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Modelling of porous metal-organic framework (MOF) materials used in catalysis

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Abstract

This paper presents a review of modern modelling of porous materials such as metal-organic frameworks used in catalysis. The authors' own research approach using the nano-design of metal-organic frameworks is included in this review.

Keywords: DFT modelling, metal-organic frameworks

1. Introduction

Describing and classifying classic structures as networks has been a recognised approach for a long time (Hoffmann, Fröba, 2016). This description was introduced in 1954 by A.F. Wells in a two-part paper entitled 'Acta Crystallographica' (Wells, 1954). A consequence of the development of the description of the crystal structure was the emergence of crystal engineering allowing the prediction and design of appropriate building molecules that provide the crystal lattice (Hoffmann, Fröba, 2016). This approach was called mesh synthesis and was described by the research team of O.M. Yaghi in 2003 (Yaghi et al., 2003). The authors proposed building the desired crystal lattice using a well-defined and stable building unit that maintains an intact structure throughout the entire process of creating the target coordination.

The formation of open skeletal structures based on coordination chemistry that mimic zeolite or other microporous solids has been studied by several research groups (Lu et al. 1997; Hoskins & Robson, 1990; Milward & Yaghi, 2005). Metal-organic frameworks (MOFs) can be divided into four groups (Fig. 1) (Abrahams, Hoskins, Michail, Robson, 1994; Kitagawa, Kondo, 1998). The first generation has an unstable porous structure due to the skeleton-inclusions relationship. After the removal of the inclusions, the structure breaks down. This is often the case when MOF contains charged structures with pores filled by ions with the opposite charge. However, in the second generation, after removal of the atom from the interior, the porous structure is preserved and is stable. The third generation is characterised by its high flexibility and dynamic structure and is able to change under the influence of external factors such as light or pressure. The fourth and last generation can be defined as a structure that demonstrates the maintenance of topology and stability relative to various types of modification after synthesis. MOFs from the 3rd and 4th generations are most often used in catalysis. Depending on their generations, it is possible for the MOFs have hundreds of highly porous structures with different open-space channels, which creates an exceptionally high capacity for molecule storage e.g. H_2 or CO_2 (Milward, Yaghi, 2005).

The concept of post-synthetic modifications (PSM) was proposed as early as 1990 (Hoskins, Robson, 1990), but for MOFs, it was relatively limited. First of all, the challenge was the breaking and rearrangement of the covalent bonds in the structure of the body with coordination groups (Wang, Cohen, 2009). However, studies have shown that MOF crystals subjected to modification can be treated as substrates and transformed in reactions by, for example, using organic chemical reagents (Wang, Cohen, 2007). New methods for the synthesis of desirable structures are based on various types of modifications, including the transformation of coordination bonds (Wu, Hu, Zhang, Lin, 2005; Vimont et al., 2006; Kaye, Long, 2008; Hwang et al., 2008), as well as the introduction or exchange of metal atoms or ions (Mulfort, Hupp, 2007; Mulfort, Hupp, 2008; Li, Yang, 2006: 726–727; Schroder et al., 2008; Proch et al., 2008). Further development of MOF modifications using the PSM

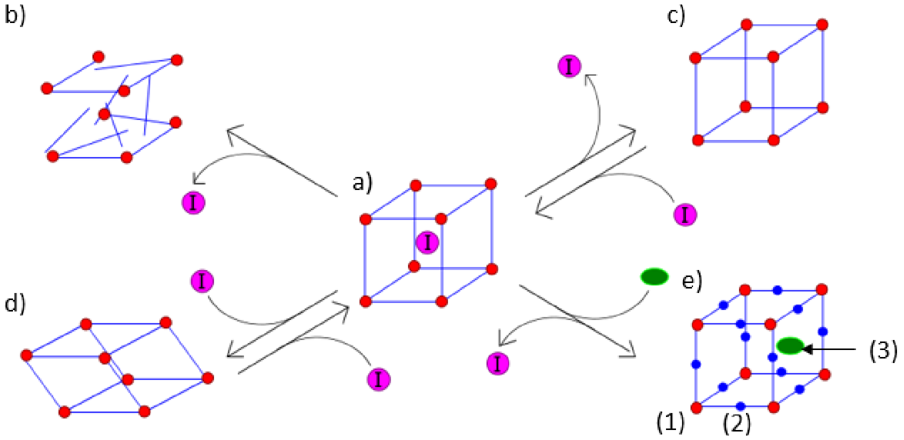

Fig. 1. MOF classification: a) skeleton-inclusion structure, b) first-generation MOFs, c) second--generation MOFs, d) third-generation MOFs, e) fourth-generation MOFs – modified (1) metallic cluster, (2) organic linker, and (3) vacancy (source: Abrahams, Hoskins, Michail, Robson, 1994)

concept enables planned structure modification, which translates into improved chemical stability and growth or directed to specific properties such as gas sorption or catalysis (Wang, Cohen, 2009).

2. Construction and types of MOFs

Organometallic structures appeared as an extensive group of crystalline materials with high porosity (up to 90% free space) and a large internal surface exceeding 6000 m^2/g (Zhou, Long, Yaghi, 2012). These properties and the variability of MOF organic and inorganic components make them an object of interest for potential applications as high-performance sorbents in ecological processes, and as catalysts for many reactions.

Organometallic structures consist of secondary metal-building units (SBUs) with rigid or semi-rigid organic ligands. Depending on the geometry and the method of connection of individual SBUs, they can create diverse structures with high porosity (Bosch, Zhang, Zhou, 2014). The structure of these compounds is often strong enough to survive the desolvation process (heating under vacuum or normal conditions), which leads to activation and, consequently, to obtaining a material with an extremely large specific surface. The connection method also influences the dimensionality of the formed structure (Pettinari, Marchetti, Mosca, Tosia, Drozdov, 2017).

A rapid development of MOF occurred in 1998 after describing MOF-2 (Fig. 2) or Zn(BDC), where (BDC) = 1,4-Benzenedicarboxylate (Li, Eddaoudi, Groy, Yaghi, 1998). On the basis of the structure obtained, it was concluded that further development may contribute to a full understanding of the physical and chemical properties of these type of compounds and will allow the design of a structure with the tailored properties.

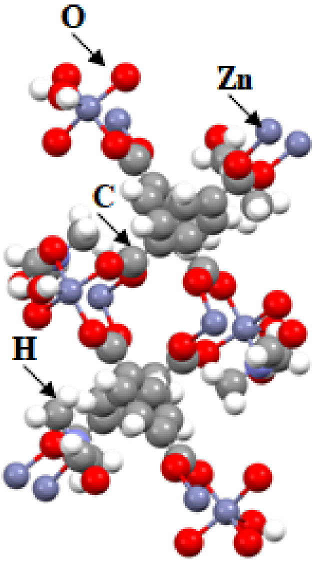

Fig. 2. Structure of the MOF-2 unit cell (CCDC, Access Structures)

As the next step, Yaghi et al. (Li, Eddaoudi, O'Keeffe, Yaghi, 1999) studied one of the important MOF groups – 3D structures based on zinc carboxylates. These included, among others structures, MOF-5 (Fig. 3) consisting of tetrahedron Zn_4O clusters connected in a cubic structure with terephthalate binders. The description of the structure with $Zn_4(CO_2)_6$ units containing four Zn_4O tetrahedrons (bound with a common vertex) and six carboxylic carbon atoms connected via benzene groups and defining the SBU octahedron (Yaghi et al., 2003) can be considered to be an important milestone in the field. This combination has exceptional porosity confirmed by sorption and stability (thermal analysis and X-ray diffraction tests).

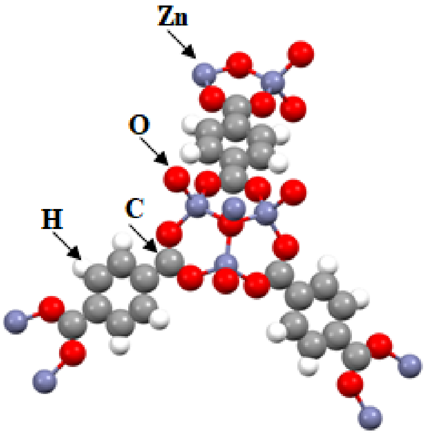

Fig. 3. Structure of the MOF-5 unit cell (CCDC, Access Structures)

MOFs based on zinc tetrahedra also include a group of structures called IRMOF (Eddaoudi et al., 2002). All of IRMOF come from the base structure of IRMOF-1 (another name MOF-5), and the differences result from the modification of the benzene ring connecting zinc tetrahedrons. This primarily affects the structure of the compound, and thus its porosity, as well as the properties they have.

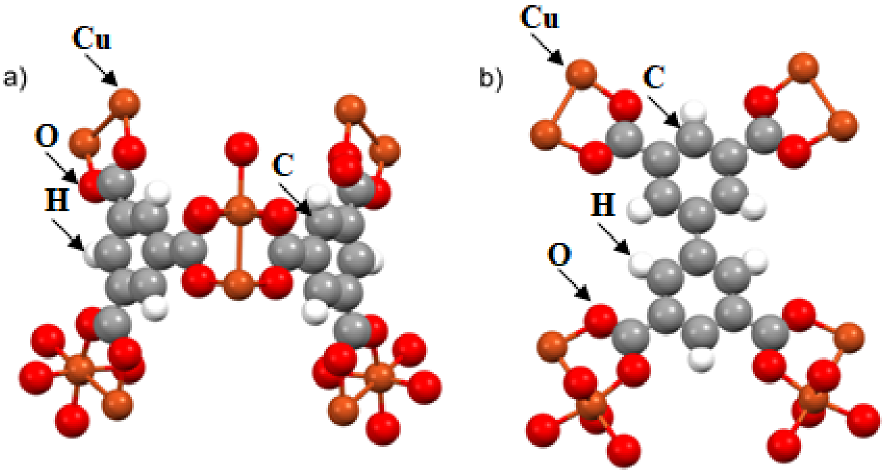

Fig. 4. Structure of the unit cell a) HKUST-1 and b) MOF-505 (CCDC, Access Structures)

An equally interesting structure that contains zinc atoms in its skeleton is ZIF-8, belonging to the family of MOFs called ZIF, which were described in an literature (Hayashi, Côté, Furukawa, O'Keeffe, Yaghi, 2007; Chizallet et al., 2010; Park et al., 2006). These types of materials have units enriched with organic units similar to those found in zeolites in their construction, for example, imidazole connectors which significantly increase the porosity of such systems and their thermal and chemical stability. In addition to zinc, the main metals in the network can also be iron, copper, or cobalt. ZIF-8 is primarily characterised by good sorption and separation properties; however, there are also reports of its use as a catalyst for various chemical reactions (Zhao, Chen, 2018; Wanga, Zenga, Wua, Mu, Chen, 2018; Miralda, Macias, Zhu, Ratnasamy, Carreon, 2012).

Another known group of MOFs have metallic copper clusters in their structure (Hendona, Walsh, 2015). The most important representant in this group is HKUST-1 (Fig. 4a), also called Cu-BTC, which was first described in 1999 and consists of duplicated units of the formula $[Cu_3(TMA)_2(H_2O)_3]_n$ (where TMA is benzene-1,3,5-tricarboxylate). This structure shows, among other properties, sorption properties comparable with the values shown by zeolites, such as fujazite or zeolite A. Moreover, HKUST-1 also has the potential to be used in organic synthesis as a catalyst due to its well-defined oxidation states (Chui, Lo, Charmant, Orpen, Williams, 1999). Another MOF containing a copper atom in its structure is MOF-505 (Fig. 4b) which can also be expressed as $[Cu_2(BPTC)(H_2O)_2(DMF)_3(H_2O)]_n$, where BPTC is 3,3', 5,5'-biphenyl tetracarboxylate and DMF – N. N'-dimethylformamide. MOF-505 is characterised by good sorption properties, especially of H_2 (Chen, Ockwig, Milward, Contreras, Yaghi, 2005; Zheng, Liang, Li, Huo, Liu, 2010).

In the context of these two systems (MOF-5 and HKUST-1), interesting studies have been conducted in which the combination of these two components and the formation of a structure called nHKUST-1⊂MOF-5 is described (Min Choi, Hyo Park, Ku Kang, 2015). HKUST-1 nanocrystals are inside the MOF-5 crystal giving this rare structure many interesting properties, including the ability to adsorb CH_4 and the ability to reverse this process without the appearance of a hysteresis loop.

The next important group includes organometallic structures based on zircon (DeCoste, Demasky, Katz, Farha, Hupp, 2015). These are particularly important as sorbents due to their significant increase of chemical and thermal stability compared to other MOF groups. These types of compounds include structures named successively UiO-66, UiO-67 and UiO-68 (UiO – University of Oslo) (Schaate et al., 2011). They contain a very stable SBU unit in their structure which is made of six zirconium cations forming an octahedron and connected with oxygen and hydroxyl bridges (Piszczek, Radtke, Grodzicki, Wojtczak, Chojnacki, 2007). Individual UiO systems differ from each other with regard to their connectors, which are dicarboxylic acids (Schaate et al., 2011). For UiO-66 it is bdc-2 (H2bdc: terephthalic acid), UiO-67 – bpdc-2 (H2bpdc: biphenyl-4,4’-dicarboxylic acid), UiO-68 - tpdc-2 (H2tpdc: terphenyl acid 4,4’’ – dicarboxylic acid). In addition, it has been shown that in addition to sorption properties, the UiO-66 system has a catalytic activity after modification at the synthesis stage (Vermoortele et al., 2013; Vandichel et al., 2015).

The next large group of MOFs are structures commonly called MIL-n (Materials Institute Lavoisier) (Ferey, 2008). These constitute a group that consists mainly of carboxyl ligands and trivalent metal ions such as V, Cr, Fe, Al, Ga, W and lanthanides (Pettinari, Marchetti, Mosca, Tosia, Drozdov, 2017). Several systems deserve attention in this family, and two of them are MIL-100 and MIL-101 (Hupp, Poeppelmeier, 2005; Ferey et al., 2005; Bromberg, Diao, Wu, Speakman, Hatton, 2012; Ferey et al., 2004). These are highly porous and therefore have a well-developed internal surface which promotes catalytic activity. The structure of the MIL-100 crystal (Fig. 5a) may contain a chromium atom, and the structure of a single crystal is so complicated that it is difficult to describe it with one formula. However, the chemical composition is determined by the general formula $Cr_3F(H_2O)_3O[C_6H_3\text{-}(CO_2)_3]_2 \cdot nH_2O$ (n ~ 28). In addition, in the MIL-100 system, the metal atom can be iron (Fig. 5b), which makes it a potentially interesting photocatalyst (Mahmoodi, Abdi, Oveisi, Asli, Vossoughi, 2018).

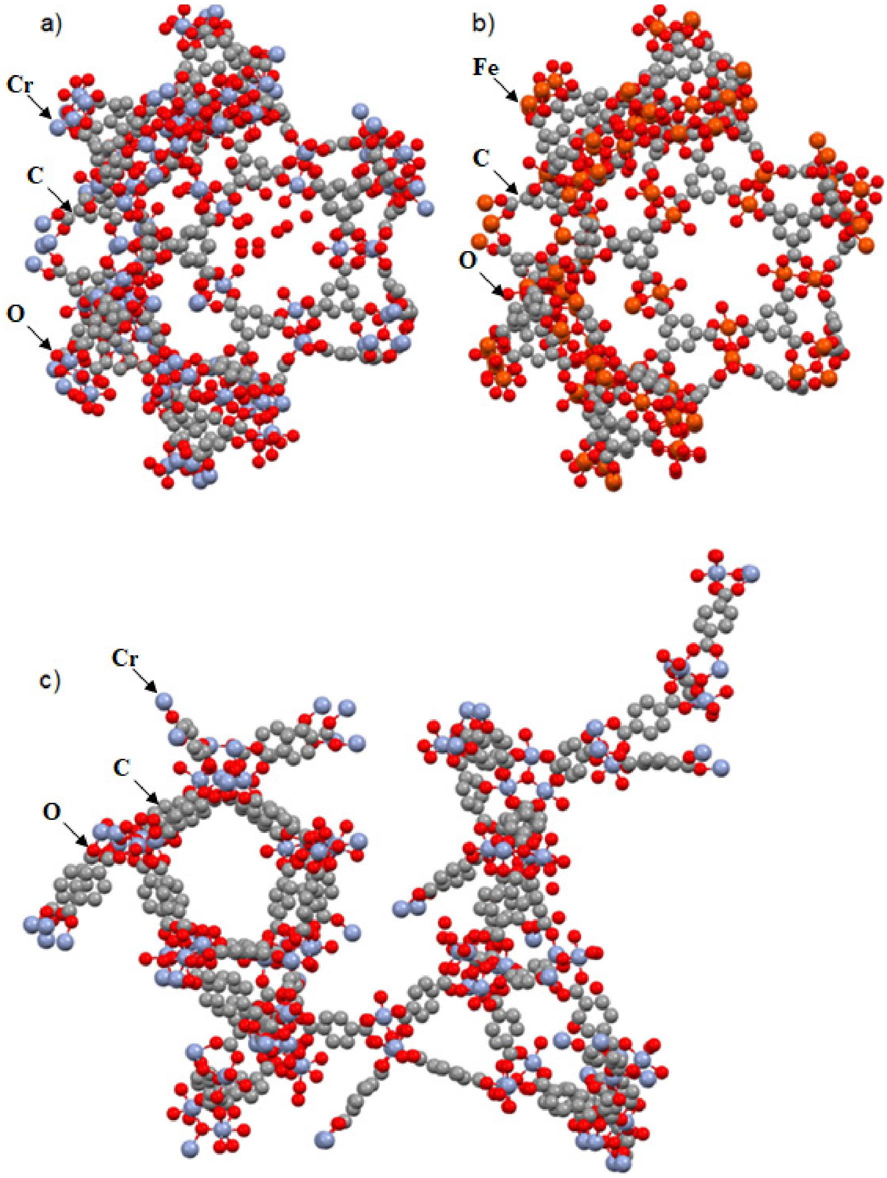

Fig. 5. Elemental cell structure a) MIL-100 (Cr), b) MIL-100 (Fe) and c) MIL-101 (CCDC, Access Structures)

In the structure of MIL-101 (Fig. 5c), the metal atom is chromium, and the general formula of this compound is $Cr_3F(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3 \cdot nH2O$ (n ~ 25) (Ferey et al., 2005). The ease of synthesis and the exceptional stability, as well as the reactivity of this system, makes it a promising research object for many catalytic reactions (Bromberg, Diao, Wu, Speakman, Hatton, 2012). Interesting observations regarding MIL-100 have been made by Khan et al. (Khan, Lee, Jen, Jun, Jhung, 2012). They found that the MIL-100, in the network of which an aluminum atom is located, can transform into other structures – MIL-96 and MIL-110 – which allows the obtaining of equal structures from one reaction mixture depending on the time of crystallisation and the method of heating.

Another structure from this family worthy of attention is MIL-125 with the general formula $Ti_8O_8(OH)_4\text{-}(O_2C\text{-}C_6H_4\text{-}CO_2)_6$, consisting of titanium oxohydroxy clusters and dicarboxylic linkers (Dan-Hardi et al., 2009). Prior to the synthesis of this system, the introduction of titanium into porous compounds was limited to the exchange of silicon in zeolites and the formation of phosphates or diphosphates with limited porosity. This compound primarily offers the opportunity to customise its use in various fields, e.g., photonic devices, sensors or in catalysis.

Further structures belonging to this group were presented by Barthelet et al. (Barhelet, Riou, Ferey, 2002; Barhelet, Marrot, Riou, Ferey, 2002), and they are based on vanadium III or IV dicarboxylates. The first of these is MIL-59 containing vanadium octahedral trimmers with the formula $[V^{III}(H_2O)]_3O(O_2CC_6H_4CO_2)_3 \cdot (Cl, 9H_2O)$. The other structure is MIL-47 with the formula $V^{IV}O\{O_2C\text{-}C_6H_4\text{-}CO_2\}$.

The last structure worth mentioning is the first synthesised system containing chromium – MIL-53 (Serre et al., 2002). This deserves attention due to its magnetic properties, high thermal stability, and promising sorption abilities.

3. Synthesis of MOFs

Over the past thirty years, the production of MOFs has aroused great interest in many research groups due to the possibility of synthesising many different structures with the desired parameters, and due to the wide range of applications of such systems, for example, in sorption, catalysis and even in medicine (Stock, Biswas, 2012).

An important aspect of MOF synthesis is the selection of an appropriate method. The chosen method affects not only both the size and morphology of the structure but also the reaction time and its efficiency. The choice of synthesis methods is broad and includes synthesis at room temperature, synthesis with electric or microwave heating, electrochemistry, mechanochemistry, as well as synthesis using the ultrasonic method (Fig. 6). Most syntheses are performed in the liquid phase (Dey, Kundu, Biswal, Mallick, Banerjee, 2014). The mixture is a salt with a selected metal, organic ligands, and a solvent. The selection of the right solvent for a specific reaction primarily affects thermodynamics and activation energy.

The traditional and simplest method of obtaining crystalline MOF structures is the slow evaporation method (Dey, Kundu, Biswal, Mallick, Banerjee, 2014; Halper, Do, Stork, Cohen 2006; Du, Li, Zhao, 2006). Its key advantage is the obtaining of a product without energy input (evaporation mainly at room temperature). The use of a solvent mixture has a positive effect on the solubility of individual components of the mixture and thus facilitates the evaporation of low boiling solvents (Yoo, Varela-Guerrero, Jeong, 2011). The great disadvantage of this method is the much longer crystallisation process time compared to other methods.

Another method for the synthesis of organometallic compounds is the solvothermal method, which also includes hydrothermal (in which water is

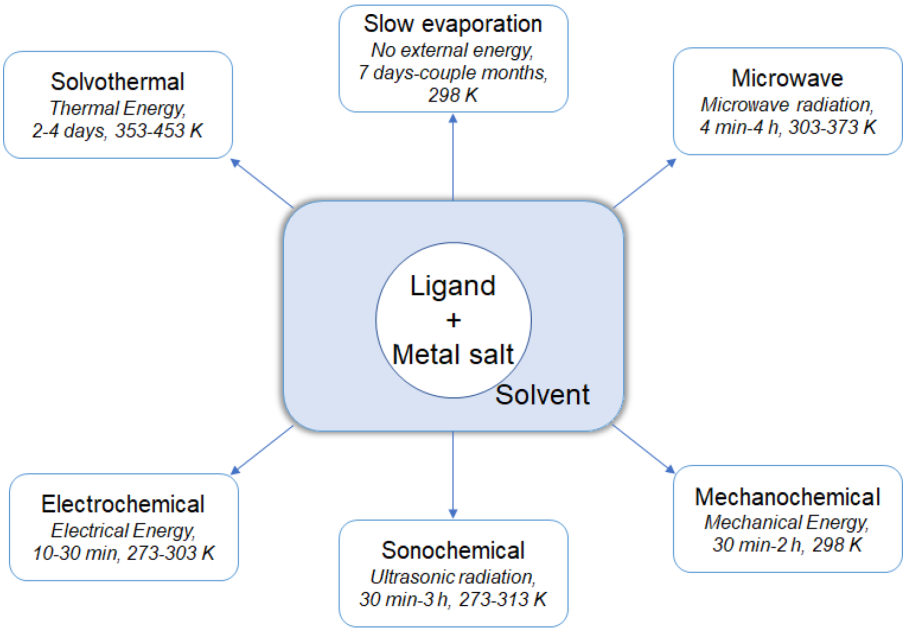

Fig. 6. Synthesis methods used in the preparation of organometallic structures together with reaction conditions (source: Dey, Kundu, Biswal, Mallick, Banerjee, 2014)

the solvent) and ionothermal (in which ionic liquid is the solvent) (Dey, Kundu, Biswal, Mallick, Banerjee, 2014; Banerjee, et al., 2011; Pachfule, Das, Poddar, Banerjee, 2011; Rowsell, Yaghi, 2004; Yaghi, Li, 1995; Morris, 2009; Parnham, Morris, 2007). This method is widely used and involves performing the process above the boiling point of the solvent in closed pressurised vessels. The time taken for this type of synthesis is significantly shorter than the time required for evaporation.

In the case of microwave-based MOF production, the synthesis is relatively fast (Klinowski, Paz, Silva, Rocha, 2011; Ni, Masel, 2006; Bux et al., 2009; Liang, D'Alessandro, 2013). It was named as 'solvothermal synthesis assisted by microflora' and allows obtaining nanocrystals. The quality of products obtained by this method does not differ significantly from those produced in the classic solvothermal process.

The next method for the synthesis of organometallic structures is the electrochemical method (Al-Kutubi, Gascon, Sudholter, Rassaei, 2014; Joaristi, Juan-Alcañiz, Serra-Crespo, Kapreijn, Gascon, 2012). This method has several advantages: 1) short reaction time, 2) controlled conditions, 3) relatively mild synthesis conditions. However, despite these advantages, this method is used relatively rarely. The occurrence of an electric field and side reactions have the greatest impact, although this has not been thoroughly studied.

The sonochemical method of obtaining MOF seems interesting due to the reduction of crystallisation time and the uniform nucleation of nanocrystals compared to classical methods (Son, Kim, Kim, Ahn, 2008; Jung, Yang, Kim, Kim, Ahn, 2010; Li et al., 2009). The general principle of sonochemical synthesis is the growth and bursting of bubbles that form in the liquid, which is called acoustic cavitation, the consequence of which is the local generation of high temperatures and high pressures. Such conditions favour chemical reactions and the formation of crystal nuclei. This method is also in line with current trends in conducting environmentally friendly processes.

The last of the synthesis methods belongs to solvent-free methods, the process of obtaining structures consists of a chemical reaction performed by applying mechanical force by, among other strategies, grinding and mixing ingredients, as a result of which this method is clean and energy-saving (Beldon et al., 2010; Tröbs, Wilke, Szczerba, Reinholz, Emmerling, 2014; Garay, Pichona, James, 2007; Friscic et al., 2010).

4. Application of MOFs

In recent years, the use of organometallic structures has received considerable interest from various research groups (Kuppler et al., 2009). This is due to the fact that structures of this type of porous system can be used in many areas, including gas storage and separation, selective catalysis as luminescent or fluorescent materials, and drug carriers.

The main application described in the literature is the storage of gases, particularly hydrogen, methane and carbon dioxide (Janiak, Vieth, 2010). It has been shown that the method of obtaining a given system and the manner of its activation have an influence on the adsorption capacity. The first research on the use of MOF for hydrogen storage was performed by Rosi et al. (Rosi et al., 2003). They described the adsorption analysis for the MOF-5 structure, which showed an adsorption capacity similar to carbon nanotubes. Due to the possibility of hydrogen storage in organometallic structures at room temperature, they have become the subject of very intensive research (Suh, Park, Prasad, Lim, 2012; Li, Yang, 2006: 8136–8137; Proch et al., 2008; Wong-Foy, Matzger, Yaghi, 2006). Attempts to use organometallic compounds as a storage medium for methane or carbon dioxide were trialled more than twenty years ago by Kondo et al. (Kondo, Yoshitomi, Seki, Matzuzaka, Kitagawa, 1997), and then they were continued with the use of various structures by other teams, for example, MOF-5 and IRMOF-6 mentioned earlier (Eddaoudi et al., 2002), and MOF-2, MOF-505 or MOF-74 at room temperature (Millward, Yaghi, 2005). An interesting review about that topic was written by Ma and Zhou in 2010, in which the organometallic structures were described as H_2, CO_2 and CH_4 adsorbents for clean energy applications (Ma, Zhou, 2010).

Catalysis is another field in which organometallic structures are studied extensively (Gascon, Corma, Kapteijn, Llabrés & Xanema, 2014). MOFs can act as catalysts in three main ways: 1) through metallic centres, 2) through ligands that contain organic groups, and 3) through space and the arrangement of pores. Some organometallic structures can catalyse chemical reactions immediately after synthesis, but unfortunately, many MOFs need to be modified after synthesis to adapt the system for use in catalytic reactions.

One of the first reports on the use of MOF-type structures as a catalyst was an article from 1994 by Fujita et al., in which the catalytic application of a 2D structure containing cadmium and 4,4'-bipyridine in the network was described (Fujita, Kwon, Washizu, Ogura, 1994). This material showed catalytic activity and shape selectivity. Research on this structure was continued, it has been confirmed that metallic centres embedded in the porous system network provide new opportunities for the design of catalysts at the molecular level (Ohmori, Fujita, 2004).

As with classic homogeneous catalysts, acid (which may be either Lewis or Brønsted) or basic centres play an important role in catalytic activity (Farrusseng, Aguado, Pinel, 2009). HKUST-1 containing copper metal is one of the carefully researched examples of structures with Lewis acid properties (Alaerts, 2006; Schlichte, 2004). The active centres have been characterised as Lewis acids through isomerisation reactions of α-pinene oxide and citronellal, as well as through the cyanosilylation of benzaldehyde. Catalytic tests and infrared analysis have shown that the HKUST-1 structure has numerous Lewis centres and virtually no Brønsted centres, but they are only available after heat treatment, which removes trapped water in the catalyst network. This catalyst is effective in the selective sulfoxidation reaction of aryl sulfides and may also become a catalyst for other oxidation reactions (Hwang et al., 2009).

In addition to the above, MOF structures from the MIL series, e.g. MIL-53, MIL-88, MIL-100 or MIL-101 have been tested extensively for Lewis centres and catalysis (Yuan et al., 2018). The aforementioned α-pinene oxide isomerisation reaction was performed on several types of catalysts, and especially those containing iron in the skeleton showed interesting catalytic properties of this reaction, the presence of Lewis acid centres was also confirmed (Dhakshinamoorthy et al., 2012). The catalytic abilities of MIL-100 (Fe) and MIL-101 structures have been thoroughly studied (Dhakshinamoorthy, Alvaro, Garcia, 2010: 8530–8536; Dhakshinamoorthy, Alvaro, Garcia, 2010: 711–717; Henschel, Gedrich, Kraehnert, Kaskel, 2008). In the case of the first system, iron atoms as active Lewis centres allow the epoxy ring-opening reaction to be performed in a regioselective manner and enable the reaction to obtain chalcones, i.e., Claisen-Schmidt condensation. In both of these reactions, the MIL-100 catalyst performance is improved in comparison to a classic iron-containing heterogeneous catalyst.

MIL-100 (Fe) and MIL-100 (Cr) have also been used in the Friedel-Crafts benzylation reaction. A very interesting property of these systems was detected, which, depending on the treatment, may show Lewis centre activity (after temperature activation and the removal of bound water in the structure) or Brønsted centres (after attachment of OH groups under the influence of water or alcohol) (Vimont et al., 2007; Vimont et al., 2006; Horcajada et al., 2007). The structure of MIL-101 (Cr) has been studied, inter alia, in the cyanosilylation reaction, cyclic carbonate synthesis, or tetralin oxidation (Henschel, Gedrich, Kraehnert, Kaskel, 2008; Zalomaeva et al., 2013; Kim, Bhattacharjee, Jeong, Jeong, Ahn, 2009). In all cases, the use of this type of catalyst has resulted in high reaction yields.

Another interesting structure that, due to its chemical stability, has been proposed as a catalyst is UiO-66 (Vermoortele, Ameloot, Vimont, Serrec, De Vos, 2011; Vermoortele et al., 2012; Vermoortele et al., 2013; Lammert et al., 2015). Its catalytic activity and the possibilities of its increase have been thoroughly studied by the team of Vermoortele et al. This structure has proven itself as a catalyst in, inter alia, the aldol condensation reaction between benzaldehyde and heptanal and in the oxidation of benzyl alcohol.

The numerous publications on this topic have recently been summarised by Kang et al. (Kang et al., 2019) and by Hall and Bollini (Hall, Bollini, 2019). The first mentioned publication described in detail the reactions that were performed using MOF as a catalyst. These are, inter alia, cyanosilylation reactions [e.g. $Cu_3(BTC)_2$, $Mn_3[(Mn_4Cl)_3(\text{-}BTT)_8(CH_3OH)_{10}]_2$], transesterification [e.g. Zn-MOF], condensation [e.g. Fe(BTC), Ba-MOF, Mg-MOF, UiO-66], ring-opening [e.g. $Cu_2(5,5'\text{-}BDA)_2(H_2O)_2]\bullet MeOH\bullet 2H_2O$, Zn-MOF, Co/Zn-MOF], Friedel-Crafts reaction [e.g. Cu-MOF-74, UiO-66–SO_3H] and cycloaddition [e.g. $Ag_2(L)_2(CF_3CO_2)_2$, $Cu_2(S)\text{-}L)_2(H_2O)_2$]. Reactions catalysed by metal in MOF structure are also described, these are CO_2 conversions [UiO-67, $Zn_4O[Cu(NHC)_2]_2$], reductions [e.g. Zr(Ti)–NDC MOF, Mg–IRMOF-74], oxidation [$Sc_2(C_8H_4O_4)_3$, MIL-100(Fe), MIL-101(Fe)], and cross-coupling [e.g. Pd–MOF, Cu–MOF]. It has been described that the active sites in the MOF catalyst can occur both on the metallic part and in the organic ligand, in which, due to the diversity of functional groups, the sites may have an acidic or basic character. The coexistence of acidic and basic sites diversity provides an opportunity for the multitude of catalysed reactions.

Hall and Bollini (Hall, Bollini, 2019) focused more on the description of the relationship between the structure and properties of MOFs, as well as the formation of ‘an open metal site’, wherein the removal of the labile ligand during thermal treatment enables the creation of a catalytically active site. They presented four MOF structures, MIL-100, MIL-101, Cu-BTC and UiO-66, combining carboxyl bridge nodes with metallic clusters and labile ligands. The authors were unable to clearly state the structure-properties relationship, where the open metal sites would significantly affect its catalytic properties. Therefore, research into understanding the catalytic mechanisms occurring on MOF structures requires further development and detailed interpretation.

5. Modeling and design of MOFs

The discovery and design of catalysts ideally suited to a given reaction became the foundation of modern chemistry (Bernales, Ortuño, Truhlar, Cramer, Gagliardi, 2018). For this purpose, computational methods and molecular modelling are used. These types of design techniques allow both the determination of the structure and characteristics of a given catalyst and the accurate definition of individual atoms, clusters and the interactions between them. Modelling catalysis using MOFs is, however, a much bigger challenge than classical heterogeneous catalysis. This is due to the fact that in the case of MOFs, the essence of the catalyst is not only the local catalytic site but also the entire structure and its impact on local as well as long-range interactions, and thus also on reactivity and selectivity. The main tool that allows studying the catalyst in the reaction and its course is the Kohn-Sham density functional theory (KS-DFT) (Kohn, Becke, Parr, 1996).

The modeling of MOF structures dedicated to catalysis assumes four main goals: 1) structure characteristics and the possibility of its modification after the synthesis stage and the impact of these factors on reactivity; 2) understanding energy and dynamics of catalytically active sites; 3) understanding and describing functional relationships within the structure; 4) the design of completely new materials with desirable catalytic properties (Bernales, Ortuño, Truhlar, Cramer, Gagliardi, 2018). Classical molecular mechanics methods are adequate and accurate for achieving the first goal, i.e. structure characteristics (Getman, Bae, Wilmer, Snurr, 2012; Fang, Demir, Kamakoti, Sholl, 2014). More advanced molecular modeling calculations (e.g. DFT) that are able to analyse the creation of new bonds are necessary for achieving goals 2-4 (Odoh, Cramer, Truhlar, Gagliardi, 2015; Coudert, Fuchs, 2016; Evans et al., 2017).

Up until now, there have been two approaches in the context of designing MOFs with specific properties (Odoh, Cramer, Truhlar, Gagliardi, 2015). The first of these is, for the most part, concerned with experimental tests based on crystal research (Yaghi et al., 2003; Eddaoudi et al., 2002; Ferey, 2008; Eddaoudi et al., 2001; Dinca, Yu, Long, 2006; Burnett, Barron, Hu, Choe, 2011; Farha, Hupp, 2010; Lee, Kim, Ahn, 2013; Sabo, Henschel, Frode, Kemm, Kaskel, 2007). The designed and synthesised crystal was analysed for gas adsorption, storage and separation, and only then in the context of applications in catalysis. This approach allowed great insights into MOFs, but it has proven to be costly and time intensive. The second alternative approach relies on designing MOF structures based on certain predictions of how metals, metal oxides or organic ligands can combine with each other (Martin, Lin, Jariwala, Smit, Haranczyk, 2013; Farrusseng et al., 2009; Frost, Snurr, 2007; Wilmer et al., 2012; First, Floudas, 2013). Such predictions result in the formation of huge libraries with potential systems in which their properties are analysed computationally, including pore size or volume, stability, the presence of unsaturated metallic centres or efficiency and selectivity regarding gas sorption. Structures designed and characterised in this way can be synthesised experimentally and then characterised to confirm the calculated properties. An example of a system that was first planned and described by molecular calculations is NU-100 (Farhaet al., 2010). After synthesising this relationship, it turned out that the computational data converged with the experimental data.

In order to design and analyse both the MOF morphology itself and subsequent adsorption or reaction involving a given structure, it is necessary to choose the appropriate calculation method. According to the generally accepted principles of molecular modelling, a balance must be found between the accuracy of the calculations and the duration of these calculations. The Evans research group (Evans et al., 2017) way described the structure, physical and chemical properties very comprehensively using various computational methods.

The problem of computational accuracy, particularly for systems containing transition metals, can be described by two aspects: 1) the accuracy of the method chosen to determine the electronic structure of a given system, and 2) the accuracy or quality of the chemical model that is used to explain the phenomena associated with the properties of the system (Vogiatzis et al., 2019). A large number of MOF structures bound with transition metals exhibit catalytic properties. Looking at the complexity of such structures in catalytic systems in both chemical and electronic terms, it is practically impossible to adjust the method and model in such a way that they perfectly reflect reality. Therefore, all relationship models are based on certain approximations and simplifications. This type of approximation includes a selection of the density functional for the DFT method, the level of correlation used in the Hartree-Fock method, and the size or type of a set of function bases.

The most widely used computational technique in heterogeneous catalysis is the density functional theory (DFT). This method has been very precisely described in terms of its theory and applications in many scientific articles (Seminario, 1995; Nørskov, Abild-Pedersen, Studt, Bligaard, 2011; Cohen, Mori-Sanchez, Yang, 2012; Becke, 2014; Cramer, Truhlat, 2009). The basis of the DFT method are two Hohenberg theorems. The first states that the ground state energy is determined by the electron density. The second theorem states that if the exact electron density is known, the calculated energy is equal to or higher than real energy (Hohenberg, Kohn, 1964). The method using the self--agreed field theory (SCF) was introduced by Kohn and Sham and it forms the basis of the current KS-DFT (Kohn, Sham, 1965).

As mentioned earlier, at the beginning of the development of the branch of chemistry associated with MOF structures, these systems were synthesised and then studied. However, the development and the growing interest in this type of structure meant that many MOFs that are popular today also received theoretical analysis using computational methods.

In the case of the MOF-5 structure, bond lengths, angles between these bonds (Mattesini, Soler, Yndurāin, 2006), parameters determining the crystal lattice and the position of atoms in this lattice (Samanta, Furuta, Li, 2006) were calculated to a very high level of accuracy. Mattesini et al. proved that despite the assumption that the MOF-5 structure should be rigid, it behaves like soft, plastic material, as illustrated by its Young's modulus, the value of which is comparable to the modulus of oak. Subsequent theoretical studies of MOF-5 particularly concerned its sorption and storage properties for hydrogen molecules (Samanta, Furuta, Li, 2006; Sagara, Klassen, Ganz, 2005; Mueller, Ceder, 2005). Samanta et al. performed calculations to determine the most energy-efficient place in the MOF-5 structure for the hydrogen adsorption process in their publication in addition to confirming the experimentally obtained structural data. Four possible positions for the hydrogen molecule were depicted: near the benzene ring perpendicularly; parallel to the ring; near the zinc atom perpendicular to one of the oxygen atoms in the organic linker, at a distance from the metallic centre. The location of the hydrogen molecule near the metal fragment containing zinc atoms showed the lowest adsorption energy. This confirms the results of the experiment presented earlier by T. Muller and G. Ceder, who proved the existence of twenty adsorption sites near the Zn_4O cluster with sixteen places filled with a hydrogen molecule (after filling, the storage activity for the metal cluster was dropped). In addition, theoretical studies were performed in which alkaline metals (Li, Na, K) (Ha, Lefedova, Ha, 2016) and transition metals (Fe, Co, Ni, Cu, Zn) (Venkataramanan, Sahara, Mizuseki, Kawazoe, 2009) were introduced into the MOF-5 structure, which stabilised in the middle of the benzene ring of the organic linker. The addition of these metals had a positive effect on MOF-5 adsorption properties.

The structure of HKUST-1 (Cu-BTC) described earlier was also compared with regard to experimental and theoretical findings. Zhao et al. performed an analysis of HKUST-1 structural parameters, vibration frequency, and a selected process of adsorption of a CO_2 molecule in a new force field (Zhao et al., 2011). The calculations were in agreement with the experimental data, which showed that HKUST-1 is a less flexible structure than MOF-5, and additionally, it has good adsorption properties. Calculations related to adsorption and using a force field opened up the possibilities of theoretical research for other types of MOF structures. Lukose et al., in his calculations, presented two types of models: cluster and periodic (Lukose et al., 2012). The calculated bond lengths, bond angles and basic unit cell parameters in both models coincide well with the data obtained experimentally. It was also found that the cluster model is good for studying catalytic and adsorption properties. An aspect regarding the structural properties of HKUST-1 was also studied – the formation of structure derivatives by changing the organic linker from BTC to BTC with additional functional groups: methyl, methoxy, nitro, ethyl, bromine and acetamide (Cai, Kulkarni, Huang, Sholl, Walton, 2014). First of all, after the introduction of functional groups, the calculations showed a decrease in the accessible surface area of the examined structure compared to the base version of Cu-BTC without a functional group. Additionally, these studies showed that the introduction of the functional group can change the topology of the crystal structure, which enables the design of structures with specific desired topologies and properties. Theoretical studies were also conducted regarding the adsorption of various molecules by the HKUST-1 structure. Supronowicz et al. investigated several small gas molecules important in environmental processes (Supronowicz, Mavrandonakis, Heine, 2013). For this purpose, interaction and adsorption energies and the vibration frequency of adsorbed particles were calculated. It has been demonstrated that primarily the interaction with the metal centre is more intense than the organic ligand. It was also determined that these interactions can be divided into three categories: 1) weak physisorption, 2) polarising and electrostatic interactions, and 3) strong acid-base interactions. Adsorption of CO_2 was also studied in detail on the HKUST-1 bimetallic structure formed by exchanging one of the copper atoms with another metal (Dong, Liu, Chen, Zhang, 2018). The two structures which showed the best properties were Mo-Cu-BTC and W-Cu-BTC, which can additionally be used as CO_2 hydrogenation catalysts. Interesting studies have also been conducted in the context of toxic gas capture by structure HKUST-1 (Zong et al., 2018). The adsorption of NO, NO_2 and NH_3 was analysed, and the structure was modified by exchanging copper atoms in Cu-BTC for other metal atoms. A total of nineteen structures were tested and three showed particularly good adsorption properties: Ti-HKUST-1, Sn-HKUST-1 and Be-HKUST-1.

Other structures of MOF were also investigated using computational methods. The structure of UiO-66 mentioned earlier was tested, inter alia, for the adsorption of ammonia (Phikulthai et al., 2017) both on the basic structure and modified with a sulfone group. Furthermore, the structure of MIL-101 was studied both in terms of structure modification (e.g. with aluminum atoms or NH_2 group) (Sugimoto, Mizushima, Okamoto, Kurita, 2014; Goesten et al., 2014), and as a catalyst in the cyanosilylation reactions of aldehydes (Oliveira, Mavrandonakis, de Lima, De Abreu, 2017).

As visible from the results presented in the literature, examples of theoretical studies for MOF structures show that the potential of these materials is almost unlimited, and determining their potential applications constitutes an enormous field of research for scientists.

6. Conclusion

Only a few MOF groups and their members are listed above. However, recent advances in the development and characterisation of new structures based on computer modelling allow virtually unlimited possibilities to design MOF structures with the desired properties for various applications. Research on MOFs as catalysts has been particularly active and will probably continue to be of great interest to research teams from various fields of chemistry.

References

Abrahams, B.F., Hoskins, B.F., Michail, D.M., Robson, R. (1994). Assembly of porphyrin building blocks into network structures with large channels. *Nature*, *369*, 727–729. https://doi.org/10.1038/369727a0

Alaerts, L., Seguin, E., Poelman, H., Thibault-Starzyk, F., Jacobs, P.A., De Vos, D.E. (2006). Probing the Lewis Acidity and Catalytic Activity of the Metal–Organic Framework [Cu_3 $(btc)_2$] (BTC=Benzene-1,3,5-tricarboxylate). *Chemistry. A European Jurnal*, *12*, 7353–7363. https://doi.org/10.1002/chem.200600220

Al-Kutubi, H., Gascon, J., Sudholter, E.J.R., Rassaei, L. (2014). Electrosynthesis of Metal–Organic Frameworks: Challenges and Opportunities. *Chemelektrochem*, *2*, 462–474. https://doi.org/10.1002/celc.201402429

Banerjee, D., Finkelstein, J., Smirnov, A., Forster, P.M., Borkowski, L.A., Teat, S.J., Parise, J.B. (2011). Synthesis and Structural Characterization of Magnesium Based Coordination Networks in Different Solvents. *Crystal Growth & Design*, *11*(6), 2572–2579. http://doi.org/10.1021/cg200327y

Barthelet, K., Marrot, J., Riou, D., Ferey, G. (2002). A Breathing Hybrid Organic Inorganic Solid with Very Large Pores and High Magnetic Characteristics. *Angewandte Chemie International Edition*, 41(2), 281–284. https://doi.org/10.1002/1521-3773(20020118)41:2<281::AID-ANIE281>3.0.CO;2-Y

Barthelet, K., Riou, D., Férey, G. (2002). $[VIII(H_2O)]_3O(O_2CC_6H_4CO_2)_3$•$(Cl,9H_2O)$ (MIL-59): a rare example of vanadocarboxylate with a magnetically frustrated three-dimensional hybrid framework. *Chemical Communications*, (14), 1492–1493. https://doi.org/10.1039/B202749F

Becke, A.D., (2014). Perspective: Fifty years of density-functional theory in chemical physics. *The Journal of Chemical Physics*, *140*(18), 18A301. https://doi.org/10.1063/1.4869598

Beldon, P.J., Fabian, L., Stein, R.S, Thirumurugan, A., Cheetham, A.K., Fricic, T. (2010). Rapid Room-Temperature Synthesis of Zeolitic Imidazolate Frameworks by Using Mechanochemistry. *Angewandte Chemie International Edition*, *49*, 9640–9643. https://doi.org/10.1002/anie.201005547

Bernales, V., Ortuño, M.A., Truhlar, D.G., C. J. Cramer, C.J., Gagliardi, L. (2018). Computational Design of Functionalized Metal-Organic Framework Nodes for Catalysis. *ACS Central Science*, *4*(1), 5–19. https://doi.org/10.1021/acscentsci.7b00500

Bosch, M., Zhang, M., Zhou, H-C. (2014). Increasing the Stability of Metal-Organic Frameworks. *Advances in Chemistry*, *2014*, 1–8. https://doi.org/10.1155/2014/182327

Bromberg, L., Diao, Y., Wu, H., Speakman, S.A., Hatton, T.A. (2012). Chromium(III) Terephthalate Metal Organic Framework (MIL-101): HF-Free Synthesis, Structure, Polyoxometalate Composites, and Catalytic Properties. *Chemistry of Materials*, *24*(9), 1664–1675. https://doi.org/10.1021/cm2034382

Burnett, B.J., Barron, P.M., Hu, C., Choe, W. (2011). Stepwise Synthesis of Metal--Organic Frameworks: Replacement of Structural Organic Linkers. *Journal of the American Chemical Society*, *133*(26), 9984–9987. https://doi.org/10.1021/ja201911v

Bux, H., Liang, F., Li, Y., Cravillon, J., Wiebcke, M., Caro, J. (2009). Zeolitic Imidazolate Framework Membrane with Molecular Sieving Properties by Microwave--Assisted Solvothermal Synthesis. *Journal of the American Chemical Society*, *131*(44), 16000–16001. https://doi.org/10.1021/ja907359t

Cai, Y., Kulkarni, A.R., Huang, Y-G., Sholl, D.S., Walton, K.S., (2014). Control of Metal--Organic Framework Crystal Topology by Ligand Functionalization: Functionalized HKUST-1 Derivatives. *Crystal Growth & Design*, *14*, 6122–6128. https://doi.org/10.1021/cg501285q

CCDC. Access Structure. Retrieved form https://www.ccdc.cam.ac.uk/structures/ (date of access: 2020/03/19).

Chen, B., Ockwig, N.W., Millward, A.R., Contreras, D.S., Yaghi, O.M. (2005). High H_2 Adsorption in a Microporous Metal-Organic Framework with Open Metal Sites. *Angewandte Chemie International Edition*, *44*, 4745–4749. https://doi.org/10.1002/anie.200462787

Chizallet, C., Lazare, S., Bazer-Bachi, D., Bonnier, F., Lecocq, V., Soyer, E., Quoineaud, A.A., Bats, N. (2010). Catalysis of Transesterification by a Nonfunctionalized Metal-Organic Framework: Acido-Basicity at the External Surface of ZIF-8 Probed by FTIR and ab Initio Calculations. *Journal of the American Chemical Society*, *132*(35), 12365–12377. https://doi.org/10.1021/ja103365s

Chui, S. S-Y., Lo, S. M-F., Charmant, J.P.H., Orpen, A.G., Williams, I.D. (1999). A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H_2O)_3]n$. *Science*, *283*, 1148–1150. https://doi.org/10.1126/science.283.5405.1148

Cohen, A.J., Mori-Sanchez, P., Yang, W. (2012). Challenges for Density Functional Theory. *Chemical Reviews*, *112*(1), 289–320. https://doi.org/10.1021/cr200107z

Coudert, F.X., Fuchs, A.H. (2016). Computational characterization and prediction of metal-organic framework properties. *Coordination Chemistry Reviews*, *307*, 211–236. https://doi.org/10.1016/j.ccr.2015.08.001

Cramer, C.J., Truhlar, D.G. (2009). Density functional theory for transition metals and transition metal chemistry. *Physical Chemistry Chemical Physics*, *11*, 10757–10816. https://doi.org/10.1039/B907148B

Dan-Hardi, M., Serre, C., Frot, T., Rozes, L., Maurin, G., Sanchez, C., Ferey, G. (2009). A New Photoactive Crystalline Highly Porous Titanium(IV) Dicarboxylate. *Journal of the American Chemical Society*, *131*(31), 10857–10859. https://doi.org/10.1021/ja903726m

DeCoste, J.B., Demasky, T.J., Katz, M.J., Farha, O.K., Hupp, J.T. (2015). A UiO--66 analogue with uncoordinated carboxylic acids for the broad-spectrum removal of toxic chemicals. *New Journal of Chemistr*, *39*, 2396–2399. https://doi.org/10.1039/C4NJ02093F

Dey, C., Kundu, T., Biswal, B.P., Mallick, A., Banerjee, R. (2014). Crystalline metal-organic frameworks (MOFs): synthesis, structure and function. *Acta Crystallographica Section B*, *70*, 3–10. https://doi.org/10.1107/S2052520613029557

Dhakshinamoorthy, A., Alvaro, M., Chevreau, H., Horcajada, P., Devic, T., Serre, C., Garcia, H. (2012). Iron(III) metal-organic frameworks as solid Lewis acids for the isomerization of α-pinene oxide. *Catalysis Science Technology*, *2*, 324–330. https://doi.org/10.1039/C2CY00376G

Dhakshinamoorthy, A., Alvaro, M., Garcia, H. (2010). Claisen-Schmidt Condensation Catalyzed by Metal-Organic Frameworks. *Advanced Synthesis & Catalysis*, *352*, 711–717. https://doi.org/10.1002/adsc.200900747

Dhakshinamoorthy, A., Alvaro, M., Garcia, H. (2010). Metal-Organic Frameworks as Efficient Heterogeneous Catalysts for the Regioselective Ring Opening o Epoxides. *Chemistry A European Journal*, *16*, 8530–8536. https://doi.org/10.1002/chem.201000588

Dinca, M., Yu, A.F., Long, J.R., (2006). Microporous Metal-Organic Frameworks Incorporating 1,4-Benzeneditetrazolate: Syntheses, Structures, and Hydrogen Storage Properties [J. Am. Chem. Soc. 2006, 128, 8904–8913]. *Journal of the American Chemical Society*, *128*(51), 17153–17153. https://doi.org/10.1021/ja068019a

Dong, X., Liu, X., Chen, Y., Zhang, M. (2018). Screening of bimetallic M-Cu-BTC MOFs for CO_2 activation and mechanistic study of CO_2 hydrogenation to formic acid: A DFT study. *Journal of CO_2 Utilization*, *24*, 64–72. https://doi.org/10.1016/j.jcou.2017.11.014

Du, M., Li, C.P., Zhao, X.J. (2006). Metal-Controlled Assembly of Coordination Polymers with the Flexible Building Block 4-Pyridylacetic Acid (Hpya). *Crystal Growth & Design*, *6*(1), 335–341. https://doi.org/10.1021/cg0502542

Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M., Yaghi, M.O. (2002). Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science*, *295*, 469–472. https://doi.org/10.1126/science.1067208

Eddaoudi, M., Moler, D.B., Li, H., Chen, B., Reineke, T.M., O'Keeffe, M., Yaghi, O.M., (2001). Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Accounts of Chemical Research*, *34*(4), 319–330. https://doi.org/10.1021/ar000034b

Evans, J.D., Fraux, G., Gaillac, R., Kohen, D., Trousselet, F., Vanson, J.M., Coudert, F.X. (2017). Computational Chemistry Methods for Nanoporous Materials. *Chemistry of Materials*, *29*(1), 199–212. https://doi.org/10.1021/acs.chemmater.6b02994

Fang, H., Demir, H., Kamakoti, P., Sholl, D.S., (2014). Recent developments in first--principles force fields for molecules in nanoporous materials. *Journal of Materials Chemistry A*, *2*, 274–291. https://doi.org/10.1039/C3TA13073H

Farha, O.K., Hupp, J.T. (2010). Rational Design, Synthesis, Purification, and Activation of Metal-Organic Framework Materials. *Accounts Of Chemical Research*, *43*(8), 1166–1175. https://doi.org/10.1021/ar1000617

Farha, O.K., Yazaydın, A.O., Eryazici, I., Malliakas, C.D., Hauser, B.G., Kanatzidis, M.G., Nguyen, S.T., Snurr, R.Q., Hupp, J.T. (2010). De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities. *Nature Chemistry*, *2*, 944–948. https://doi.org/10.1038/nchem.834

Farrusseng, D., Aguado, S., Pinel, C. (2009). Metal-Organic Frameworks: Opportunities for Catalysis. *Angewandte Chemie International Edition*, *48*, 7502–7513. https://doi.org/10.1002/anie.200806063

Farrusseng, D., Daniel, C., Gaudillere, C., Ravon, U., Schuurman, Y., Mirodatos, C., Dubbeldam, D., Frost, H., Snurr, R.Q. (2009). Heats of Adsorption for Seven Gases in Three Metal-Organic Frameworks: Systematic Comparison of Experiment and Simulation. *Langmuir*, *25*(13), 7383–7388. https://doi.org/10.1021/la900283t

Ferey, G. (2008). Hybrid porous solids: past, present, future. *Chemical Society Reviews*, *37*, 191–214. https://doi.org/10.1039/B618320B

Ferey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble, S., Margiolaki, I., (2005). A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. *Science*, *309*, 2040–2042. https://doi.org/10.1126/science.1116275

Ferey, G., Serre, C., Mellot-Draznieks, C., Millange, F., Surble, S., Dutour, J., Margiolaki, I. (2004). A Hybrid Solid with Giant Pores Prepared by a Combination of Targeted Chemistry, Simulation, and Powder Diffraction. *Angewandte Chemie International Edition*, *43*, 6296–6301. https://doi.org/10.1002/anie.200460592

First, E.L., Floudas, C.A. (2013). MOFomics: Computational pore characterization of metal-organic frameworks. *Microporous and Mesoporous Materials*, *2013*(165), 32–39. https://doi.org/10.1016/j.micromeso.2012.07.049

Friscic, T., Reid, D.G., Halasz, I., Stein, R.S., Dinnebier, R.E., Duer, M.J. (2010). Ion- and Liquid-Assisted Grinding: Improved Mechanochemical Synthesis of Metal-Organic Frameworks Reveals Salt Inclusion and Anion Templating. *Angewandte Chemie International Edition*, *49*, 712–715. https://doi.org/10.1002/anie.200906583

Frost, H., Snurr, R.Q. (2007). Design Requirements for Metal-Organic Frameworks as Hydrogen Storage Materials. *The Journal of Physical Chemistry C*, *111*(50), 18794–18803. https://doi.org/10.1021/jp076657p

Fujita, M., Kwon, Y.J., Washizu, S., Ogura, K. (1994). Preparation, Clathration Ability, and Catalysis of a Two-Dimensional Square Network Material Composed of Cadmium(II) and 4,4'-Bipyridine. *Journal of the American Chemical Society*, *116*(3), 1151–115. https://doi.org/10.1021/ja00082a055

Garay, A.L., Pichona, A., James, S.L. (2007). Solvent-free synthesis of metal complexes. *Chemical Society Reviews*, *36*, 846–855. https://doi.org/10.1039/b600363j

Gascon, J., Corma, A., Kapteijn, F., Llabrés i Xanema, F.X. (2014). Metal Organic Framework Catalysis: Quo vadis? *ACS Catalysis*, *4*(2), 361–378. https://doi.org/10.1021/cs400959k

Getman, R.B., Bae, Y.S., Wilmer, C.E., Snurr, R.Q. (2012). Review and Analysis of Molecular Simulations of Methane, Hydrogen, and Acetylene Storage in Metal-Organic Frameworks. *Chemical Reviews*, *112*(2), 703–723. https://doi.org/10.1021/cr200217c

Goesten, M.G., Magusin, P.C.M.M., Pidko, E.A., Mezari, B., Hensen, E.J.M., Kapteijn, F., Gascon, J. (2014). Molecular Promoting of Aluminum Metal-Organic Framework Topology MIL-101 by N,N-Dimethylformamide. *Inorganic Chemistry*, *53*(2), 882–887. https://doi.org/10.1021/ic402198a

Ha, N.T.T., Lefedova, O.V., Ha, N.N. (2016). Theoretical Study on the Adsorption of Carbon Dioxide on Individual and Alkali-Metal Doped MOF-5s. *Russian Journal of Physical Chemistry A*, *90*, 220–225. https://doi.org/10.1134/S0036024415120201

Hall, J.N., Bollini, P., (2019). Structure, characterization, and catalytic properties of open-metal sites in metal organic frameworks. *Reaction Chemistry Engineering*, *4*, 207–222. https://doi.org/10.1039/C8RE00228B

Halper, S.R., Do, L., Stork, J.R., Cohen, S.M. (2006). Topological Control in Heterometallic Metal-Organic Frameworks by Anion Templating and Metalloligand Design. *Journal of the American Chemical Society*, *128*(47), 15255–15268. https://doi.org/10.1021/ja0645483

Hayashi, H., Côté, A.P., Furukawa, H., O'Keeffe, M., Yaghi, O.M., (2007). Zeolite A imidazolate frameworks. *Nature Materials*, *6*, 501–506. https://doi.org/10.1038/nmat1927

Hendona, C.H., Walsh, A, (2015). A Chemically Functionalizable Nanoporous Material $[Cu_3(TMA)_2(H_2O)_3]n$. *Chemical Science*, *6*, 3674–3683. https://doi.org/10.1039/C5SC01489A

Henschel, A., Gedrich, K., Kraehnert, R., Kaskel, S. (2008). Catalytic properties of MIL-101. *Chemical Communications*, (35), 4192–4194. https://doi.org/10.1039/B718371B

Hoffmann, F., Fröba, M. (2016). Network Topology. In S. Keskel (Ed.), *The Chemistry of Metal-Organic Frameworks*, (p. 5-38). Weinheim, Germany.

Hohenberg, P., Kohn, W. (1964). Inhomogeneous Electron Gas. *Physical Review*, *136*, B864. https://doi.org/10.1103/PhysRev.136.B864

Horcajada, P., Surble, S., Serre, C., Hong, D.Y., Seo, Y.K., Chang, J.S., Greneche, J.M., Margiolaki, I., Ferey, G. (2007). Synthesis and catalytic properties of MIL-100(Fe), an iron(III) carboxylate with large pores. *Chemical Communications*, (27), 2820–2822. https://doi.org/10.1039/B704325B

Hoskins, B.F., Robson, R. (1990). Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks $[N(CH3)_4][CuIZnII(CN)_4]$ and CuI[4,4',4'',4'''-tetracyanotetraphenylmethane] $BF_4{\bullet}xC_6H_5NO_2$. *Journal of the American Chemical Society*, *112*(4), 1546–1554. https://doi.org/10.1021/ja00160a038

Hupp, J.T., Poeppelmeier, K.R. (2005), Better Living Through Nanopore Chemistry. *Science*, *2005*(309), 2008–2009. https://doi.org/10.1126/science.1117808

Hwang, Y.K., Hong, D.Y., Chang, J.S., Jhung, S.H., Seo, Y.K., Kim, J., Vimont, A., Daturi, M., Serre C., Ferey, G. (2008). Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation. *Angewandte Chemie International Edition*, *47*, 4144–4148. https://doi.org/10.1002/anie.200705998

Hwang, Y.K., Hong, D.Y., Chang, J.S., Seo, H., Yoon, M., Kim, J., Jhung, S.H., Serre, C., Ferey, G. (2009). Selective sulfoxidation of aryl sulfides by coordinatively unsaturated metal centers in chromium carboxylate MIL-101. *Applied Catalysis A: General*, *358*, 249–253. https://doi.org/10.1016/j.apcata.2009.02.018

Janiak, C., Vieth, J.K. (2010). MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs). *New Journal of Chemistry*, *34*, 2366–2388. https://doi.org/10.1039/C0NJ00275E

Joaristi, A.M., Juan-Alcañiz, J., Serra-Crespo, P., Kapteijn, F., Gascon, J. (2012). Electrochemical Synthesis of Some Archetypical Zn^{2+}, Cu^{2+}, and Al^{3+} Metal Organic Frameworks. *Crystal Growth & Design*, *12*(7), 3489–3498. https://doi.org/10.1021/cg300552w

Jung, D.W., Yang, D.A., Kim, J., Kim, J., Ahn, W.S. (2010). Facile synthesis of MOF-177 by a sonochemical method using 1-methyl-2-pyrrolidinone as a solvent. *Dalton Transactions*, *39*, 2883–2887. https://doi.org/10.1039/b925088c

Kang, Y.S., Lu, Y., Chen, K., Zhao, Y., Wang, P., Sun, W.Y. (2019). Metal-organic frameworks with catalytic centers: From synthesis to catalytic application. *Coordination Chemistry Reviews*, *378*, 262–280. https://doi.org/10.1016/j.ccr.2018.02.009

Kaye, S.S., Long, J.R. (2008). Matrix Isolation Chemistry in a Porous Metal-Organic Framework: Photochemical Substitutions of N_2 and H_2 in $Zn_4O[(\eta 6\text{-}1,4\text{-Benzenedicarboxylate})Cr(CO)_3]_3$. *Journal of the American Chemical Society*, *130*, 806–807. https://doi.org/10.1021/ja7102108

Khan, N.A., Lee, J.S., Jeon, J., Jun, C.H., Jhung, S.H. (2012). Phase-selective synthesis and phase-conversion of porous aluminum-benzenetricarboxylates with microwave irradiation. *Microporous and Mesoporous Materials*, *152*, 235–239. https://doi.org/10.1016/j.micromeso.2011.11.025

Kim, J., Bhattacharjee, S., Jeong, K.E., Jeong, S.Y., Ahn, W.S. (2009). Selective oxidation of tetralin over a chromium terephthalate metal organic framework, MIL-101. *Chemical Communications*, (26), 3904–3906. https://doi.org/10.1039/B902699A

Kitagawa, S., Kondo, M. (1998). Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds. *Bulletin of the Chemical Society of Japan*, *71*, 1739–1753. https://doi.org/10.1246/bcsj.71.1739

Klinowski, J., Paz, F.A.A., Silva, P., Rocha, J. (2011). Microwave-Assisted Synthesis of Metal-Organic Frameworks. *Dalton Transactions*, *40*, 321–330. https://doi.org/10.1039/C0DT00708K

Kohn, W., Becke, A.D., Parr, R.G. (1996). Density Functional Theory of Electronic Structure. *The Journal of Physical Chemistry*, *100*(31), 12974–12980. https://doi.org/10.1021/jp960669l

Kohn, W., Sham, L.J. (1965). Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review*, *140*, A1133. https://doi.org/10.1103/PhysRev.140.A1133

Kondo, M., Yoshitomi, T., Seki, K., Matsuzaka, H., Kitagawa, S. (1997). Three-Dimensional Framework with Channeling Cavities for Small Molecules: $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\bullet xH_2O\}_n$ (M = Co, Ni, Zn). *Angewandte Chemie International Edition*, *36*(16), 1725–1727. https://doi.org/10.1002/anie.199717251

Kuppler, R.J., Timmons, D.J., Fang, Q.R., Li, J-R., Makal, T.A., Young, M.D., Yuan, D., Zhao, D., Zhuang, W., Zhou, H.C. (2009). Potential applications of metal-organic frameworks. *Coordination Chemistry Reviews*, *253*, 3042–3066. https://doi.org/10.1016/j.ccr.2009.05.019

Lammert, M., Wharmby, M.T., Smolders, S., Bueken, B., Lieb, A., Lomachenko, K.A., De Vos, D., Stock, N. (2015). Cerium-based Metal Organic Frameworks with UiO-66 Architecture: Synthesis, Properties and Redox Catalytic Activity. *Chemical Communications*, *51*, 12578–12581. https://doi.org/10.1039/C5CC02606G

Lee, Y.R., Kim, J., Ahn, W.S. (2013). Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical Engineering*, *30*, 1667–1680. https://doi.org/10.1007/s11814-013-0140-6

Li, H., Eddaoudi, M., Groy, T.L., Yaghi, O.M. (1998). Establishing Microporosity in Open Metal-Organic Frameworks: Gas Sorption Isotherms for Zn(BDC) (BDC) 1,4-Benzenedicarboxylate). *Journal of the American Chemical Society*, *120*(33), 8571–8572. https://doi.org/10.1021/ja981669x

Li, H., Eddaoudi, M., O'Keeffe, M., Yaghi, O.M. (1999). Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*, *402*, 276–279. https://doi.org/10.1038/46248

Li, Z.Q., Qiu, L.G., Xu, T., Wu, Y., Wang, W., Wu, Z.Y., Jiang, X. (2009). Ultrasonic synthesis of the microporous metal-organic framework $Cu_3(BTC)_2$ at ambient temperature and pressure: An efficient and environmentally friendly method. *Materials Letters*, *63*, 78–80. https://doi.org/10.1016/j.matlet.2008.09.010

Li, Y., Yang, R.T., (2006). Hydrogen Storage in Metal-Organic Frameworks by Bridged Hydrogen Spillover. *Journal of the American Chemical Society*, *128*(25), 8136–8137. https://doi.org/10.1021/ja061681m

Li, Y.W., Yang, R.T. (2006). Significantly Enhanced Hydrogen Storage in Metal--Organic Frameworks via Spillover. *Journal of the American Chemical Society*, *128*(3), 726–727. https://doi.org/10.1021/ja056831s

Liang, W., D'Alessandro, D.M. (2013). Microwave-assisted solvothermal synthesis of zirconium oxide based metal-organic frameworks. *Chemical Communications*, *49*, 3706–3708. https://doi.org/10.1039/c3cc40368h

Lu, J., Paliwala, T., Lim, S.C., Yu, C., Niu, T., Jacobson, A.J. (1997). Coordination Polymers of Co(NCS)2 with Pyrazine and 4,4′-Bipyridine: Syntheses and Structures. *Inorganic Chemistry*, *36*(5), 923–929. https://doi.org/10.1021/ic961158g

Lukose, B., Supronowicz, B., Petkov, P.St., Frenzel, J., Kuc, A.B., Seifert, G., Vayssilov, G.N., Heine, T. (2012). Structural properties of metal-organic frameworks within the density-functional based tight-binding method. *Physica status solidi B*, *249*, 335–342. https://doi.org/10.1002/pssb.201100634

Ma, S., Zhou, H.C., (2010). Gas storage in porous metal-organic frameworks for clean energy applications. *Chemical Communications*, *46*, 44–53. https://doi.org/10.1039/B916295J

Mahmoodi, N.M., Abdi, J., Oveisi, M., Asli, M.A., Vossoughi, M. (2018). Metal--organic framework (MIL-100 (Fe)): Synthesis, detailed photocatalytic dye degradation ability in colored textile wastewater and recycling. *Materials Research Bulletin*, *100*, 357–366. https://doi.org/10.1016/j.materresbull.2017.12.033

Martin, R.L., Lin, L.C., Jariwala, K., Smit, B., Haranczyk, M. (2013). Mail-Order Metal-Organic Frameworks (MOFs): Designing Isoreticular MOF-5 Analogues Comprising Commercially Available Organic Molecules. *The Journal of Physical Chemistry C*, *117*(23), 12159–12167. https://doi.org/10.1021/jp401920y

Mattesini, M., Soler, J.M., Ynduráin, F. (2006). Ab initio study of metal-organic framework-5 Zn4O(1,4-benzenedicarboxylate)3: An assessment of mechanical and spectroscopic properties, *Physical Review B*, *2006*(73), 094111. https://doi.org/10.1103/PhysRevB.73.094111

Millward, A.R., Yaghi, O.M. (2005). Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *Journal of the American Chemical Society*, *127*(51), 17998–17999. https://doi.org/10.1021/ja0570032

Min Choi, K., Hyo Park, J., Ku Kang, J. (2015). Nanocrystalline MOFs embedded in the crystals of other MOFs and their multifunctional performance for molecular encapsulation and energy-carrier storage. *Chemistry of Materials*, *27*, 5088–5093. https://doi.org/10.1021/acs.chemmater.5b01786

Miralda, C.M., Macias, E.E., Zhu, M., Ratnasamy, P., Carreon, M.A., (2012). Zeolitic Imidazole Framework-8 Catalysts in the Conversion of CO_2 to Chloropropene Carbonate. *ACS Catalysis*, *2*, 180–183. https://doi.org/10.1021/cs200638h

Morris, R.E. (2009). Ionothermal synthesis—ionic liquids as functional solvents in the preparation of crystalline materials. *Chemical Communications, 21*, 2990–2998. https://doi.org/10.1039/B902611H

Mulfort, K.L., Hupp, J.T. (2007). Chemical Reduction of Metal-Organic Framework Materials as a Method to Enhance Gas Uptake and Binding. *Journal of the American Chemical Society*, *129*(31), 9604–9605. https://doi.org/10.1021/ja0740364

Mulfort, K.L., Hupp, J.T. (2008). Alkali Metal Cation Effects on Hydrogen Uptake and Binding in Metal-Organic Frameworks. *Inorganic Chemistry*, *47*(18), 7936–7938. https://doi.org/10.1021/ic800700h

Mueller, T., Ceder, G. (2005). A Density Functional Theory Study of Hydrogen Adsorption in MOF-5. *The Journal of Physical Chemistry B*, *109*(38), 17974–17983. https://doi.org/10.1021/jp051202q

Ni, Z., Masel, R.I. (2006). Rapid Production of Metal-Organic Frameworks via Microwave-Assisted Solvothermal Synthesis. *Journal of the American Chemical Society*, *128*(38), 12394–12395. https://doi.org/10.1021/ja0635231

Ni, Z., Masel, R.I. (2006). Rapid Production of Metal-Organic Frameworks via Microwave-Assisted Solvothermal Synthesis. *Journal of the American Chemical Society*, *128*(38), 12394–12395. https://doi.org/10.1021/ja0635231

Nørskov, J.K., Abild-Pedersen, F., Studt, F. (2011). Density functional theory in surface chemistry and catalysis. *Proceedings of the National Academy of Sciences*, *108*(3), 937–943. https://doi.org/10.1073/pnas.1006652108

Odoh, S.O., Cramer, C.J., Truhlar, D.G., Gagliardi, L. (2015). Quantum-Chemical Characterization of the Properties and Reactivities of Metal–Organic Frameworks. *Chemical Reviews*, *115*(12), 6051–6111. https://doi.org/10.1021/cr500551h

Ohmori, O., Fujita, M. (2004). Heterogeneous catalysis of a coordination network: cyanosilylation of imines catalyzed by a Cd(II)-(4,4‘-bipyridine) square grid complex. *Chemical Communications*, (14), 1586–1587. https://doi.org/10.1039/B406114B

Oliveira, A., Mavrandonakis, A., de Lima, G.F., De Abreu, H.A. (2017). Cyanosilylation of Aldehydes Catalyzed by MIL-101(Cr): A Theoretical Investigation. *Chemistry Select*, *2*, 7813–7820. https://doi.org/10.1002/slct.201700946

Pachfule, P., Das, R., Poddar, P., Banerjee, R. (2011). Solvothermal Synthesis, Structure, and Properties of Metal Organic Framework Isomers Derived from a Partially Fluorinated Link. *Crystal Growth & Design*, *11*(4), 1215–1222. https://doi.org/10.1021/cg101414x

Park, K.S., Ni, Z., Cote, A.P., Choi, J. Y., Huang, R., Uribe-Romo, F.J., Chae, H.K., O’Keeffe, M., Yaghi, O.M. (2006). Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proceedings of the National Academy of Sciences*, *103*, 10186–10191. https://doi.org/10.1073/pnas.0602439103

Parnham, E.R., Morris, R.E. (2007). Ionothermal Synthesis of Zeolites, Metal--Organic Frameworks, and Inorganic–Organic Hybrids. *Accounts of Chemical Research*, *40*(10), 1005–1013. https://doi.org/10.1021/ar700025k

Pettinari, C., Marchetti, F., Mosca, N., Tosia, G., Drozdov, A. (2017). Application of Metal-organic Frameworks. *Polymer International*, *66*, 731–744. https://doi.org/10.1002/pi.5315

Phikulthai, S., Injongkol, Y., Maihom, T., Treesukol, P., Maitarad, P., Tangsermvit, V., Kongpatpanich, K., Boekfa, B. (2017). Adsorption of Ammonia on Zirconium-Based Metal-Organic Framework: A Combined Experimental and Theoretical Study. *Key Engineering Materials*, *757*, 93–97. https://doi.org/10.4028/www.scientific.net/KEM.757.93

Piszczek, P., Radtke, A., Grodzicki, A., Wojtczak, A., Chojnacki, J. (2007). The new type of $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]$ cluster core: Crystal structure and spectral characterization of $[Zr_6O_4(OH)_4(OOCR)_{12}]$ (R = But, C(CH3)2Et). *Polyhedron*, *26*, 679–685. https://doi.org/10.1016/j.poly.2006.08.025

Proch, S., Herrmannsdorfer, J., Kempe, R., Kern, C., Jess, A., Seyfarth, L., Senker, J. (2008). Pt@MOF-177: Synthesis, Room-Temperature Hydrogen Storage and Oxidation Catalysis. *Chemistry A European Journal*, *14*, 8204–8212. https://doi.org/10.1002/chem.200801043

Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., Kim, J., O'Keeffe, M., Yaghi, O.M. (2003). Hydrogen Storage in Microporous Metal-Organic Frameworks. *Science*, *300*(5622), 1127–1129. https://doi.org/10.1126/science.1083440

Rowsell, J.L.C., Yaghi, O.M. (2004). Metal-organic frameworks: a new class of porous materials. *Microporous and Mesoporous Materials*, *73*, 3–14. https://doi.org/10.1016/j.micromeso.2004.03.034

Sabo, M., Henschel, A., Frode, H., Klemm, E., Kaskel, S. (2007). Solution infiltration of palladium into MOF-5: synthesis, physisorption and catalytic properties. *Journal of Materials Chemistry*, *17*, 3827–3832. https://doi.org/10.1039/B706432B

Sagara, T., Klassen, J., Ganz, E. (2005). Computational study of hydrogen binding by metal-organic framework-5. *The Journal of Chemical Physics*, *121*, 12543–12547. https://doi.org/10.1063/1.1809608

Samanta, A., Furuta, T., Li, J. (2006). Theoretical assessment of the elastic constants and hydrogen storage capacity of some metal-organic framework materials. *The Journal Of Chemical Physics, 125*, 084714. https://doi.org/10.1063/1.2337287

Schaate, A., Roy, P., Godt, A., Lippke, J., Waltz, F., Wiebcke, M., Behrens, P. (2011). Modulated Synthesis of Zr-Based Metal-Organic Frameworks: From Nano to Single Crystals. *Chemistry A European Journal*, *17*, 6643–6651. https://doi.org/10.1002/chem.201003211

Schlichte, K., Kratzke, T., Kaskel, S. (2004). Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound Cu3(BTC)2. *Microporous and Mesoporous Materials*, *73*, 81–88. https://doi.org/10.1016/j.micromeso.2003.12.027

Schroder, F., Esken, D., Cokoja, M., van den Berg, M.W.E., Lebedev, O.I., van Tendeloo, G., Walaszek, B., Buntkowsky, G., Limbach, H.H., Chaudret, B., Fischer, R.A. (2008). Ruthenium Nanoparticles inside Porous [Zn4O(bdc)3] by Hydrogenolysis of Adsorbed [Ru(cod)(cot)]: A Solid-State Reference System for Surfactant-Stabilized Ruthenium Colloids. *Journal of the American Chemical Society*, *130*(19), 6119–6130. https://doi.org/10.1021/ja078231u

Seminario, J.M. (1995). An Introduction to Density Functional Theory in Chemistry. *Theoretical and Computational Chemistry*, *2*, 1–27. https://doi.org/10.1016/S1380-7323(05)80031-7

Serre, C., Millange, F., Thouvenot, C., Nogues, M., Marsolier, G., Louer, D., Ferey, G. (2002). Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or $CrIII(OH)\bullet\{O_2C\text{-}C_6H_4\text{-}CO_2\}\bullet\{HO_2C\text{-}C_6H_4\text{-}CO_2H\}_x\bullet H_2O_y$. *Journal of the American Chemical Society*, *124*, 13519–13526. https://doi.org/10.1021/ja0276974

Son, W.J., Kim, J., Kim, J., Ahn, W.S. (2008). Sonochemical synthesis of MOF-5. *Chemical Communications*, (48), 6336–6338. https://doi.org/10.1039/B814740J

Stock, N., Biswas, S. (2012). Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chemical Reviews*, *112*(2), 933–969. https://doi.org/10.1021/cr200304e

Sugimoto, T., Mizushima, T., Okamoto, A., Kurita, N. (2014). Structures and electronic properties of metal organic frameworks: DFT and ab initio FMO calculations for model systems. *Chemical Physics Letters*, *612*, 295–301. https://doi.org/10.1016/j.cplett.2014.08.012

Suh, M.P., Park, H.J., Prasad, T.K., Lim, D.W. (2012). Hydrogen Storage in Metal--Organic Frameworks. *Chemical Reviews*, *112*(2), 782–835. https://doi.org/10.1021/cr200274s

Supronowicz, B., Mavrandonakis, A., Heine, T. (2013). Interaction of Small Gases with the Unsaturated Metal Centers of the HKUST-1 Metal Organic Framework. *The Journal of Physical Chemistry*, *117*(28), 14570–14578. https://doi.org/10.1021/jp4018037

Tröbs, L., Wilke, M., Szczerba, W., Reinholz, U., Emmerling, F. (2014). Mechanochemical synthesis and characterization of two new bismuth metal organic frameworks. *CrystEngComm*, *16*, 5560–5565. https://doi.org/10.1039/C3CE42633E

Vandichel, M., Hajek, J., Vermoortele, F., Waroquier, M., De Vosb, D.E., Van Speybroeck, V. (2015). Active site engineering in UiO-66 type metal–organic frameworks by intentional creation of defects: a theoretical rationalization. *CrystEngComm*, *17*, 395–406. https://doi.org/10.1039/C4CE01672F

Venkataramanan, N.S., Sahara, R., Mizuseki, H., Kawazoe, Y. (2009). Probing the Structure, Stability and Hydrogen Adsorption of Lithium Functionalized Isoreticular MOF-5 (Fe, Cu, Co, Ni and Zn) by Density Functional Theory. *International Journal of Molecular Sciences*, *10*, 1601–1608. https://doi.org/10.3390/ijms10041601

Vermoortele, F., Ameloot, R., Vimont, A., Serrec, C., De Vos, D. (2011). An amino-modified Zr-terephthalate metal-organic framework as an acid--base catalyst for cross-aldol condensation. *Chemical Communications*, *47*, 1521–1523. https://doi.org/10.1039/c0cc03038d

Vermoortele, F., Bueken, B., Bars, G.L., Voorde, B.V., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., Speybroeck, V.V., Kirschhock, C., De Vos, D.E. (2013). Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal-Organic Frameworks: The Unique Case of UiO--66(Zr). *Journal of the American Chemical Society*, *135*(31), 11465–11468. https://doi.org/10.1021/ja405078u

Vermoortele, F., Vandichel, M., de Voorde, B.V., Ameloot, R., Waroquier, M., Van Speybroeck, V., De Vos, D.E. (2012). Electronic Effects of Linker Substitution on Lewis Acid Catalysis with Metal-Organic Frameworks. *Angewandte Chemie International Edition*, *51*, 1–5. https://doi.org/10.1002/anie.201108565

Vimont, A., Goupil, J.M., Lavalley, J.C., Daturi, M., Surble, S., Serre, C., Millange, F., Ferey, G., Audebrand, N. (2006). Investigation of Acid Sites in a Zeotypic Giant Pores Chromium(III) Carboxylate. *Journal of the American Chemical Society*, *128*(10), 3218–3227. https://doi.org/10.1021/ja056906s

Vimont, A., Leclerc, H., Mauge, F., Daturi, M., Lavalley, J.C., Surble, S., Serre, C., Ferey, G. (2007). Creation of Controlled Brønsted Acidity on a Zeotypic Mesoporous Chromium(III) Carboxylate by Grafting Water and Alcohol Molecules. *The Journal of Physical Chemistry C*, *111*(1), 383–388. https://doi.org/10.1021/jp064686e

Vogiatzis, K.D., Polynski, M.V., Kirkland, J.K., Townsend, J., Hashemi, A., Liu, C., Pidko, E.A. (2019). Computational Approach to Molecular Catalysis by 3d Transition Metals: Challenges and Opportunities. *Chemical Reviews*, *119*(4), 2453–2523. https://doi.org/10.1021/acs.chemrev.8b00361

Wang, Z., Cohen, S.M. (2007). Postsynthetic Covalent Modification of a Neutral Metal-Organic Framework. *Journal of the American Chemical Society*, *129*, 12368–12369. https://doi.org/10.1021/ja074366o

Wang, Z., Cohen, S.M. (2009). Postsynthetic modification of metal–organic frameworks. *Chemical Society Reviews*, *38*, 1315–1329. https://doi.org/10.1039/B802258P

Wanga, Y., Zenga, Y., Wua, X., Mu, M., Chen, L. (2018). A novel Pd-Ni bimetallic synergistic catalyst on ZIF-8 for Sonogashira coupling reaction. *Materials Letters*, *220*, 321–324. https://doi.org/10.1016/j.matlet.2018.03.006

Wells, A.F., (1954). The Geometrical Basis of Crystal Chemistry. Part 1. *Acta Crystallographica*, *7*, 535–544. https://doi.org/10.1107/S0365110X5400182X

Wells, A.F., (1954). The Geometrical Basis of Crystal Chemistry. Part 2. *Acta Crystallographica*, *7*, 545–554. https://doi.org/10.1107/S0365110X54001831

Wilmer, C.E., Leaf, M., Lee, C.Y., Farha, O.K., Hauser, B.G., Hupp, J.T., Snurr, R.Q. (2012). Large-scale screening of hypothetical metal–organic frameworks. *Nature Chemistry*, *4*, 83–89. https://doi.org/10.1038/nchem.1192

Wong-Foy, A.G., Matzger, A.J., Yaghi, O.M. (2006). Exceptional H_2 Saturation Uptake in Microporous Metal-Organic Frameworks. *Journal of the American Chemical Society*, *128*(11), 3494–3495. https://doi.org/10.1021/ja058213h

Wu, C.D., Hu, A., Zhang, L., Lin, W. (2005). A Homochiral Porous Metal-Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis. *Journal of the American Chemical Society*, *127*(25), 8940–8941. https://doi.org/10.1021/ja052431t

Yaghi, O.M., Li, H. (1995). Hydrothermal Synthesis of a Metal-Organic Framework Containing Large Rectangular Channels. *Journal of the American Chemical Society*, *117*(41), 10401–10402. https://doi.org/10.1021/ja00146a033

Yaghi, O.M., O'Keeffe, M., Ockwig, N.W., Chae, H.K., Eddaoudi, M., Kim, J. (2003). Reticular synthesis and the design of new materials. *Nature*, *423*, 705–714. https://doi.org/10.1038/nature01650

Yoo, Y., Varela-Guerrero, V., Jeong, H.K. (2011). Isoreticular Metal-Organic Frameworks and Their Membranes with Enhanced Crack Resistance and Moisture Stability by Surfactant-Assisted Drying. *Langmuir*, *27*(6), 2652–2657. https://doi.org/10.1021/la104775d

Yuan, S., Feng, L., Wang, K., Pang, J., Bosch, M., Lollar, C., Sun, Y., Qin, J., Yang, X., Zhang, P., Wang, Q., Zou, L., Zhang, Y., Zhang, L., Fang, Y., Li, J., Zhou, H.C. (2018). Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Advanced Materials*, 30(37), 1704303. https://doi.org/10.1002/adma.201704303

Zalomaeva, O.V., Chibiryaev, A.M., Kovalenko, K.A., Kholdeeva, O.A., Balzhinimaev, B.S., Fedin, V.P., (2013). Cyclic carbonates synthesis from epoxides and CO2 over metal–organic framework Cr-MIL-101. *Journal of Catalysis*, *298*, 179–185. https://doi.org/10.1016/j.jcat.2012.11.029

Zhao, S., Chen, J. (2008). Metal organic framework-derived Ni/Zn/Co/NC composites as efficient catalyst for oxygen evolution reaction. *Journal of Porous Materials*, *26*, 381–387. https://doi.org/10.1007/s10934-018-0612-5

Zhao, L., Yang, Q., Ma, Q., Zhong, C., Mi, J., Liu, D. (2011). A force field for dynamic Cu-BTC metal-organic framework. *Journal of Molecular Modeling*, *17*, 227–234. https://doi.org/10.1007/s00894-010-0720-x

Zheng, B., Liang, Z., Li, G., Huo, Q., Liu, Y. (2010). Synthesis, Structure, and Gas Sorption Studies of a Three-Dimensional Metal-Organic Framework with NbO Topology. *Crystal Growth & Design*, *10*(8), 3405–3409. https://doi.org/10.1021/cg100046j

Zhou, H-C., Long, J.R., Yaghi, O.M. (2012). Introduction to Metal–Organic Frameworks. *Chemical Reviews*, *112*(2), 673–674. https://doi.org/10.1021/cr300014x

Zong, S., Zhang, Y., Lu, N., Ma, P., Wang, J., Shi, X-R. (2018). A DFT Screening of M-HKUST-1 MOFs for Nitrogen-Containing Compounds Adsorption. *Nanomaterials*, *8*, 958–973. https://doi.org/10.3390/nano8110958

Modelowanie porowatych materiałów metaloorganicznych (MOF) stosowanych w katalizie

Streszczenie

W niniejszym artykule przedstawiamy przegląd nowoczesnego modelowania materiałów porowatych, takich jak struktury metaloorganiczne, stosowanych w katalizie. Uwzględnione zostały również nasze własne prace badawcze wykorzystujące projektowanie struktur metaloorganicznych.

Słowa kluczowe: modelowanie, teoria funkcjonałów gęstości, struktury metalo-organiczne

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