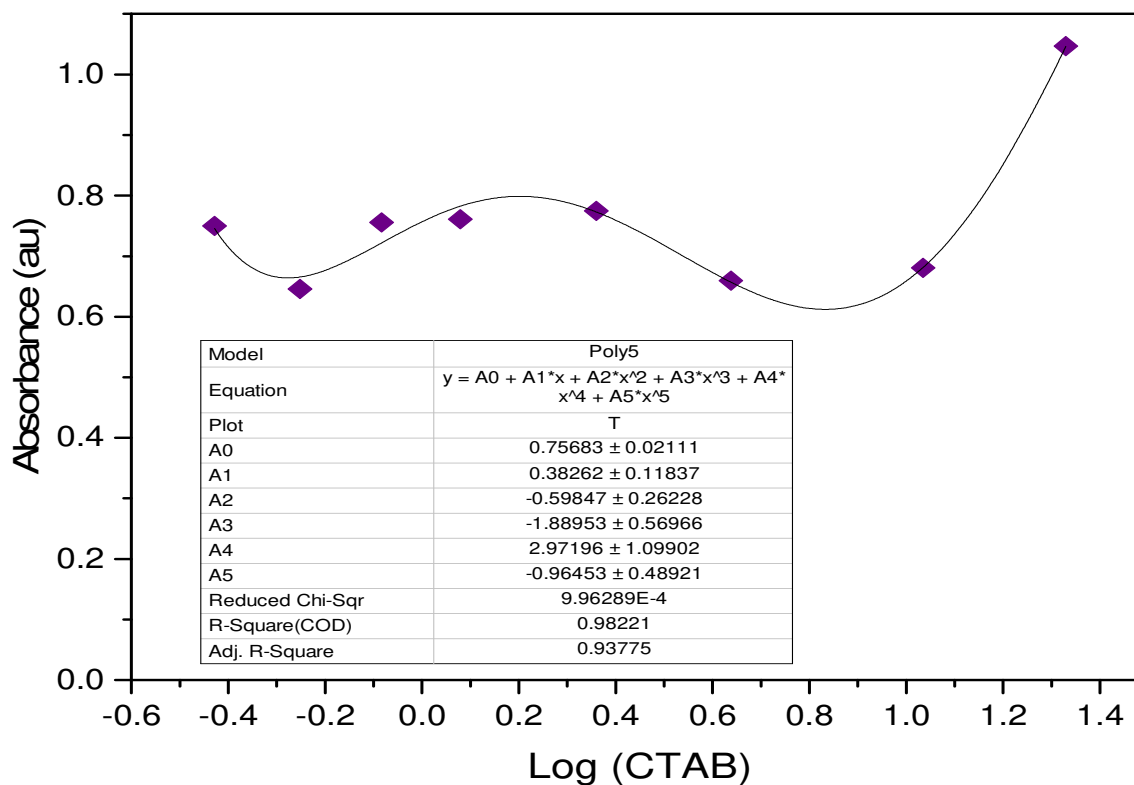
Plot showing the 4th order polynomial curve fit of the absorbance as a function of the CTAB concentration aqueous solutions, $\lambda = 397$ nm.



Accordingly, we performed the same experiment for the DMF/Acetic Acid mixture (8:3 v/v), which corresponds to the reaction mixture of the MOFs synthesis. In this case, two different absorbance maximums were detected: $\lambda = 392$ and 493 nm. The data collected for $\lambda = 392$ nm were plotted and fitted according to Figure S11. After the calculation of the function minimum, the calculated CMC of CTAB is 6.8 mM. This value is lower than the concentrations of CTAB, **13,02** and **26,037** mM, employed for the synthesis of ZrBTC-AE1 and ZrBTC-AE2, respectively. Thus, the CTAB concentrations employed during the MOFs synthesis induced its self-assembly for the formation of the micelles.

Figure D-11.

Plot showing the 5th order polynomial curve fit of the absorbance as a function of the CTAB concentration in the DMF/Acetic Acid mixture (8:3 v/v), $\lambda = 397$ nm.



D-2.5. Molecular structure

The bands around $1600-1400\text{ cm}^{-1}$ are associated with the C-O of carboxylates linked to the metal centers. Further, the bands in the region of $1480-1420\text{ cm}^{-1}$ corresponded to the C=C in the aromatic compound of the organic linker (Q. Zhang et al., 2014). The bands observed in the region of $750-655\text{ cm}^{-1}$ are related to the asymmetric vibration of the Zr-(μ_3 -O) bridges in the framework building blocks. The band at 640 cm^{-1} is assigned to a vibration of the hexanuclear cluster, and the band around $545-555\text{ cm}^{-1}$ is assigned to the Zr-(OC) asymmetric stretching vibration (Piszczyk et al., 2007).

D-2.6. Surface chemistry

Surface chemical state by XPS

The empirical formulas were estimated on a hydrogen-free basis and according to our previous works (Ardila Suárez, Díaz, et al., 2019; Ardila Suárez, Rodríguez Pereira, et al., 2019): $\text{CO}_{0.843}\text{Zr}_{0.182}\text{N}_{0.001}\text{Cl}_{0.011}$, $\text{CO}_{1.002}\text{Zr}_{0.211}\text{N}_{0.003}\text{Cl}_{0.010}$, and $\text{CO}_{1.001}\text{Zr}_{0.203}\text{N}_{0.004}\text{Cl}_{0.014}$ for ZrBTC-F, ZrBTC-A, and ZrBTC-P, respectively. Related to the materials synthesized using surfactant, the empirical formulas were estimated as $\text{CO}_{0.961}\text{Zr}_{0.199}\text{N}_{0.001}$, and $\text{CO}_{0.956}\text{Zr}_{0.209}\text{N}_{0.003}\text{Cl}_{0.008}$ for ZrBTC-AE1, and ZrBTC-AE2, respectively. Compared to the

previously reported formula $\text{CO}_{1.848}\text{Zr}_{0.25}\text{H}_{0.25}$ (Hiroyasu Furukawa et al., 2014), the materials synthesized herein exhibited deficiencies at the surfaces of ca. 46% and 20%, respectively. These findings are in agreement with our previous discussion (Ardila Suárez, Rodríguez Pereira, et al., 2019).

Chemical surface composition through ToF –SIMS

Figure D-12.

Spectra of the surface (a) Positive (b) Negative Secondary Ion Polarity of ZrBTC-AE2 MOF.

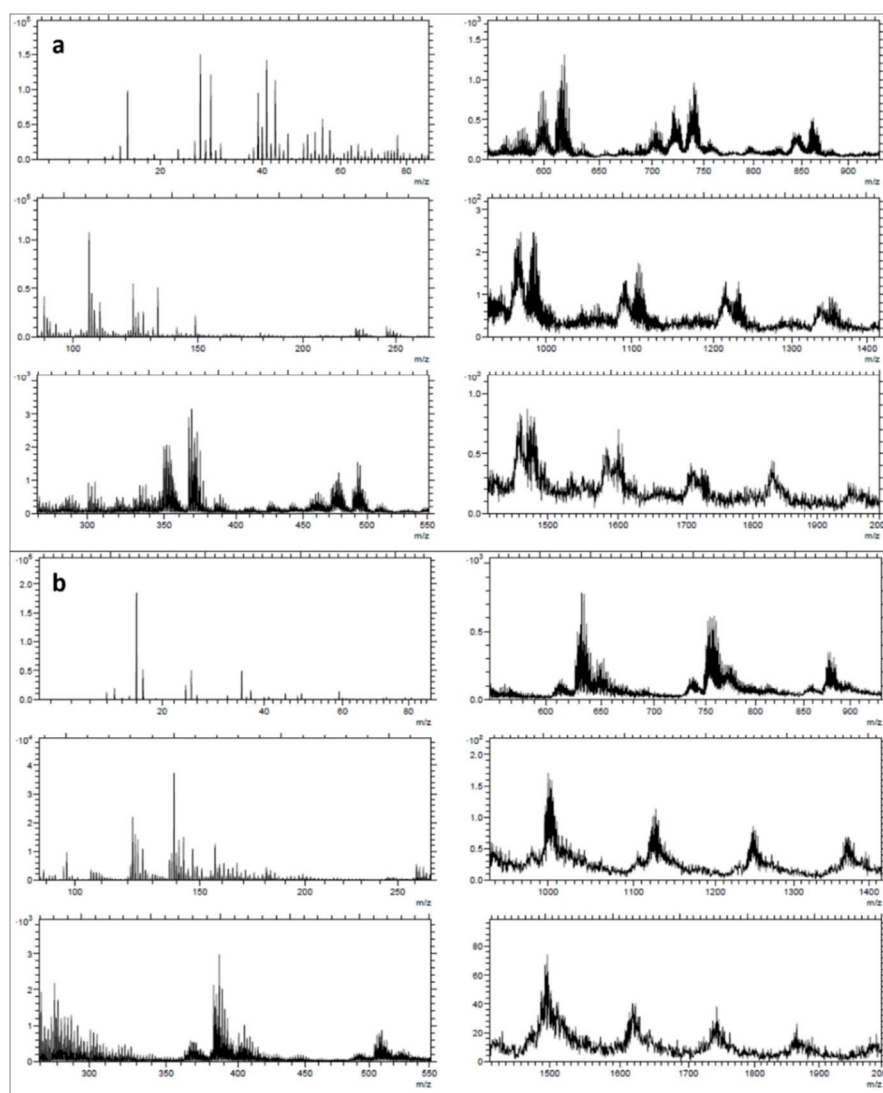
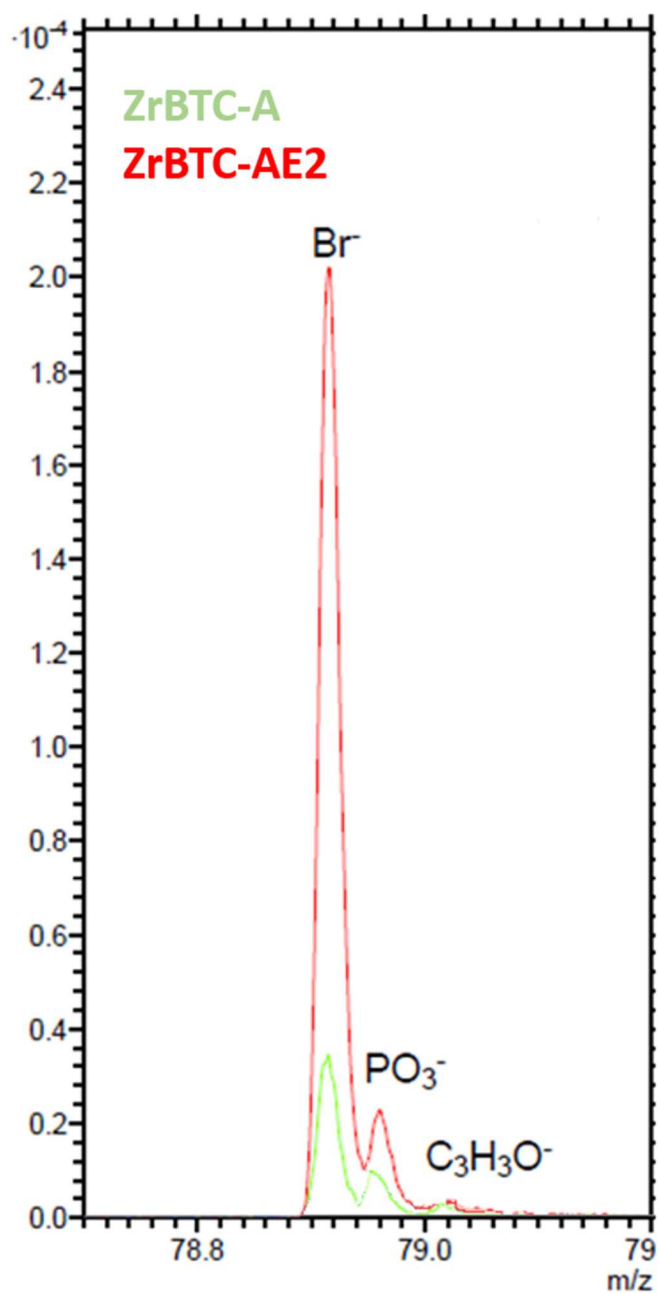


Figure D-13.

Spectra comparison of the surface Negative Secondary Ion Polarity of ZrBTC-A and ZrBTC-AE2 MOFs.



Appendix E. Supplementary Information Chapter 5

E-1. Experimental Methods

Thermal stability was studied by recording thermal gravimetric analysis profiles. Tests were performed in a Discovery 5500 TA instrument. Samples were heated to 900°C at a rate of 5°C/min under an air (Linde, 4.7, 99.997% purity) flow of 25 mL/min. Morphology was studied by recording scanning electron microscopy images in a Quanta FEG 650 equipment. The acceleration voltage was set to 2.5 kV through an everhart Thornley detector (secondary electrons detector). Samples were prepared by spreading them on a carbon tape in a Quorum 150ES equipment. Besides, transmission electron microscopy images were recorded with a Philips CM200 microscope operating at 200 kV and equipped with an Energy-dispersive X-ray spectrometer. The porosity and surface of the materials were evaluated after recording Ar adsorption-desorption isotherms at 87 K using a 3Flex (Micromeritics) apparatus. The relative pressure range went from 1.82×10^{-5} to 0.995 with equilibrium intervals of 10 s. Isotherms for the materials were recorded twice in independent experiments. Before measurements, the materials were degassed at a temperature of 120°C under vacuum for 12 h. Surface area calculations were performed using the methods based on the χ theory (James B Condon, 2006). The crystalline structure of the materials was assessed by recording X-ray diffraction patterns with a Bruker AXS D8 Advance DaVinci geometry instrument equipped

with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). This instrument was operated at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ value range from 3.0 to 50.0° (with a step time of 0.6 s). For gaining further insight into the molecular structure of the materials, we wanted to identify and quantify the concentration of the modulators coordinated to the zirconium node. This was made by dissolution/ ^1H NMR spectroscopy. For this purpose, MOFs are digested in a deuterated medium (Shearer et al., 2016). During the experiment, hydroxyls digest the organic part of the MOF, i.e., the organic linker, the modulator, and the solvent that may still be trapped inside the pores of the materials. The digested product can then be analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy while the inorganic component, namely ZrO_2 , of the material precipitates. Further details for this experiment are included in Section 1.2. of the Supporting information. Liquid ^1H NMR spectra were recorded in a Bruker Ultrashield 400 MHz (Avance III, 400) using a relaxation delay (D1) of 20 s and 64 scans (Shearer et al., 2016). The identification of functional groups of the as-synthesized and modified MOFs was performed by Infrared spectroscopy on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. The surface chemistry of the materials was analyzed by X-ray photoelectron spectroscopy. Analyses were performed in the XPS/ISS/UPS-A.Centeno surface characterization platform (SPECS). The platform is provided with a PHOIBOS 150 2D-DLD energy analyzer package. A monochromatized Al K α X-ray source (Focus 500) operated at 100 W was employed. The pressure in the analysis chamber was approximately $1 \times 10^{-7} \text{ Pa}$. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 54°. Samples were mounted on carbon conductive tape over metallic sample holders for analysis. Surface charge compensation was controlled with a flood gun (FG 15/40-PS FG500 device) operated at 58 μA and 1.0 eV. Spectra were collected in the Fixed Analyzer Transmission mode. The spot

area for analyses was $3.5 \times 1.0 \text{ mm}^2$. The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and to 15 eV for high-resolution spectra. The energy step for the acquisition was set to 0.050 eV. General spectra were recorded first for all samples followed by high-resolution spectra. The C 1s peak was recorded both at the beginning and the end of the measurements for checking the evolution of surface charge during the analyses. High-resolution spectra were recorded following elements identification in the general spectra and according to samples chemistry and history. Data analysis was performed with the CasaXPS program (Casa Software Ltd) using the SPECS Prodigy library for R.S.F. values. A U 3 Tougaard baseline (J. Walton et al., 2016) was employed for background modeling together with a Lorentzian line shape, LA(1.53,243) in CasaXPS, for peak decomposition. The peak decomposition for the quantification of surface chemical species was performed according to our previous works (Ardila Suárez, Díaz, et al., 2019; Ardila Suárez, Rodríguez Pereira, et al., 2019). For the C 1s peak, the following chemical species, ordered from lower to higher binding energies (BEs), were considered: (i) Carbon belonging to an aromatic ring, labeled as C-Ar. Under the analysis conditions employed herein, this component is indistinguishable from the peak from the C-(C,H) species from aliphatic hydrocarbons. In consequence, a single component centered at 284.8 eV (Rouxhet & Genet, 2011) was assumed for both species. This component was employed as a reference for correcting the BE scale of the spectra (Rouxhet & Genet, 2011). (ii) Carbon from the carboxylic acid group linked to the Zr cluster labeled as Ar-(C-O)-Zr, [286.14, 286.54] eV. (iii) Carbon belonging to the carboxylic acid group of H3BTC, labeled as Ar-Carboxy. Based on literature references (Genet et al., 2008; Rouxhet & Genet, 2011), it was fixed at 288.0 eV. (iv) Carbon from the carboxylic acid group linked to an aliphatic chain labeled as Aliph-Carboxy and fixed at 289.0 eV (Genet et al., 2008). (iv) Carbon linked to a sulfonic group,

C-S-O (Ardila Suárez, Díaz, et al., 2019), that under the analysis conditions of this work, this component is indistinguishable from the C-O-H contribution (Rouxhet & Genet, 2011), [286.3-286.5] eV. An additional peak corresponding to the $\pi - \pi^*$ from the aromatic ring was considered for peak decomposition (Briggs & Beamson, 1992), [290.6, 291.0] eV. For this component, the R.S.F. was set to 0 for quantification. The same FWHM was considered for all carbon species and the $\pi - \pi^*$ transition peak. For the O 1s peak, three species were considered. The first was oxygen linked to Zr in the inorganic cluster, labeled O-Zr, [530.5, 531.2] eV. The second was oxygen belonging to a carboxylic acid functional group, [531.9, 532.4] eV. In the O 1s peak, this component, labeled as R-(C=O)-OH, cannot be further decomposed into carboxylates linked to an aromatic or aliphatic chain (Rouxhet & Genet, 2011). The third oxygen component, [533.8, 534.2] eV, was ascribed to oxygen belonging to the Zr-O-C bonds in the MOF. The oxygen bound to the sulfate group O-S chemical species was also considered. Its position was set around 530 eV according to the literature (Poo-arporn et al., 2015). This proposal is coherent with the BE shifts expected when comparing the parent carbon components described before, in the sense that if the corresponding carbon is more oxidized, the oxygen must be more reduced. No constraints were imposed during peak decomposition except for assuming the same FWHM for all components. For the Zr 3d peak, three species were considered. The first was Zr coordinated to an organic group through oxygen, labeled Zr-O-C, the Zr 3d_{5/2} peak = [181.6, 182.5] eV, the second Zr belonging to inorganic clusters, the Zr 3d_{5/2} peak = [182.0, 183.0], labeled Zr-O, and the third one, the Zr linked to the sulfate group and labeled as Zr-O-S. The average position of the Zr 3d_{5/2} peak for this last contribution was 184.5 eV. The above BE assignation was also made considering the relative BE shifts expected from the corresponding oxygen and carbon components. The following constraints were imposed during peak decomposition: a) the area

of the Zr 3d_{3/2} core level is equal to two-thirds of the area of the Zr 3d_{5/2} core level, and, b) separation of 2.37 eV between both core levels was assumed (Moulder et al., 1995). Besides, four components corresponding to overlapping loss features from the Zr 3d core levels of each assigned species were considered for peak decomposition but not accounted for in quantification; i.e., R.S.F. fixed to 0. Finally, for the S 2p peak of the sulfated sample, the S–O–Zr corresponding to sulfur linked to inorganic Zr moieties. In this case, the average of the S 2p_{3/2} peak was centered around 165.5 eV, associated with S–O bonds in (SO₄)²⁻ species in which sulfur remains in a hexavalent oxidation state (S⁶⁺) (Zhichao Miao et al., 2017). For the S 2p core level, the following constraints were imposed during peak decomposition: a) the area of the S 2p_{1/2} core level is equal to half of the area of the S 2p_{3/2} core level and b) separation of 1.16 eV between these two peaks was assumed ("Thermo Scientific XPS,").

Additional insights into the surface chemistry were gained by performing a series of time-of-flight secondary ion mass spectrometry analyses. Spectra were recorded using an IONTOF TOF.SIMS 5 instrument in both positive and negative ion secondary ion polarity applying Bi₃⁺ primary ions with 30 keV and a pulsed primary ion beam current of 0.3 pA. The analysis area varied from 66 x 66 μm² to 141 x 141 μm² over which the Bi₃⁺ beam was rastered. The resulting primary ion dose density was below 3.4E12 cm⁻² for all measurements so that the corresponding spectra mainly contain chemical information on the sample surface. In order to stabilize the surface potential, the charge compensation device of the instrument was used during the analyses. The imaging mode was also employed for this study.

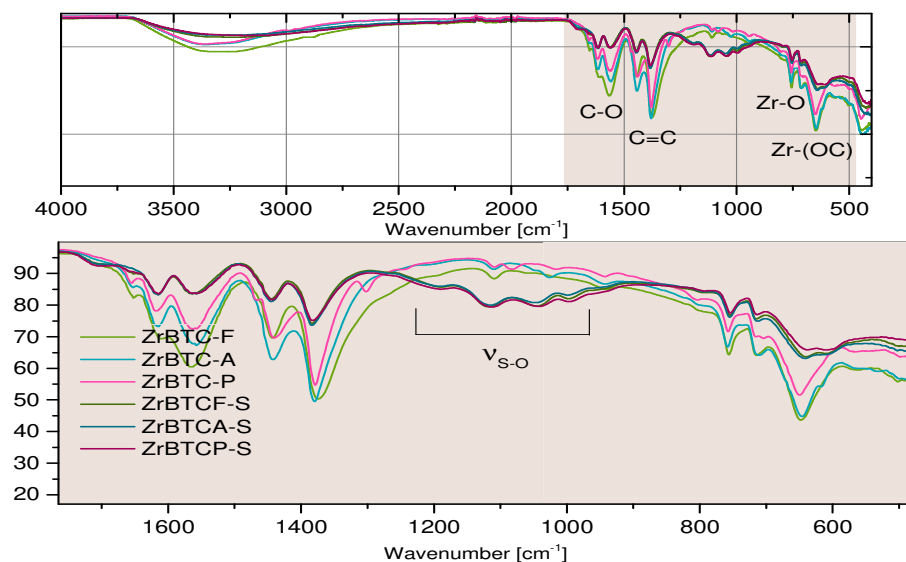
E-2. Results and Discussion

E-2.1. Molecular Structure

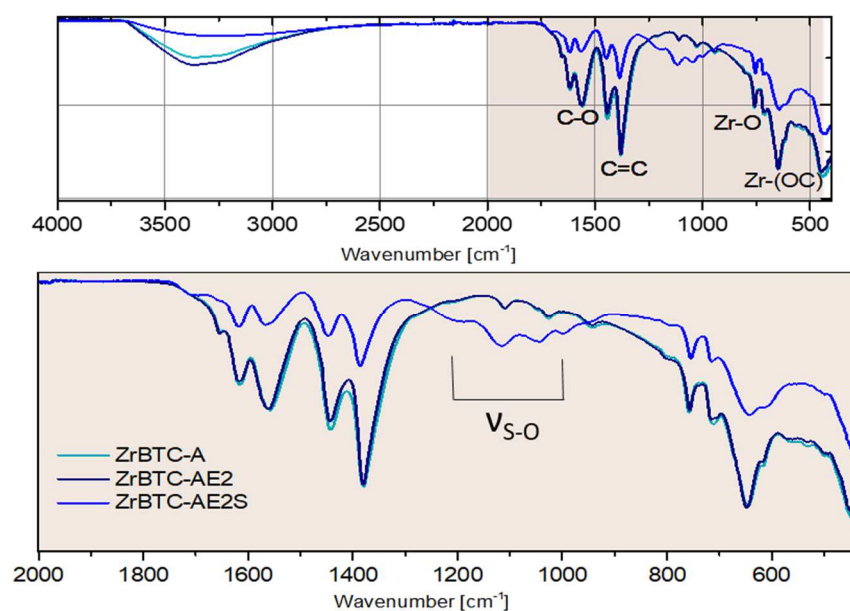
The bands in the region from 1600 to 1500 cm^{-1} are related to the C-O of the carboxylates linked to the zirconium clusters. Also, the bands around 1480-1420 cm^{-1} are associated with the C=C of the organic ligand (**Q. Zhang et al., 2014**). The bands observed in the region from 750-655 cm^{-1} correspond to the asymmetric vibration of the Zr-(μ_3 -O) bridges in the framework building units. The band around 640 cm^{-1} is associated with the vibration of the hexanuclear cluster and finally, the band in the 545-555 cm^{-1} is assigned to the Zr-(OC) asymmetric stretching vibration (**Piszcdek et al., 2007**).

Figure E-1.

Infrared spectra of synthesized ZrBT-F, ZrBTC-A, and ZrBTC-P materials before and after the sulfation process.

**Figure E-2.**

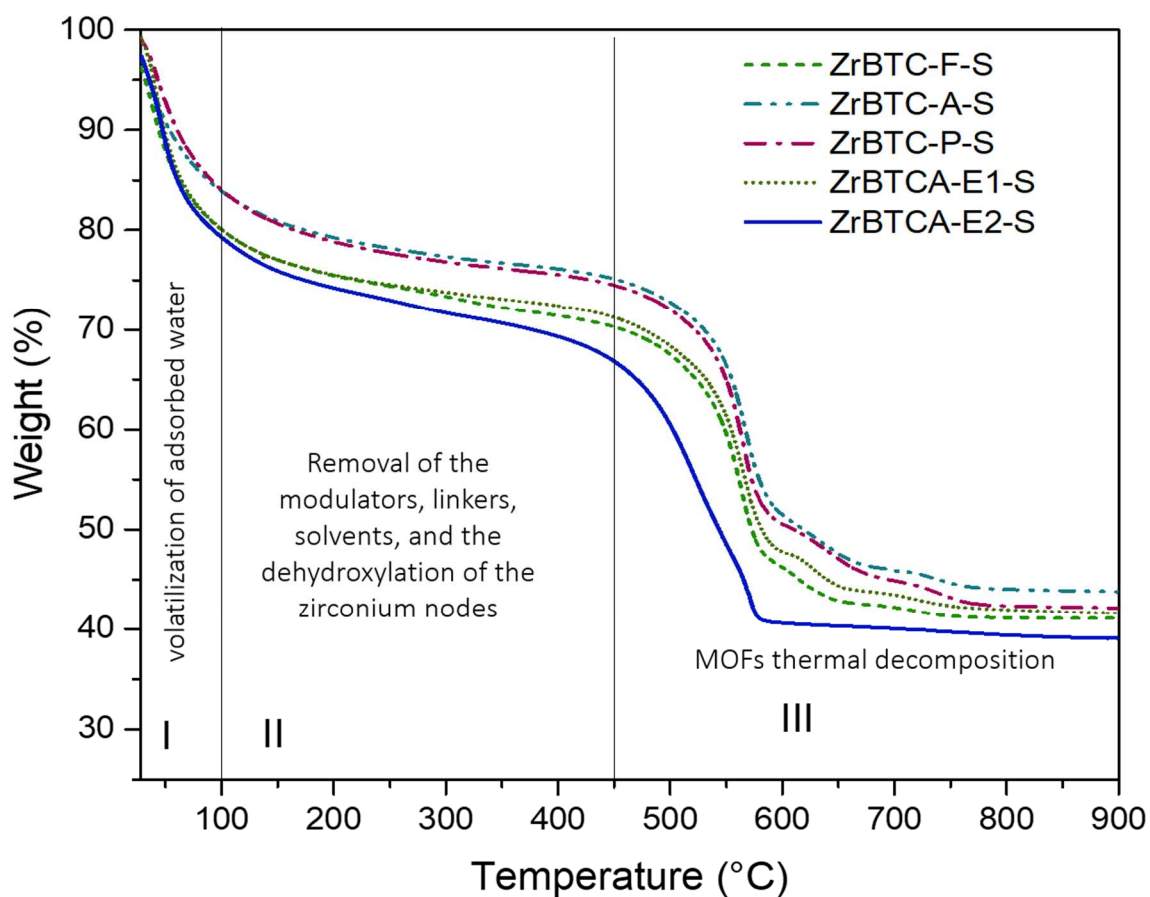
Infrared spectra of synthesized ZrBTC-A, ZrBTC-AE1, and ZrBTC-AE2 materials before and after the sulfation process.



E-2.2. Thermal stability

Figure E-3.

Thermogravimetric analysis (TGA) in an air atmosphere of synthesized MOFs.



E-2.3. Crystallinity

The crystalline structure analysis done by powder X-ray diffraction showed that the materials synthesized have the previously reported set of reflections of MOF-808, i.e., $2\theta = 4.34^\circ$ which

was assigned to the (111) plane of MOF-808 and $2\theta = 8.32^\circ$ and 8.69° which were assigned to diffraction from the planes (311) and (222), respectively. Although the ZrBTC-P material exhibited more defined peaks compared to the ZrBTC-F and ZrBTC-A MOFs, the three materials exhibited a certain degree of amorphicity, that could be related to their significant mesoporosity caused by missing linker defects. The synthesized materials crystallized in the cubic space group $Fd\bar{3}m$, Table S1. The lattice parameters of the materials synthesized herein are very similar to the previously reported for MOF-808 and as postulated by Liang et al. (W. Liang et al., 2014). The differences between them, according to the LeBail treatment results, could be related to the differences of solvent molecules that remain occluded inside the structure.

Table E-1.

Crystallinity data and structure treatment of the ZrBTC-F, ZrBTC-A, ZrBTC-P, ZrBTCAE-1, and ZrBTC-AE-2 material.

	Crystal system	Space group	Cell parameters (Å)	Volume (Å ³)	Chi2
ZrBTC-FS	Cubic	$Fd\bar{3}m$	35.31888(180)	43334.152(38.86)	1.32
ZrBTC-AS	Cubic	$Fd\bar{3}m$	35.04232(685)	43030.730(-----)	1.19
ZrBTC-PS	Cubic	$Fd\bar{3}m$	35.04154(525)	43027.848(111.6)	1.20
ZrBTC-AE1S	Cubic	$Fd\bar{3}m$	35.18922(391)	43574.152(83.91)	1.49
ZrBTC-AE2S	Cubic	$Fd\bar{3}m$	35.16290(316)	43476.430(67.57)	1.36

Figure E-4.

Le Bail profile fitting for ZrBTC-FS, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

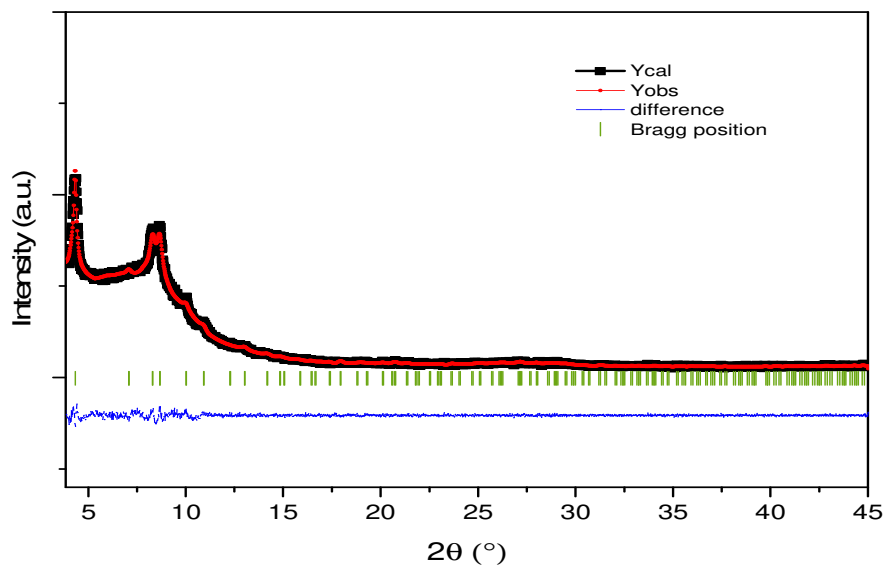


Figure E-5.

Le Bail profile fitting for ZrBTC-AS, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

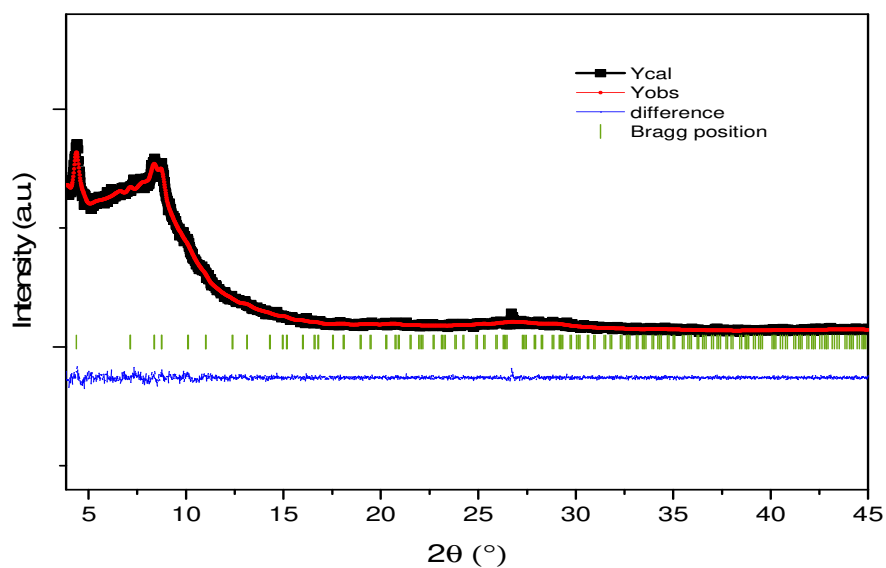


Figure E-6.

Le Bail profile fitting for ZrBTC-PS, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

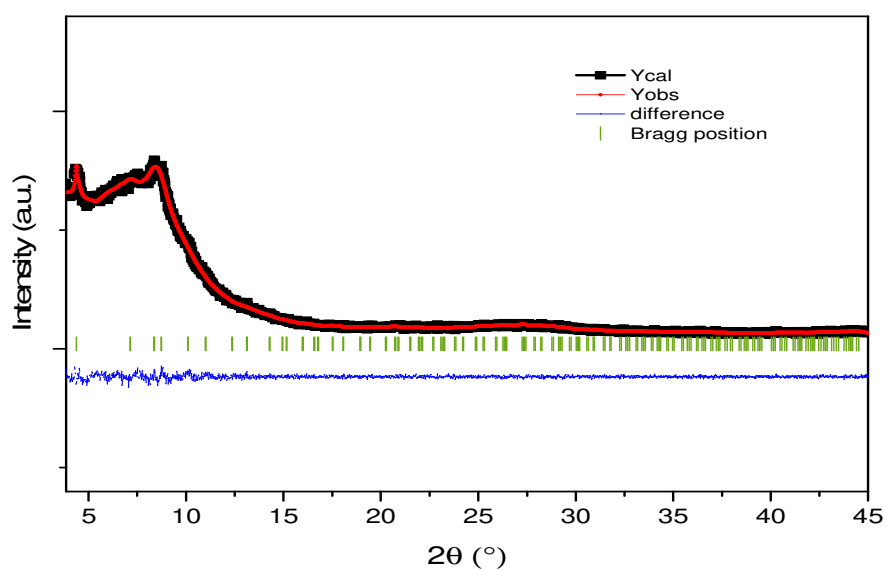


Figure E-7.

Le Bail profile fitting for ZrBTC-AEIS, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

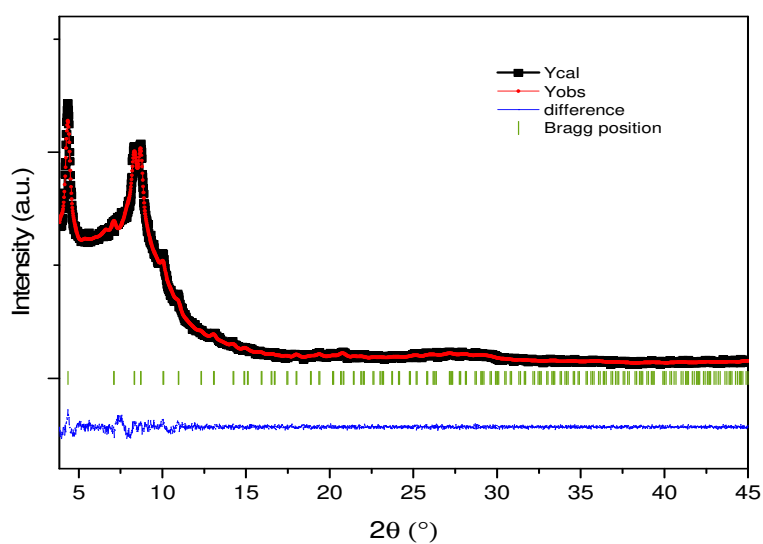
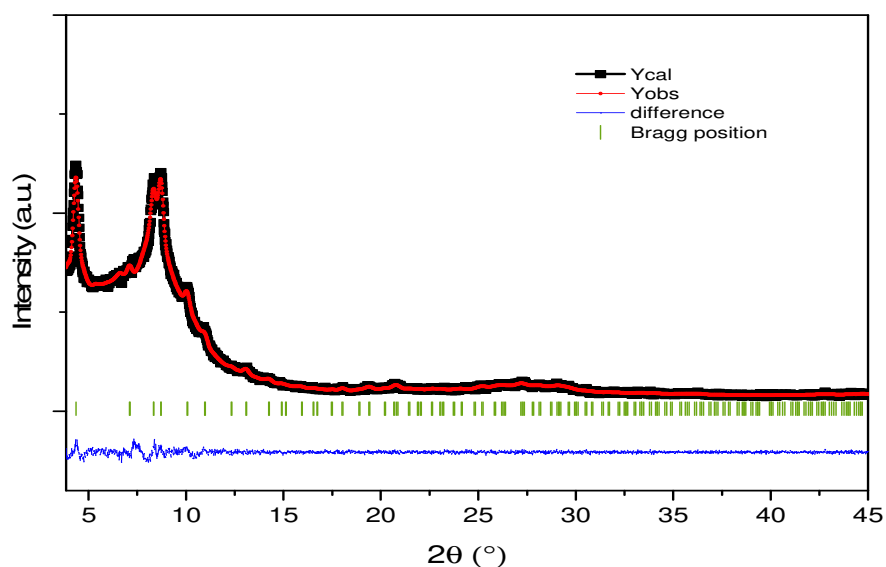


Figure E-8.

Le Bail profile fitting for ZrBTC-AE2S, using experimental PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.



E-2.4. Surface chemistry

E-2.4.1. Surface chemical state by XPS

The empirical formulas for the surface of ZrBTC-AS, ZrBTC-AE1S, and ZrBTC-AE2S were $\text{CO}_{1.468}\text{Zr}_{0.296}\text{N}_{0.002}\text{S}_{0.134}$, $\text{CO}_{1.235}\text{Zr}_{0.258}\text{N}_{0.003}\text{S}_{0.113}$, and $\text{CO}_{1.318}\text{Zr}_{0.274}\text{N}_{0.003}\text{S}_{0.135}$, respectively. Compared to the formula presented by Jiang et al. (Juncong Jiang et al., 2014), $\text{CO}_{1.736}\text{Zr}_{0.330}\text{H}_{0.714}\text{S}_{0.127}$ the sulfated materials synthesized herein exhibited oxygen deficiencies at the surface of ca. 15 and 28 % for ZrBTC-AS and CTAB-synthesized materials, respectively. Related to zirconium, the

sulfated materials of this work showed a decrease of ca. 10 and 22 % for ZrBTC-AS and CTAB-synthesized materials, respectively. Accordingly, the sulfated materials synthesized through the surfactant self-assembly strategy displayed an increase of zirconium and oxygen deficiencies at the surface compared to the blank material, the ZrBTC-AS. On the other hand, related to the presence of sulfur at the surface, the ZrBTC-A and ZrBTC-AE2S showed a higher concentration (ca. 6 %) of sulfur at its surface but contrary, the ZrBTC-AE1S decreased the amount of sulfur at the surface in around 16 %.

E-2.4.2. Chemical surface composition through ToF –SIMS

Figure E-9.

Spectra of the surface (a) Positive (b) Negative Secondary Ion Polarity of ZrBTC-AE2S MOF.

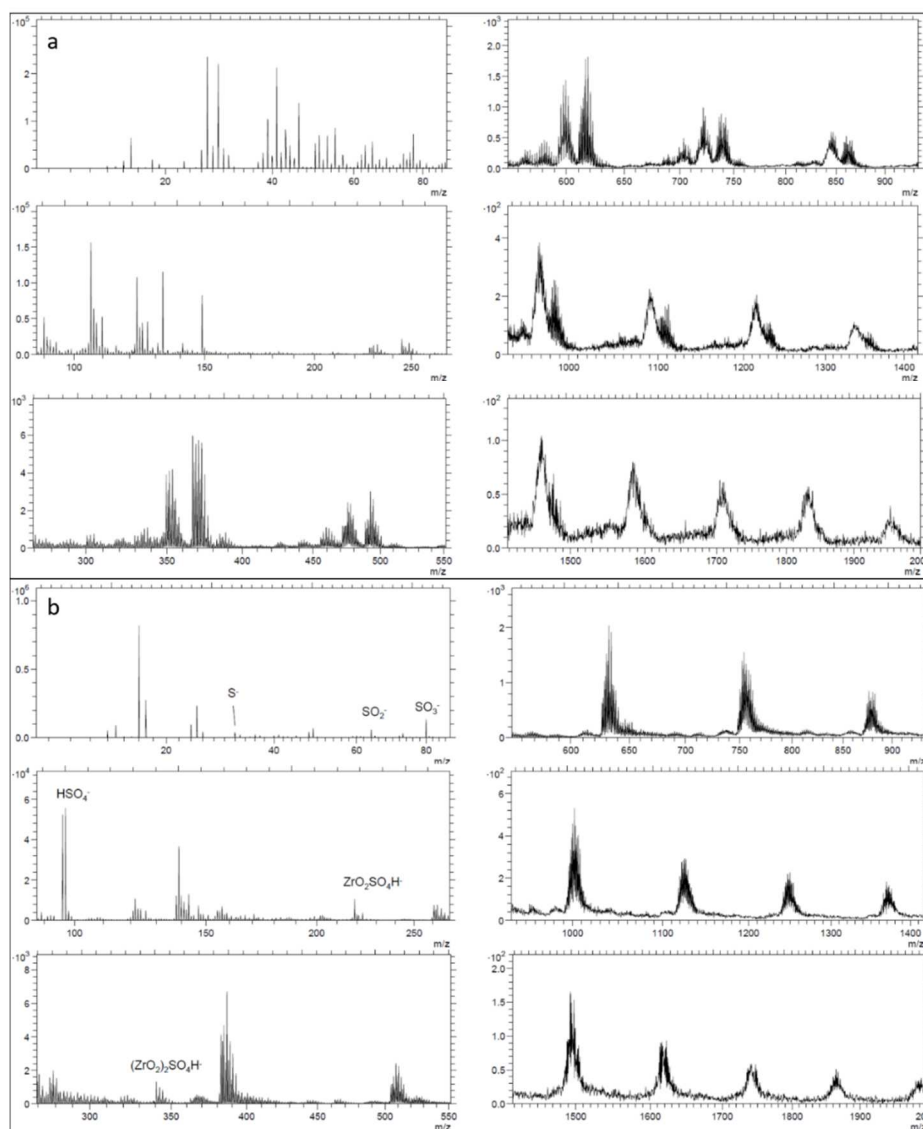
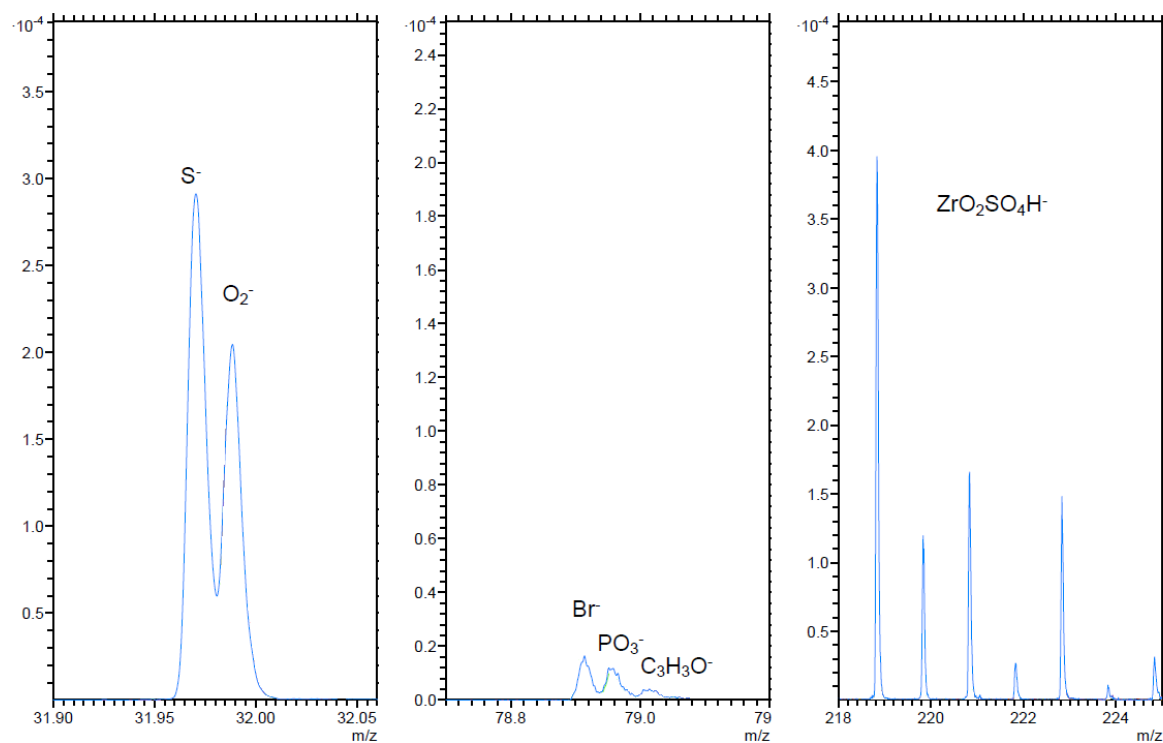
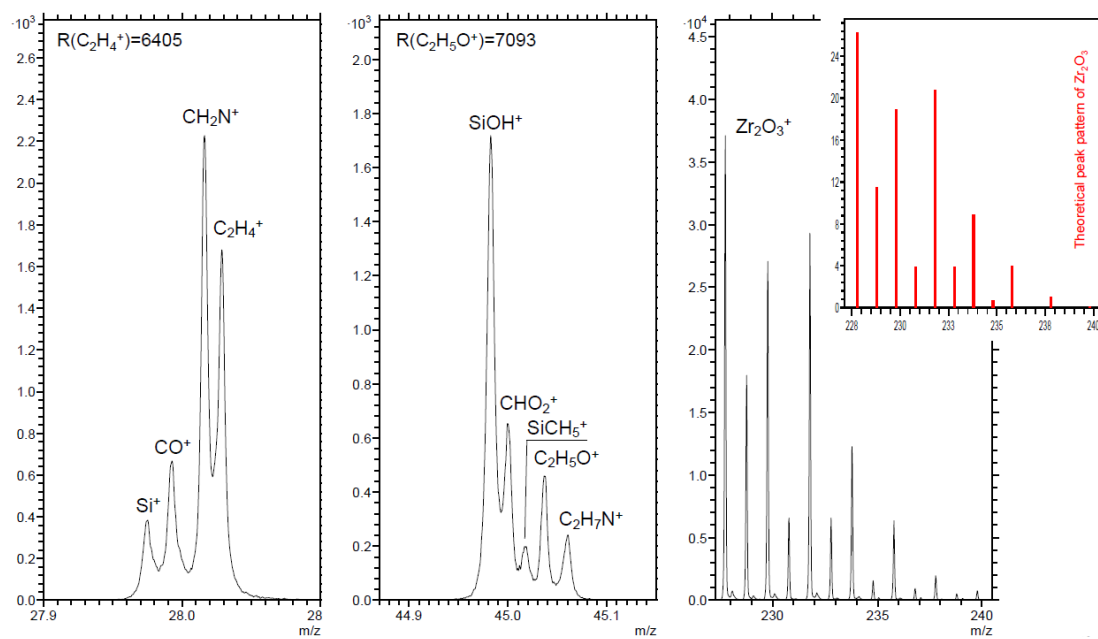


Figure E-10.*Spectra of the surface Negative Secondary Ion Polarity of ZrBTC-AE2S***Figure E-11.***Spectra of the surface Positive Secondary Ion Polarity of ZrBTC-AE2S*

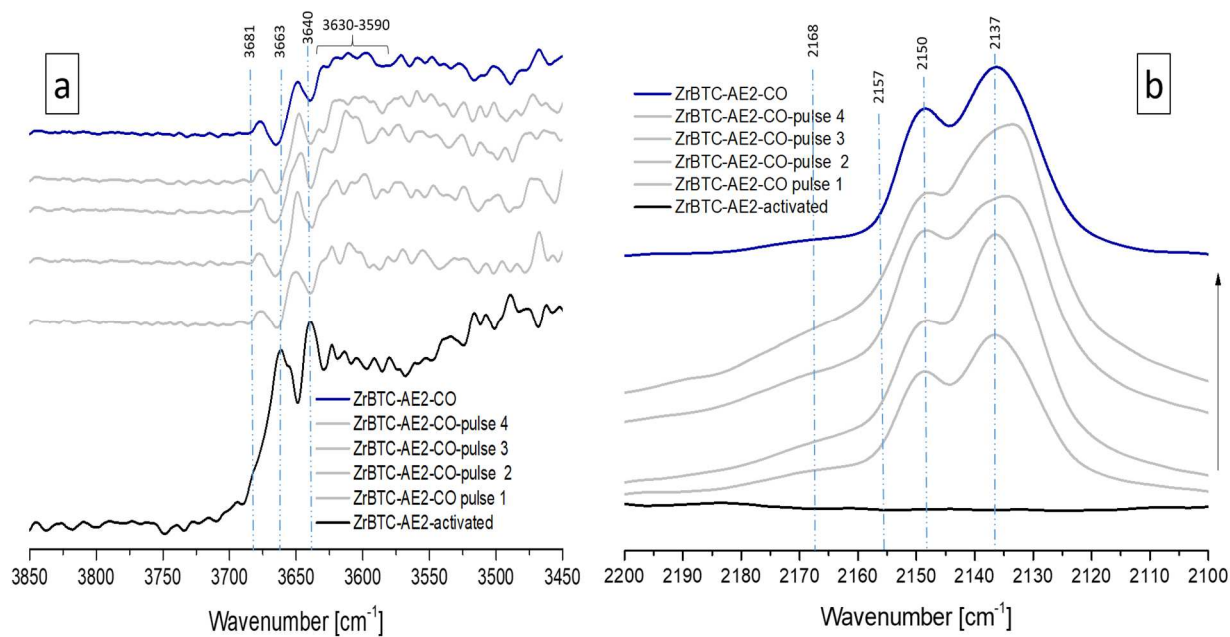
E-2.5. Assessment of the acid properties of ZrBTC MOFs

E-2.5.1. Infrared spectroscopy study of the CO adsorption.

The spectrum of the activated ZrBTC-AE2 sample is shown in Figure S12. The $\nu(\text{OH})$ zone, Figure S12a, shows hydroxyl groups at 3640 and 3663 cm^{-1} . This last contribution also exhibits two shoulders around 3654 and 3681 cm^{-1} . It shows since the first CO dose, the almost total disappearance of the 3663 and 3640 cm^{-1} bands and the simultaneous appearance of a vast contribution between 3590 and 3630 cm^{-1} indicating the presence of heterogeneous acid sites with mild strength. Related to the $\nu(\text{CO})$ region, Figure S12b, since the first addition of CO doses, a broad around 2168 cm^{-1} emerges as well as two clear peaks at 2150 and 2137 cm^{-1} . The increase of the amount of CO introduced induces a widening of the band centered at 2137 cm^{-1} . However, after the removal of CO from the cell, this peak becomes more defined, whereas the peak at 2168 cm^{-1} disappears.

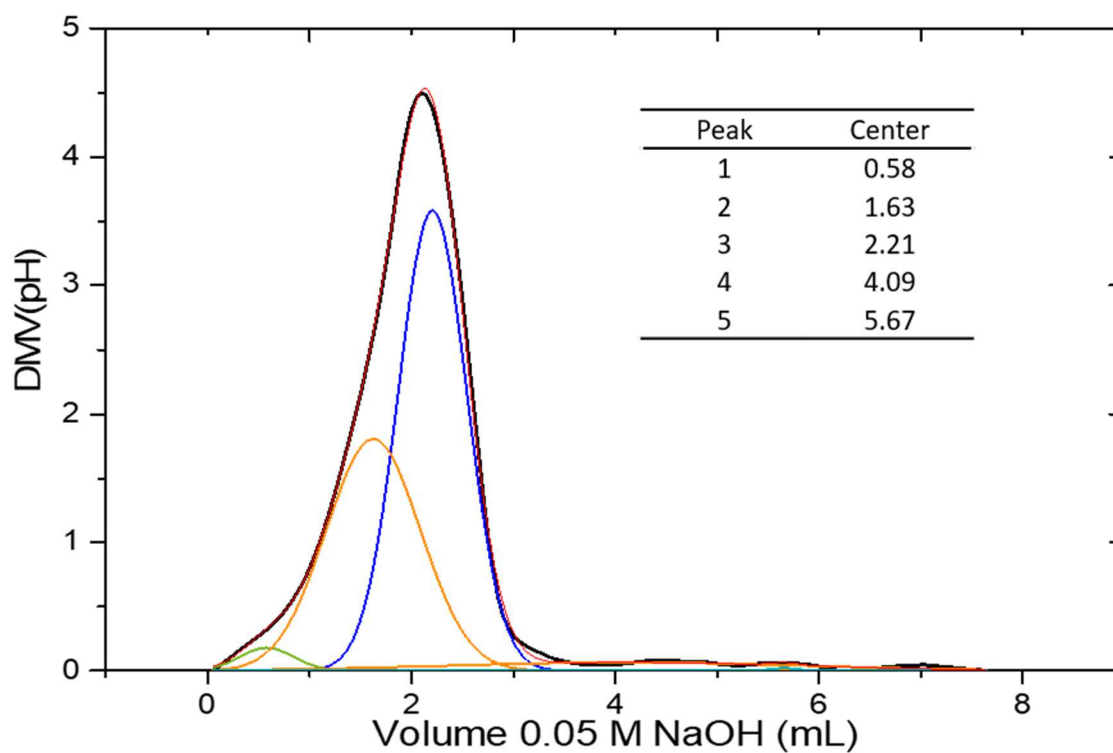
Figure E-12.

FTIR spectra of CO adsorbed at 77 K on ZrBTC-AE2 MOF in the C-O (a) and O-H (b) stretching region (after activation at 120 °C for 60 h)



E-2.5.2. Potentiometric acid-base titrations**Figure E-13.**

Peak decomposition of the first derivative curve of ZrBTC-AE2S material.



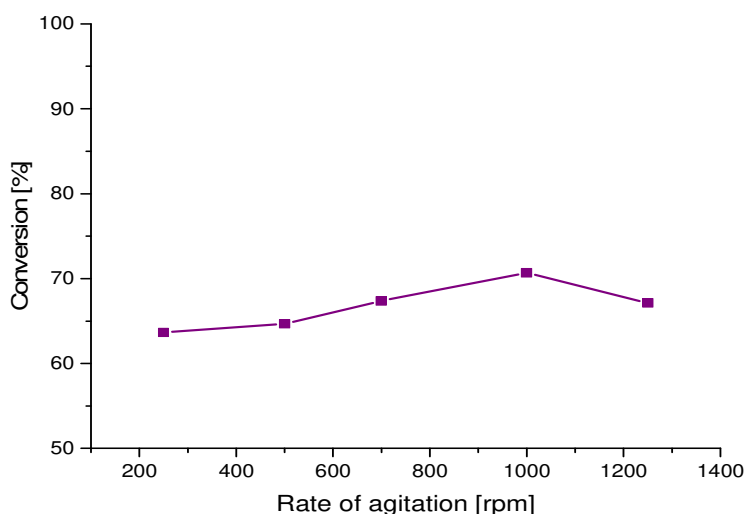
E-2.6. Catalytic Evaluation

E-2.6.1. External limitations

The mass transport could be external or internal, relying on if this phenomenon occurs in the boundary layer adjacent to the particle surface or inside the catalyst porous structure. In a “diffusion-limited” reaction, the reaction rate is not determined by the intrinsic reaction rate but by the diffusion rate. If this is the case, the external transport limitations are reduced by increasing the agitation rate of the reaction mixture (Sievers et al., 2016). Figure S14 displayed the glycerol conversion using the ZrTBTC-P catalyst as a function of the rate of agitation at the established reaction conditions. The glycerol conversion increases as the rate of agitation increase to a maximum of 1000 rpm and subsequently decline possibly due to vortex effects.

Figure E-14.

Glycerol conversion (%) as a function of the rate of agitation at the batch reaction using the ZrBTC-P as the catalyst. Reaction time: 4 hours in a batch reactor at 100 °C.

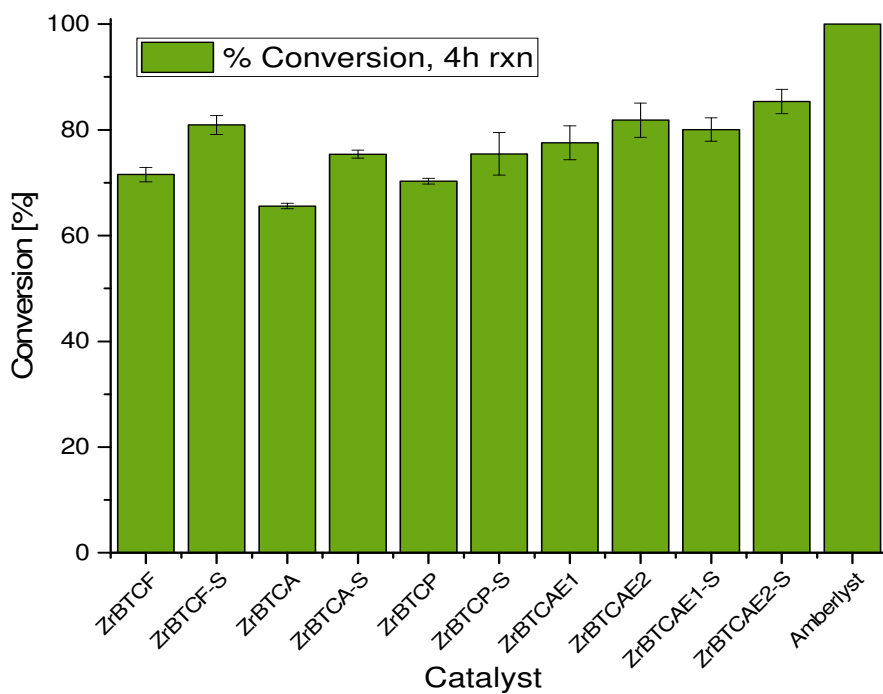


E-2.6.2. Glycerol conversion after 4 h reaction at 120 °C

Overall, it may be said that the materials synthesized using acetic acid as the modulator increases its glycerol conversion from $65.59 \pm 0.51\%$ to 77.56 ± 3.22 and $81.84 \pm 3.25\%$ for ZrBTC-AE1 and ZrBTC-AE2 materials. It is worth mentioning that despite both materials synthesized using surfactant exhibited ordered and interconnected structures, the ZrBTC-AE1 MOF showed a slightly larger surface area ($1005 \text{ m}^2/\text{g}$) and macroporous PSD (centered around 67.4 nm) compared to the ZrBTC-AE2 material ($943 \text{ m}^2/\text{g}$ and 53.9 nm). However, the increase of glycerol conversion in the latter material could be related to its greater crystallinity [H-MOF808]. More crystallinity leads to structural uniformity and the molecular specificity in catalysis (L. Ma & Lin, 2010). After sulfation, all materials improved their selectivity to diacetin. ZrBTC-F, ZrBTC-A, and ZrBTC-P increased in around 9 % their conversion, whereas the increment was slightly lower for ZrBTC-AE1 and ZrBTC-AE2, approximately 4 %. Contrary to the amberlyst commercial catalyst, none of the studied MOFs achieved the 100 % of glycerol conversion after 4 h reaction.

Figure E-15.

Glycerol conversion on the studied catalyst concerning reaction time in a batch reactor at 100 °C; catalyst loading: 1% wt (glycerol reactant basis).



E-2.6.3. Turnover frequency calculation

The turnover frequency, TOF, was calculated according to equation S1 (Boudart, 1995).

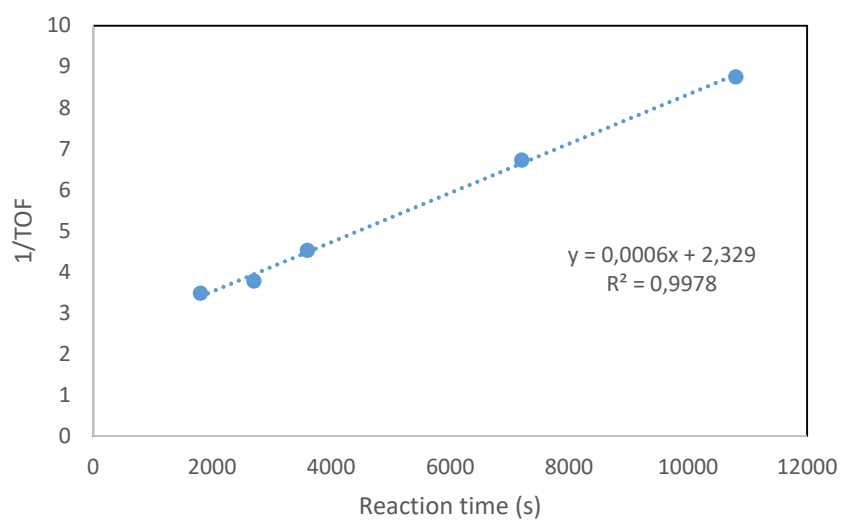
The total of active sites was calculated according to Table 3.

$$TOF [s^{-1}] = \frac{(n_{0, glycerol})(\chi_{glycerol})}{(\# \text{ active sites})(time)} \quad (S1)$$

To calculate the TOF values at zero conversion, the 1/TOF values as function reaction time was plotted, see Table E-2 and Figure E-16.

Figure E-16.

1/TOF as a function of reaction time for the ZrBTC-A catalyst.

**Table E-2.**

TOF calculations at zero conversion for ZrBTC-A, ZrBTC-AE2, and ZrBTC-AE2S catalysts.

Catalyst	1/TOF [s]	TOF [s^{-1}]	R ²
ZrBTC-A	2.329	0.4294	0.99
ZrBTC-AE	0.9908	1.0093	0.99
ZrBTC-AE2S	0.8127	1.2305	0.99

Figure E-17.

Experimental PXRD data comparison of the ZrBTC-AE2S catalyst before and after the catalytic test.

