



# Defect formation in metal–organic frameworks initiated by the crystal growth-rate and effect on catalytic performance



Somboon Chaemchuen<sup>a</sup>, Zhixiong Luo<sup>a,c</sup>, Kui Zhou<sup>a,b</sup>, Bibimaryam Mousavi<sup>a</sup>, Suphot Phatanasri<sup>e</sup>, Mietek Jaroniec<sup>f</sup>, Francis Verpoort<sup>a,b,c,d,\*</sup>

<sup>a</sup>Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China

<sup>b</sup>School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, PR China

<sup>c</sup>Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, 9000 Ghent, Belgium

<sup>d</sup>National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, Russian Federation

<sup>e</sup>Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand

<sup>f</sup>Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA

## ARTICLE INFO

### Article history:

Received 5 June 2017

Revised 12 August 2017

Accepted 15 August 2017

Available online 6 September 2017

### Keywords:

Metal-organic framework

Defect structure

Un-coordinated site

Active site

Catalyst

## ABSTRACT

The defect formation in metal–organic frameworks (MOFs) initiated by the crystal growth-rate of different synthesis procedures affects the structure, morphology and other properties of MOFs such as particle shape, gas adsorption capacity and specifically catalytic performance etc. Although the design of defect structures and the defect structures itself are well known, comparatively little is known regarding defect creation introduced by the synthesis procedure (different from mixed-linker approach, the use of acid modulators, post-synthetic treatment, etc.) and characterization of the resulting naturally occurring abnormalities (defects) in the material. Moreover, high performance of MOFs in various catalytic reactions can be correlated to the higher amount of defect structures because defects can possibly exhibit acid and/or basic properties. While studies of MOF crystallinity confirmed that for a given type of MOF different synthesis methods generate samples of similar crystal structures, their morphologies are often different due to the differences in the crystallization rates associated with these methods.

© 2017 Elsevier Inc. All rights reserved.

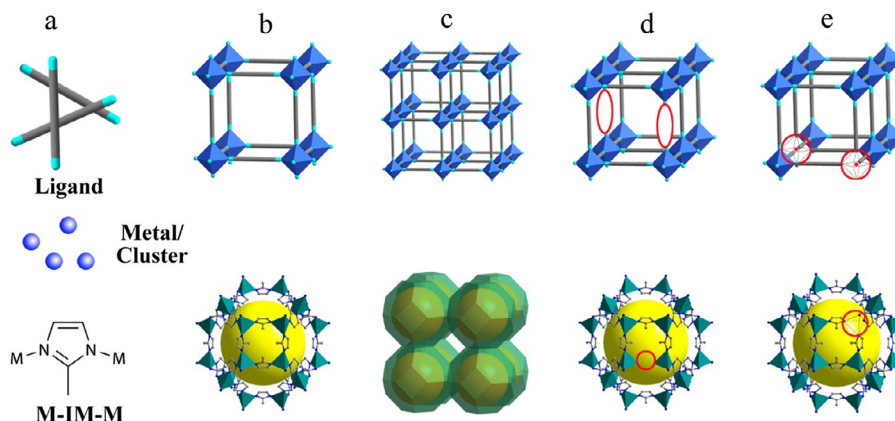
## 1. Introduction

Crystalline hybrid materials assembled by bridging metals/cluster nodes with linkers/organic compounds, well-known as Metal-Organic Frameworks (MOFs), exhibit excellent adsorption, catalytic and structural properties [1–3]. Perfect MOFs are marked by an ideal crystal structure in which the unit cells are faultlessly arranged, however, such ideal MOF structures are practically unachievable. The real crystal structures always deviate from the perfect or ideal structures due to the presence of structural defects (Fig. 1) [4]. Generally, the defect structures present in solid materials significantly affect their physical and chemical properties such as spin frustration in cooperative paramagnets [5], thermoelectric parameters [6], and formation of polar nanodomains in

relaxed or ferroelectric structures [7] and particularly the surface active sites in sensing applications [8,9]. Specifically, in case of MOF materials, defects are well-known to exist in MOFs structure and received special attention since defect structures in MOFs can drastically enhance adsorption of gases such as H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and CO, as well as catalytic applications depending on the presence of acid and/or basic sites [10,11]. The metal type and content and the variety of organic ligands in MOFs are a great source of active sites, which can act as reactive centers in many catalytic reactions [12,13]. The high accessibility of open sites such as unsaturated metal ions and uncoordinated ligands, in this work assigned as defect structures, has gained more and more interest from the catalysis field [14]. Application of MOFs in catalysis is rapidly growing, which is reflected by a wide range of catalyzed reactions such as cyanosilylation [15], isomerization, hydrogenation [16,17], oxidation [18], trans-esterification [19], photocatalysis etc. [20–22]. Notably, the advantage of applying MOFs as catalysts is related to their heterogeneous nature, which is superior to homogeneous catalysis because of easier separation, reusability, minimization of wastes, and generation of “green” and clean products.

\* Corresponding author at: Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China.

E-mail addresses: [Francis.Verpoort@UGent.be](mailto:Francis.Verpoort@UGent.be), [Francis@whut.edu.cn](mailto:Francis@whut.edu.cn) (F. Verpoort).



**Fig. 1.** A comparison of MOFs (up) and ZIFs (bottom) structures. a) The fundamental bridging unit in frameworks. b) The single unit structure. c) The linking of units (b) into an expanded face-centered-cubic structure. The structure with missed linkers (d) and missed metals (e) or defect structures.

Regardless the well-defined structure of MOFs, their catalytic applications are largely hampered because the metal/cluster is usually completely coordinated and blocked by organic linkers [23]. Therefore, the design of defect structures in MOFs can possibly enhance the amount of catalytic sites at the nodes of these frameworks [24]. Tailoring the defects in MOFs is essential for establishing the structure–property relationships for targeted applications, such as shape- and size-selective adsorption, and complex site-driven catalysis and sensing. Until today, two main strategies have been applied and investigated for the generation of defect structures. The first strategy uses a proper mixture of mono- and/or poly-dentate ligands to create the defects in MOFs [25–27]. Similarly, the ratio of linker/metal is crucial in the design and creation of defect structures, however, this is limited to certain MOFs (bearing many linkers in one secondary building unit such as UiO-66 (Zr) or UiO-66(Hf)) [28–30]. The second strategy is focused on the acceleration of synthesis via addition of a strong deprotonating agent resulting in a very fast reaction (kinetically driven process) leading to the creation of defect structures while still retaining the original MOF structure [31,32]. While numerous variations of these synthesis routes are well-known in the area of MOFs, so far the relation between various synthesis procedures and creation of different amounts of defects in MOFs has not been studied yet. Since the synthesis procedure determines often if the crystal growth is thermodynamically or kinetically driven, it has a pronounced effect on the creation of defect structures within MOF frameworks. A proper selection and/or modification of the synthesis procedure can markedly affect the morphology and properties of MOFs, since the crystallization rate is essential in the crystal growth process and formation of defect structures, which have a pronounced effect on the adsorption and catalytic properties of these materials. Nonetheless, the design of defect structures and the defect structures itself are well known, comparatively little is known regarding defect creation introduced by the synthesis procedure and characterization resulting in naturally occurring abnormalities (defects) in the material. Moreover, the available literature on the formation of defect structures during growth of MOF crystals is extremely rare and the relation between these defects and the catalytic activity is, as a consequence, poorly understood. In addition, the effect of parameters such as type of procedure, crystal growth-rate and reactivity, *etc.* affecting the defect structure creation are not yet reported. Therefore, there is still an urgent need for the procedures allowing creation of defects in MOFs in a straightforward and controllable manner and for studies of the relationship between the amount of defects and the catalytic performance of MOFs in specific catalytic reactions, gas adsorption and separation.

This report is focused on the creation of defect structures (defects) in MOFs obtained by different synthesis procedures, and on the quantitative assessment of these defects. Another aspect of this work is related to the unexpected finding that the defect structures can enhance the catalytic activity of MOFs in various chemical reactions. Furthermore, this study shows that the catalytic reactions can be successfully used to prove the presence of defect structures, while their amount can be related to the catalytic performance (activity) of MOFs. Finally, a further advancement in the design and understanding defect structures will certainly open new opportunities for multipurpose applications of MOFs.

## 2. Experimental

The MOFs synthesis, characterization and catalytic testing are provided in [Supporting Information](#).

## 3. Results and discussion

The ZIF-8 series was prepared by using different typical methods to demonstrate the effect of synthesis procedure on the amount of created defect structures. In addition, this work utilized ZIF-8 as a prototypical model of MOFs and later on, will be extended to other MOFs. Powder X-ray diffraction was used to determine the crystallinity of ZIF-8 obtained via different synthesis methods (Fig. 2a). The XRD patterns of the ZIF-8 samples obtained by different methods show only small differences in the normalized intensities using the [0 1 1] reflection plane. This figure shows that the XRD patterns obtained for the aforementioned ZIF-8 samples remain unchanged and are in excellent agreement with the simulated pattern between  $2\theta$  values of 5 and  $30^\circ$ . These results confirm that ZIF-8 crystals obtained via different synthesis procedures are isostructural with the simulated pattern and their high intensity reveal high crystallinity.

Scanning Electron Microscopy (SEM) was used to investigate the crystal morphology and to estimate the average crystal size (Fig. S1, [Supporting Information](#)). The SEM images reveal different morphologies and sizes of the crystals depending on the synthesis procedure (Fig. 2a). The cube shape was observed for the ZIF-8 sample obtained by spray drying method (ZIF-8-SP), while the microwave-assisted synthesis produced more spherical-like crystals (ZIF-8-MW) but with smaller particle size (particle sizes of ZIF-8-SP and ZIF-8-MW were  $\sim 5 \mu\text{m}$  and  $0.2 \mu\text{m}$ , respectively). The rhombic dodecahedron crystals were obtained by using conventional room temperature synthesis (ZIF-8-RT) and the well-defined truncated rhombic dodecahedral crystals were formed

Download English Version:

<https://daneshyari.com/en/article/6455498>

Download Persian Version:

<https://daneshyari.com/article/6455498>

[Daneshyari.com](https://daneshyari.com)