

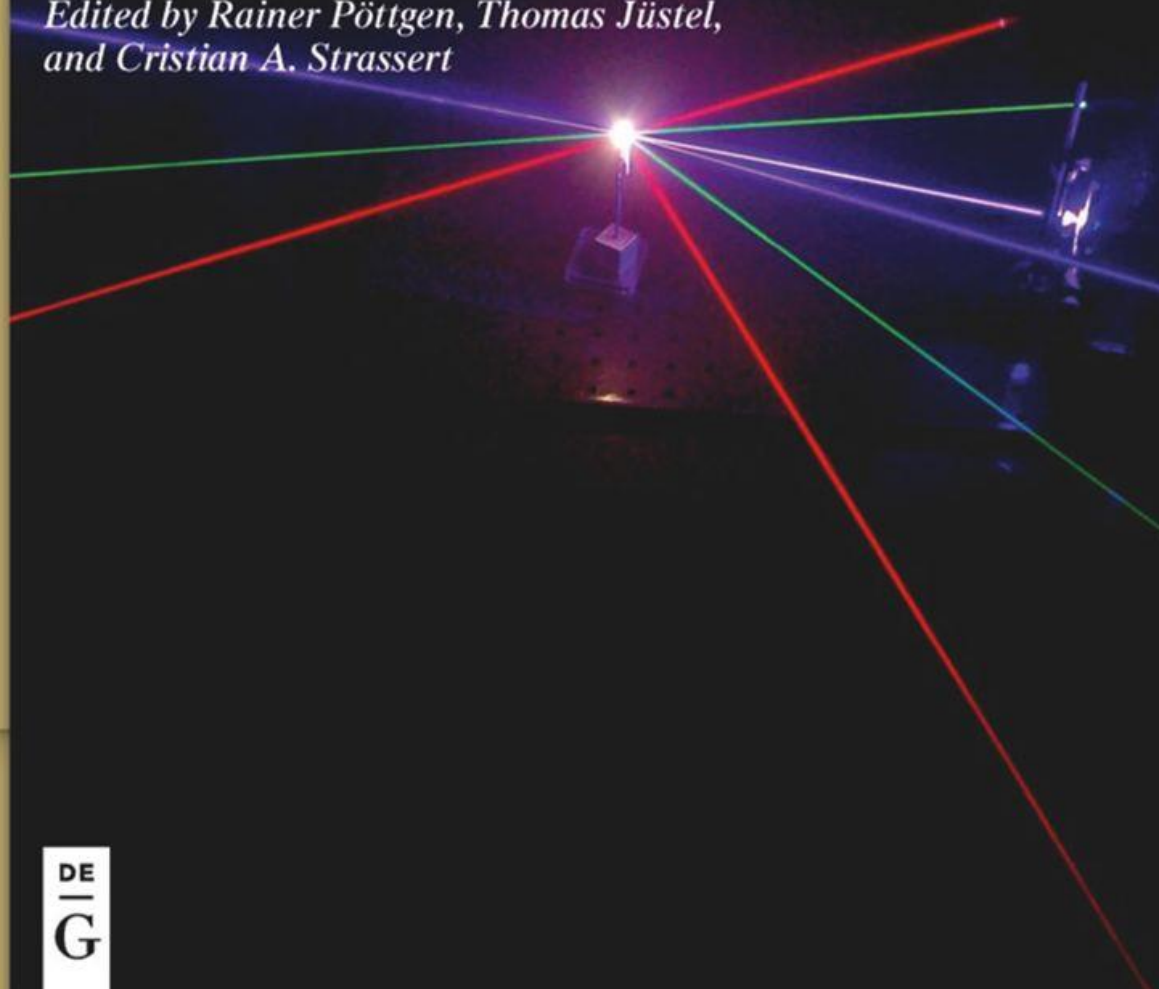
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# APPLIED INORGANIC CHEMISTRY

VOLUME 2: FROM ENERGY STORAGE TO  
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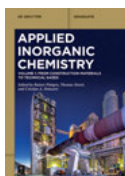
*Edited by Rainer Pöttgen, Thomas Jüstel,  
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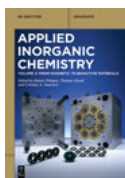
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Rainer Pöttgen, Thomas Jüstel, Cristian A. Strassert (Eds.)  
**Applied Inorganic Chemistry**

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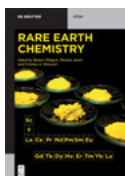
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# Applied Inorganic Chemistry

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Volume 2: From Energy Storage  
to Photofunctional Materials

Edited by  
Rainer Pöttgen, Thomas Jüstel, Cristian A. Strassert

**DE GRUYTER**

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## Preface

The Periodic Table meanwhile lists 118 chemical elements, which leads to a vast number of inorganic compounds. Many of them have well-defined physicochemical properties, which are exploited for the realization of functional materials we all comfortably use in daily life without even thinking about it, including magnetic and optical materials, construction materials, materials for energy storage and conversion – just to name a few remarkable examples. The impact of inorganic chemistry in human evolution cannot be overstated, and is proven by the designation of historical ages, such as stone, copper, bronze or iron age (even golden ages and gold rush), or by geographical locations (such as the Silicon Valley and Argentina). While carbon-based organic chemistry has provided incredible breakthroughs in medicinal chemistry and plastic materials, there is no doubt that the solution of the most urgent problems currently faced by humanity will stem from inorganic chemistry providing high-density/high-stability materials for construction, information technologies, energy storage and conversion.

Chemical sciences and industries are often demonized, but the many indispensable materials we use in daily life impressively show how significantly they influence our society. Ecosystems, metabolic and pathophysiological processes, food production, construction in its broadest sense, mobility and energy conversion are determined by chemistry – these facts cannot simply be ignored! The present book summarizes the many basic examples of inorganic materials we use on a large scale in everyday life, but also niche products with thoroughly optimized properties. Many subchapters are written by experts from academia and industry. We tried to ensure a proper balance of topics, even though it is simply impossible to cover all aspects of applied inorganic chemistry. Nonetheless, we hope that we made a good compromise – if any topic is missing, this was unintentional. The final chapter focusses on energy flows and resources, which constitutes one of the most urgent topics. As a kind of appetizer for the following 16 chapters, we briefly summarize some applications for the elements of the first four rows of the Periodic Table. Several of these topics are picked up again in the following chapters:

**Hydrogen:** energy source; **helium:** low-temperature refrigerant; ballon gas, **lithium:** anode materials for lithium-ion batteries; **beryllium:** hardening component for light-weight alloys, non-spark alloys, X-ray windows; **boron:** hardening component for intermetallics; **carbon:** electrode materials, black pigment; **nitrogen:** source for ammonia and nitrate fertilizers, protective gas, low-temperature cooling; **oxygen:** medical gas, liquid oxygen for the Linz-Donauwitzer process in steel refinement; **fluorine:** uranium hexafluoride production; **neon:** helium-neon lasers; **sodium:** reducing agent; **magnesium:** alloying component and sacrificial anodes; **aluminum:** light-weight alloys, construction material; **silicon:** semiconductors; **phosphorus:** synthesis of phosphoric acid; matches; **sulfur:** vulcanization of rubber; **chlorine:** disinfection of water; **argon:** protective gas in chemical synthesis

and arc-welding; **potassium**: liquid sodium-potassium alloys as coolants in nuclear reactors; **calcium**: reducing agent in metallurgy; **scandium**: additive for aluminum-based alloys, component of electron emitters; **titanium**: steel additive, corrosion resistant alloys; **vanadium**: high-speed tool steels; **chromium**: stainless steel and chromium plating; **manganese**: ferromanganese, activator in LED phosphors; **iron**: steel and cast iron; **cobalt**: superalloys and samarium-cobalt magnets; **nickel**: catalysis and anti-corrosion coatings; **copper**: cables and water tubes; **zinc**: facade cladding, corrosion protection; **gallium**: gallium nitride, phosphide or arsenide semiconductors; **germanium**: semiconductors and detection technology; **arsenic**: doping of semiconductors; **selenium**: II-VI semiconductors and alloy additive for free cutting steel; **bromine**: special disinfection products and synthesis of flame retardants; **krypton**: excimer lasers, KrCl excimer discharge lamps. The reader might notice that transition metals and lanthanides are not even mentioned here; there would not be sufficient space in a preface to list their impact!

Such a book project is not realizable without the help of numerous colleagues and co-workers. We thank Gudrun Lübbering for continuous help with literature search and text processing and Thomas Fickenscher for providing with many photos of materials and devices. We are especially grateful to our colleagues for their immediate agreements to write up a subchapter. It is always challenging to compile a concise Table of Contents and find the right co-authors. We are indebted to the editorial and production staff of De Gruyter. Our particular thanks go to Kristin Berber-Nerlinger, Dr. Vivien Schubert and Melanie Götz for their continuous support during conception, writing and producing the present book.

Münster, Steinfurt, June 2022

Thomas Jüstel, Rainer Pöttgen, Cristian A. Strassert

This book contains two different tokens, pointing to:



list of references



recommended literature for further reading; i.e. relevant text books, review articles or important original articles

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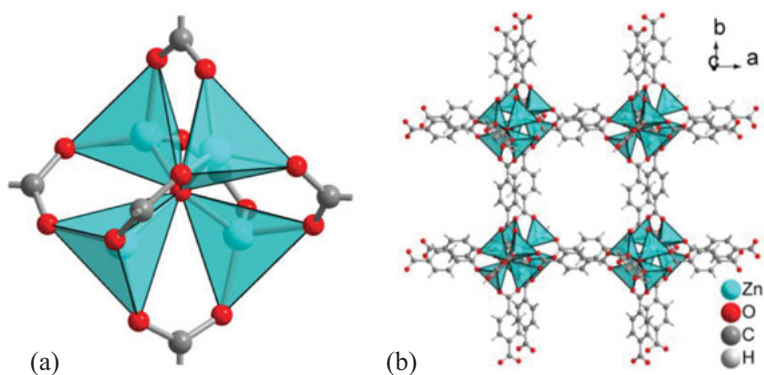
## 7.4 Metal-organic frameworks

Christoph Janiak

Metal-organic frameworks, abbreviated as MOFs, are coordination networks with organic ligands containing potential voids. Coordination networks are cross-linked metal coordination compounds extending through repeating coordination entities in two or three dimensions (2D, 3D) [1]. Porosity is usually determined after removal of the templating solvent molecules by measuring a nitrogen (or argon) sorption isotherm at 77 K (78 K) and then calculating an internal surface area and pore size distribution based on the Brunauer-Emmett-Teller (BET) theory and related to 1.0 g material (specific surface area). The four prototypical MOFs MOF-5, Cu-btc, MIL-53 (Al) and ZIF-8 will be briefly presented.

### 7.4.1 Selected MOF structures

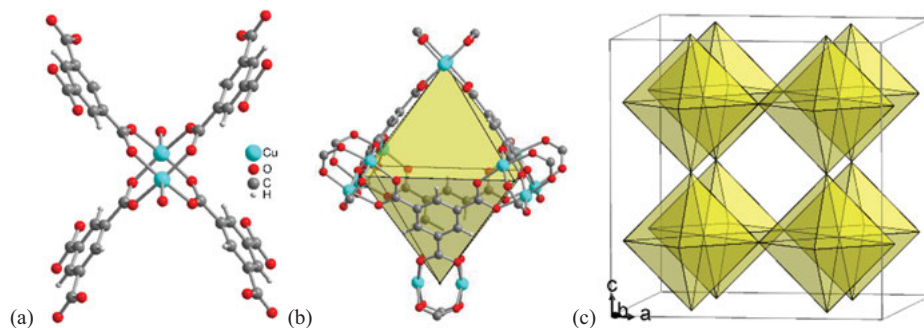
MOF-5: Based on hydrothermally obtained tetranuclear and tetrahedral  $\{Zn_4(\mu_4-O)\}$  units and aromatic para-dicarboxylate ligands such as benzene-1,4-dicarboxylate ( $bdc^{2-}$ , terephthalate), a series of similarly constructed (iso-reticular) structures, including 3D- $[Zn_4O(bdc)_3]$ , MOF-5, can be obtained [2]. The carboxylate groups span the six edges of the  $\{Zn_4(\mu_4-O)\}$  tetrahedron, and the dicarboxylate bridges are oriented at right angles to each other (Figure 7.4.1).



**Figure 7.4.1:** (a) Tetranuclear  $\{Zn_4(\mu_4-O)\}$  unit of MOF-5 with bridging carboxylate groups. The C atoms of the carboxylate bridge are located at the vertices of an octahedron. Each Zn atom is tetrahedrally coordinated by four O atoms. (b) Packing diagram of 3D- $[Zn_4O(bdc)_3]$ , MOF-5. The network is traversed by channels along the *a*, *b* and *c* axis. The specific internal surface area is  $\sim 2900 \text{ m}^2 \text{ g}^{-1}$ .



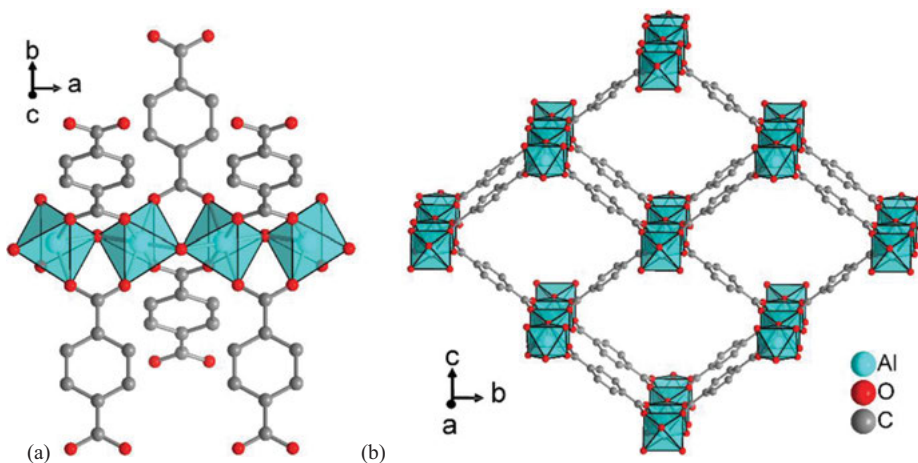
**Cu-btc:** The compound  $3\text{D}[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$  (also called HKUST-1,  $\text{btc}^{3-}$  = benzene-1,3,5-tricarboxylate, trimesate) contains two copper atoms as the metal atom assembly, which are bridged by four carboxylate groups as in copper acetate ( $[\text{Cu}_2(\text{CH}_3\text{COO})_4]$ ) to form a “paddle-wheel” unit (Figure 7.4.2). Cu-btc is stable up to 240 °C. The aqua ligands can be removed [3].



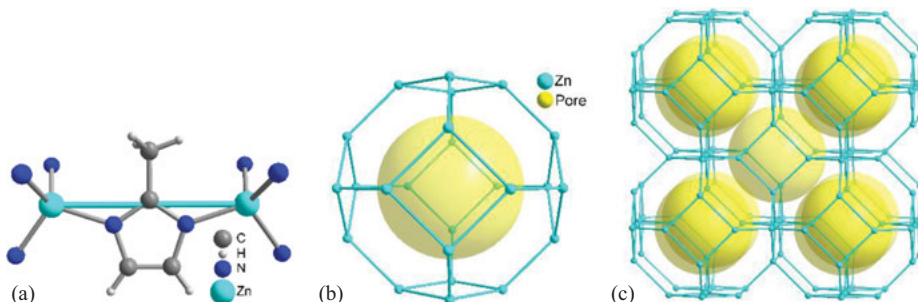
**Figure 7.4.2:** (a)  $\{\text{Cu}_2(\text{btc})_4\}$  “paddle-wheel” unit in Cu-btc (HKUST-1). (b) The  $\{\text{Cu}\}_2$  dumbbells sit at the corners of an octahedron. Four btc ligands each span opposite four of the eight faces of the octahedron. (c) These octahedra form a porous 3D network via vertex linkage. The network is traversed by channels along the  $a$ ,  $b$  and  $c$  axis. The specific surface area is  $\sim 1300 \text{ m}^2 \text{ g}^{-1}$ .

**MIL-53(Al):** Many aluminum MOFs with the formula unit  $3\text{D}[\text{Al}(\mu\text{-OH})(\text{dicarboxylate ligand})]$  such as MIL-53(Al), are built up from slightly angled strands of vertex-sharing  $\{\text{AlO}_6\}$  octahedra. In the strands, the Al atoms are connected by the oxygen atoms of  $\mu$ -hydroxido and carboxylate bridges (Figure 7.4.3) [4]. The dicarboxylate ligands connect each strand to four neighboring strands, forming microporous rhombic to square channels in the 3D framework. The dicarboxylate ligands are terephthalate in MIL-53(Al).

**ZIF-8:** Three-dimensional zeolitic imidazolate frameworks (ZIFs) with the formula  $3\text{D}[\text{Zn}(\text{imidazolate})_2]$  are obtained from  $\text{Zn}^{2+}$  and imidazolate ligands. ZIFs are one of the few porous MOFs in which individual metal atoms are bridged by ligands. In ZIFs, each Zn atom is surrounded by four N atoms from four imidazolate ligands (Figure 7.4.4). The linkage leads to zeolite-like structures in which the Zn atom occupies the position of Al/Si and the imidazolate bridges occupy the positions of the oxygen bridges in the zeolite. The best-known ZIF is ZIF-8 with 2-methylimidazolate as ligand [5, 6].



**Figure 7.4.3:** (a) Vertex-linked  $\{\text{Al}(\mu\text{-OH})(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2)_2\}$  strand in MIL-53(Al) and (b) resulting 3D framework with parallel channels in only one direction (here along a) (hydrogen atoms are not shown). The specific surface area is  $1600 \text{ m}^2 \text{ g}^{-1}$  for (the large-pore form of) MIL-53(Al).



**Figure 7.4.4:** (a) Zn and 2-methylimidazolate building groups in ZIF-8 and (b) the assembly to a  $\beta$ -cage and (c) sodalite structure showing only the Zn atoms and their topological connections. The pore represented by the yellow sphere inside the  $\beta$ -cage has a diameter of  $12 \text{ \AA}$ ; the hexagonal rings as pore openings have a diameter of  $3.4 \text{ \AA}$  (taking the van-der-Waals surface into account). The BET surface area is about  $1600 \text{ m}^2 \text{ g}^{-1}$ .

### 7.4.2 General MOF properties

MOFs are crystalline microporous to mesoporous materials (microporous  $< 2 \text{ nm}$ , mesoporous from  $2$  to  $50 \text{ nm}$  pore diameter). In contrast to the amorphous mesoporous materials silica gel and activated carbons, MOFs have defined identical pore systems due to their crystallinity. In contrast to the likewise crystalline and thus uniform microporous zeolites with only limited structural units, the pore size and shape, the hydrophilicity/hydrophobicity, the inner surface functionality up to the chirality can be tailored in many ways in MOFs by the organic bridging ligands. The

ligands can be modified by organic-chemical reactions (substitutions, additions) even after the formation of the MOF network. For this purpose, the term “post-synthetic modification” has been coined for MOFs [7].

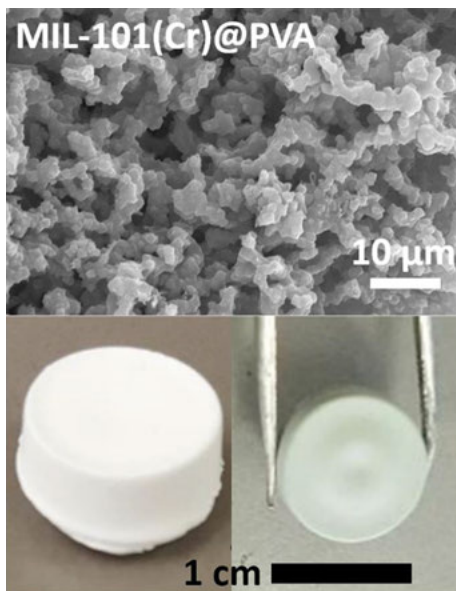
There are now about 200 zeolite structures compared to over 20000 MOF structures. The BET surface area for zeolites, silica gels and activated carbons is at most about  $1000 \text{ m}^2 \text{ g}^{-1}$ , while values of  $2000\text{--}4000 \text{ m}^2 \text{ g}^{-1}$  are reproducible and applicable for MOFs. The pore openings or channel diameters in MOFs range from 0.3 to 3.4 nm, with specific pore volumes up to  $1.5\text{--}2 \text{ cm}^3 \text{ g}^{-1}$ .

From the synthesis, the pores of the MOF scaffolds are filled with solvent molecules, which have a templating effect. Before using the porosity, the solvent guest molecules have to be removed, which is done by evacuation, if necessary after an exchange of less volatile for more volatile solvents. In this way, the MOF is first activated.

Some MOFs are already being produced industrially on a pilot scale in anticipation of applications. Without going into details of MOF synthesis, there is the problem of “greener”, cheaper and easily scalable synthesis procedures to provide access to larger amounts if these materials are to be used. The synthetic procedures for fabricating MOFs can require harsh conditions (high temperature/high pressure in autoclaves) and/or expensive organic linkers together with not environmentally benign solvents. There is the need to develop more syntheses at ambient pressures, possibly as continuous processes and without the often-used organic solvents like dimethylformamide [8, 9]. A positive example is the MOF aluminum fumarate ( $[\text{Al}(\text{OH})(\text{O}_2\text{C}-\text{C}_2\text{H}_2-\text{CO}_2)]$ , BASOLITE<sup>TM</sup> A520) [10, 11], where only aqueous solutions of aluminum sulfate and sodium fumarate are combined at ambient pressure and at a temperature of  $60 \text{ }^\circ\text{C}$ , even in a continuous flow process with a space-time-yield of  $97159 \text{ kg m}^{-3} \text{ day}^{-1}$  and a rate of  $5.6 \text{ kg h}^{-1}$  [12].

From the initial synthesis, MOFs are prepared as microcrystalline powders. Yet, powdered MOFs have limited practical interest owing to poor processability, safety problems from dusting and poor recyclability. The use of MOFs in potential applications most often requires shaping as an important aspect of their prospective use at an industrial scale. Thus, MOFs have to be formulated to obtain handable objects as deposited MOF layers on a substrate, coatings, films or 3D-structured composites such as grains, pellets, beads, areogels, hydrogels and monoliths (Figure 7.4.5) [13–15]. These shaped MOF particles have to be mechanically stable and retain the initial MOF porosity [16]. The simple use of a polymeric binder to assemble and shape MOF particles to a larger object may block the MOF pores and reduce the accessible surface area.

A possible obstacle for applications of MOFs is their often-insufficient hydrothermal stability [17] even if by now, some MOFs are known to be stable against prolonged contact with water and humid air.



**Figure 7.4.5:** MOF@polymer-monolith composites (with a scanning electron microscopy image) from the MOFs Al-fumarate (left) and MIL-101(Cr) (right) with the polymer poly(vinyl alcohol) (PVA), prepared using a phase separation technique. In the MOF@PVA monoliths, the mass-weighted BET surface area and the water vapor uptake capacity reproducibly reached 60–100% of the neat MOF values with MOF loadings of 50–80 wt%. The monoliths exhibit slightly plastic properties and a high resistance against deformation.

### 7.4.3 Potential applications of MOFs

In terms of industrial scale applications, MOFs can still be seen as an emerging class of materials. So far, most of the noted “applications” have to be regarded as potential ones and have to do with the porosity. MOFs are intensively investigated for a task- and compound-specific selective adsorption, storage and separation, sensing, catalysis, etc. For many of the applications, it is mandatory to develop robust and inexpensive MOF materials with good hydrolytic stability, excellent adsorption properties and recyclability.

The following paragraphs summarize the most important “application-oriented” developments with MOFs [18], based on review articles, but they do not present a full account of all “possible applications”. It should also be noted that there are occasional applications with “MOFs” which have no proven porosity and are rather non-porous coordination polymer/network. The noted possible applications do not only refer to pristine MOFs but also refer to MOF composites, for example, mixed-matrix membranes for gas separation with MOFs as fillers [19, 20].

Early on, MOFs came into the focus for H<sub>2</sub> storage for mobile applications. At 77 K, volume-specific storage curves of hydrogen on different MOF-materials in comparison to the compression curve of hydrogen into empty gas containers showed an up to three times higher H<sub>2</sub> uptake in g(H<sub>2</sub>)/L(container). Still, a sufficiently high amount of storage at room temperature could not be attained [21, 22]. For methane, the storage capacity of a tank filled with shaped bodies of the MOF Basolite A520 could reach a 40% increase vs. a conventional container at 35 bar and room temperature [10].

Numerous studies have demonstrated the capture and separation of carbon dioxide, CO<sub>2</sub> from binary mixtures with N<sub>2</sub>, which were simplistically viewed as flue gas [23, 24] as well as of SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub> and NO<sub>x</sub> from gas mixtures [25, 26] and even up to chemical warfare agents [27]. MOFs have addressed the adsorption-based separations of fluorocompounds [28], acetylene/ethylene [29], olefin/paraffin, linear/branched alkanes, xenon/krypton [30], acetylene/CO<sub>2</sub> [31], hydrogen isotopes [32] and adsorption-based purifications, of e.g. ethylene [33].

MOFs have been investigated for the ionic conduction of various charge carriers, such as a proton ( $>10^{-2}$  S cm<sup>-1</sup>), hydroxide ion ( $>10^{-2}$  S cm<sup>-1</sup>), lithium ion, sodium ion and magnesium ion (all about 10<sup>-4</sup> S cm<sup>-1</sup>) in their pores [34, 35] as well as for energy applications such as electrocatalysts [36], energy storage and conversion [37], supercapacitors [38], batteries and fuel cells [39].

MOFs have been developed for their possible use as sensors for the detection of many different gases and volatile organic compounds [40, 41], as signal amplification elements for electrochemical sensing [42], for the sensing and imaging of biomolecules [43, 44], environmental pollutants [45], explosives [46], ionic species [47, 48], among many others. Often, the luminescence of MOFs from the linkers, metals, incorporated luminophores or a combination thereof is utilized for the sensing application [49–51].

MOFs are used as size- and enantioselective heterogeneous catalysts [52, 53], including enzyme-MOF composites with MOFs as an enzyme immobilization platform [54, 55], as solid catalysts for liquid-phase continuous flow reactions [56], for the photocatalytic degradation of dyes in water depollution [57], etc.

MOFs are studied for the adsorptive removal of synthetic dyes in textile effluents [58] as well as of pharmaceuticals, personal care products [59] and of fluoride and arsenic [60] from (waste)water.





The porosity of MOFs enables them to be used for (self-sacrificial) drug delivery [61–63], including the sustained release of antibiotic and antimicrobial drugs [64] or bisphosphonate anti-osteoporotic drugs [65].

MOFs are investigated as materials for adsorption and desiccant cooling technologies through cyclic sorption of water or methanol in adsorption-driven heat pumps or adsorption chillers [66–70]. The aspect of cyclic water sorption extends to water harvesting from air for fresh water production [71–73].


In 2016, the first commercial application of a MOF may have materialized. The MOF (by the company MOF Technologies) was used to store and release 1-methylcyclopropene (1-MCP) to slow the fruit ripening process. 1-MCP binds and blocks ethylene receptors in the fruit, with ethylene being a ripening hormone [74, 75].

The MOF start-up NuMat is supplying MOF-filled gas storage cylinders, named ION-X, to store toxic gases (e.g. arsine, phosphine and boron trifluoride), which are used as dopants in the semiconductor industry, and doing this more safely than conventional pressurized cylinders [73, 76].

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