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Current Opinion in
Green and Sustainable Chemistry

Metal-organic frameworks for energy-related applications

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Abstract

Current micro review describes the recent progress in the energy-related MOF applications. The most outstanding research papers and reviews, which report the application of Metal-Organic Frameworks for gas storage, adsorption heat transformation, solar cells, fuel cells, hydrogen evolution reaction and supercapacitors are highlighted.

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Current Opinion in Green and Sustainable Chemistry 2017, **4**:44–49

This review comes from a themed issue on **Novel materials for energy production and storage**

Edited by **Susan Schorr**

http://dx.doi.org/10.1016/j.cogsc.2017.02.005

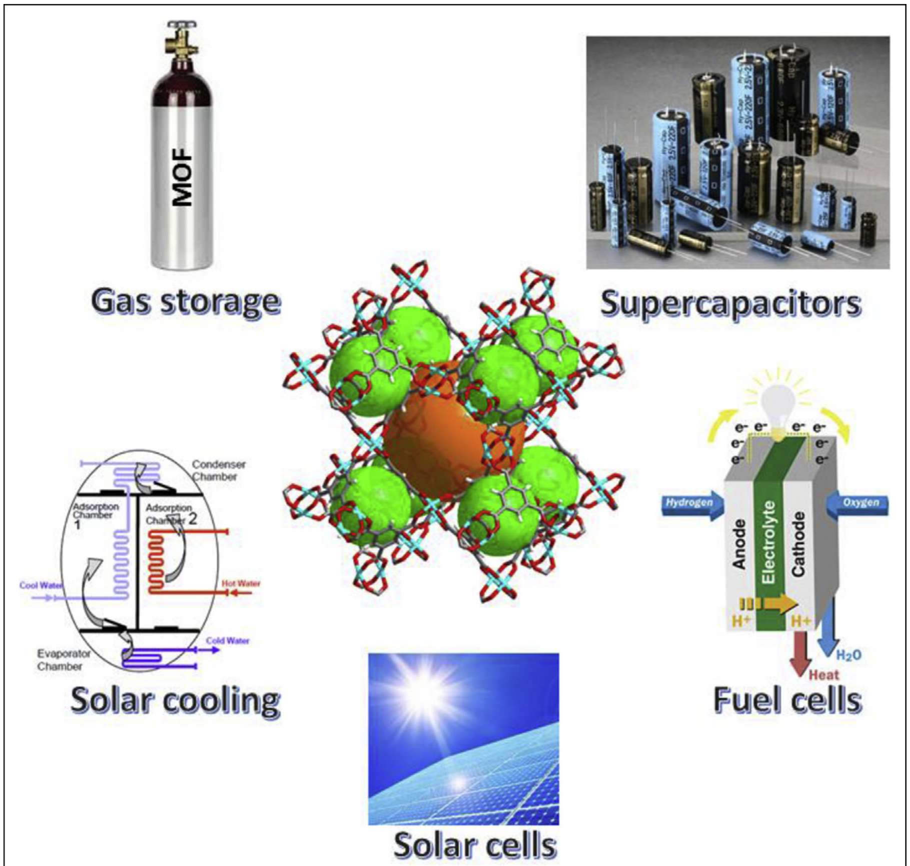
Metal-Organic Frameworks (MOFs) – well-established class of crystalline porous materials, constructed from metal ions or clusters, which are interconnected by organic ligand molecules based on a modular principle and form 3D Frameworks with various topologies [1]. This results in the formation of the precisely defined pore system, which differentiate MOFs from less ordered activated carbons, porous metal oxides and silica's. Well-defined crystal structure of MOFs opens unique functionalization possibilities, which in turns further expand their application potential ranging from catalysis, capture of the greenhouse gases and even fabrication of electronic devices etc. [2**]. Among the broad application field for MOFs, energy-related applications are connected with energy storage and transformation (Figure 1) [3**–5]. Thus, the physical adsorption of the supercritical gases in the pores of MOFs was the first recognized application of materials with record surface areas and pore volumes [6,7].

Further, improvement of the chemical and thermal stability of MOFs allowed to test them in adsorption-driven heat pumps [8**]. Introducing the proton conductivity allows to utilize MOFs in the fuel cells [9]. The use of redox-active metals provides improved charge transfer between the ligand and metal nodes and therefore makes them prospective as active materials for solar cells and water splitting. The current micro review describes the recent progress in above mentioned energy-related MOF applications, achieved in the last 2 years.

Gas storage

Ultra-high porosity of MOFs, expressed in surface areas and pore volumes prompt the community to comprehensive tests of newly synthesized materials for their gravimetric and volumetric capacities in high-pressure adsorption experiments with hydrogen and methane, which are considered as most sustainable energy carriers. The main target gravimetric and volumetric capacities to be achieved for adsorptive storage of hydrogen and methane are provided by US Department of Energy [10,11]. Currently, a large number of exhaustive review articles have been published on these topics [6,12]. With excess storage capacity of 308 mgg^{-1} of MOF at 110 bar and 298 K, DUT-49 (DUT states for Dresden University of Technology) is unbeatable record holder in terms of gravimetric excess methane storage capacity among all MOF materials [13]. In case of cryogenic hydrogen storage at 77 K, another Cu paddle-wheel based MOF NU-100 (NU – Northwestern University) occupy the first podium place with excess adsorption of 99.5 mgg^{-1} at 56 bar [14]. However, in order to achieve the optimal storage and working capacities in the real system, the volumetric capacity and the slope of the adsorption isotherm became critical characteristic properties. In this term, an interplay of porosity and density of the framework play a decisive role. Also a working capacity is a crucial parameter for adsorbents to be used in gas storage tanks. The best materials, which meets both above mentioned characteristics, MOF-519 and MOF-520 show a record of working capacity with 230 and 194 $cm^3\ cm^{-3}$ in the pressure range 5–80 bar [15]. It should be mentioned that archetypical HKUST-1 material shows working capacity of 200 $cm^3\ cm^{-3}$ in the same pressure range [7]. Very recently Yaghi and coworkers reported MOF-905, a new benchmark material, based on **ith-d** underlying net topology with working capacity of 203 $cm^3\ cm^{-3}$ [16]. Despite of ultra-high gravimetric and volumetric capacities of MOFs the real application in this field is still limited mostly by two factors: a) expensive price of the MOF materials; b) poor thermal conductivity of MOFs. The letter can be improved by introducing sophisticated

Figure 1



Current Opinion in Green and Sustainable Chemistry

Potential applications of MOFs for energy storage and transformation.

heat management systems or using flexible Metal-Organic Frameworks with intrinsic thermal managements [17**]. Recently BASF, the global leader in commercialization of MOFs, introduced a prototype truck equipped with natural gas fuel systems containing BASF MOF materials [18].

Adsorption heat transformations

Adjustable polarity of the inner surface of MOFs makes them very attractive as adsorbents for sustainable adsorption based heaters or coolers, so-called adsorption heat pumps. Although such devices are already commercialized and worked with zeolites and silica's as adsorbents, there is still a potential for efficiency improvement in terms of the optimization of adsorbents. Thus, mesoporous silica's have a moderate capacity in the working cycle, while microporous and hydrophilic zeolites required high temperatures in regeneration cycle, which is undesirable if waste heat with moderate temperatures or even solar heat is used for regeneration of adsorbent. The most prospective materials should show S-shaped isotherm of adsorptive fluid (usually water or alcohols) with intensive adsorption at moderate relative pressures. As a result, a couple of stable MOFs [19*], which meet above mentioned criteria, namely CAU-10-H (CAU – Christian-Albrechts-Universität) [20], MOF-808 [21*], CPO-27(Ni), aluminium fumarate [22] and MIL-160 (MIL - Materials Institute Lavoisier) [23*] were extensively tested for this kind of application. The results on adsorption mechanisms, use of various working fluids, evaluation of MOFs and performance analysis is summarized in the review article by Kapteijn and co-workers [8]. Besides working capacity, one of the most important material properties for such type of application is cycle stability. These properties are extensively tested by Henninger and co-workers [24–26].

Fuel cells

Because of the limited resources of fossil fuels on one hand, and constantly increasing energy demand on another hand, fuel cells could be a reasonable alternative for environmentally unfriendly internal combustion engines. The application of MOFs for the improving efficiency and decreasing the cost of the fuel cells can be considered in different aspects: a) MOFs for the hydrogen evolution reaction (see chapter below); b) MOFs as precursors for the oxygen reduction reactions; c) MOFs as proton conductive polymers for membranes [9]. Recently the group of Shimizu reports a novel water-stable Mg-based framework with abbreviation PCMOF-10 with proton conductivity exceeding 10^{-2} Scm^{-1} at 70 °C and relative humidity of 95% [27]. The hybrid composite membrane composed of sulfated MOF-808 material and Nafilon polymer shows improved long-range-order proton conductivity through utilization of superacidic sites [28]. The most important criteria, which influence the proton conductivity in MOFs, were summarized in the comprehensive review article by Kitagawa and co-workers [29**]. In the oxygen reduction reactions, MOFs appear as effective precursor for the synthesis of metal-doped nitrogen-rich porous carbons, catalytic activity of which is competing with highly effective and developed Pt-metal based oxygen reduction catalysts [30]. Very recently Dincă and co-authors reported $Ni_3(HITP)_2$ (HITP = 2, 3, 6, 7, 10, 11-hexaiminotriphenylene) as an intrinsically conductive metal-organic framework with 40 Scm^{-1}, which shows high catalytic activity in the oxygen reduction reactions comparable with M-N-C materials (M – 3d metal) [31**].

Solar cells

In the last decade the photovoltaic is considered as a prospective source of the green energy and alternative to nuclear and charcoal plants. Although the silicon-based solar panels are now widely commercialized, the search for a more efficient charge separation is still ongoing. Beside the organic perovskites with their record power conversion efficiency (PCE), MOFs, based on the redox-active metals are also considered for this type of application. Following this idea, Vinogradov and co-workers used Ti-based MOF MIL-125 (MIL – Materials Institute Lavoisier) as a composite with TiO_2 for the construction of the solar cell. As a result, authors succeed with increasing of PCE from 2.5% for pure TiO_2 to 6.4% for the composite containing 3% of MIL-125 in TiO_2 [32]. Another researcher team achieved 1.12% of PCE for Co-MOF/TiO_2 composite [33]. Different strategy to introduce the redox-center into the MOF-based solar cell was introduced by Morris and co-workers. RuDCBPY (RuDCBPY – ruthenium(II) bis-(2,2′-bipyridine)(2,2′-bipyridine-5,5′-dicarboxylic acid)) containing UiO-67 (UiO – Universitetet i Oslo) type MOFs were grown as thin films on TiO_2 as sensitizing materials [34]. The test cells, prepared using these type of materials show efficiency nearly 1%. Chang et al. show an advantage of MOF micropores for crystallization rendering of organic perovskite. Thus, using 5 v/v % of nanocrystalline Zr-based MOF-525 in the MOF/perovskite composite increases the PCE from 10.3 ± 0.3% for pure perovskite to 12.0 ± 0.5% for the composite material [35**]. The similar approach was very recently introduced by Zhang and co-authors by loading the $MAPbI_3$ (MA – methylammonium) into the orientated HKUST-1 (HKUST – Hong Kong University of Science and Technology) thin film. The composites show the comparable efficiency but improved moisture stability [36]. Summarizing, MOFs cannot compete with organic perovskites in the sense of PCE, but can improve an efficiency of the latter in the form of composites.

Hydrogen evolution reaction

One of the disadvantages of the renewable energy sources are fluctuations or discontinuity. Thus, in order to store the electrical energy, produced by solar plants, additional battery systems are required. In such case, considerable part of produced energy is losing during charging/discharging cycles. Therefore, the storage of the energy in the form of hydrogen, produced in the result of water splitting is a reasonable alternative to solar panels. In this field MOFs have been used in the several approaches: a) direct incorporation of the photosensitizer into the framework; b) adsorption of the photosensitizer into the pores of MOFs; c) the use of MOFs as precursors for the synthesis of the composite materials for electrodes. Following the first approach, Zhang and co-workers synthesized the Gd-based MOF with dye-like ligand showing prominent photocatalytic activity for hydrogen production under UV–vis irradiation. The performance of the materials could be even improved by a factor of 1.5 by depositing Ag as the co-catalyst [37]. Using the same approach, Chen et al. incorporated well known photosensitizer RuDCBPY and PtDCBPY into UiO-67, known as a water stable MOF material [38]. The second approach was followed by Hupp and co-workers. Incorporation of the NiS species into the pores of NU-1000 together with adsorbed rosa Bengal dye allows to achieve the hydrogen evolution rate of 4.8 mmol g^{-1} h^{-1} [39]. Embedding of 10 wt% CdS into the mesoporous MIL-101(Cr) material results in the evolution rate of 75.5 mmol $gCdS^{-1}$ h^{-1} [40]. Nasalevich et al. reported photosensitizer complex with composition $[Co^{III}Br_2(DOH)_2]$ (DOH – N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione 2-imine 3-oxime)), encapsulated into the pores of MIL-125 and enhance the hydrogen evolution in 20 times in comparison with pure MOF material [41**]. Some groups used MOFs as precursors for the synthesis of materials for the electrodes. Wang et al. pyrolysed the pillar-layered Ni-MOF, $Ni_2(bdc)_2$ted (bdc – 1,4-benzenedicarboxylic acid; ted – triethylene-diamine) in NH_3 with the aim of obtaining Ni nanoparticles embedded in a carbon matrix for hydrogen evolution reaction (HER) [42]. The use of the material in the electrolysis results in the production of hydrogen amount very close to theoretical value and with that ranks the material among the best noble metal free catalysts for hydrogen evolution reactions. The similar strategy was used independently by two different groups for obtaining in one case Co@N-C [43] and in another case Co@BCN [44] materials as catalysts for HER. In both cases ZIF-67 (ZIF – Zeolitic Imidazolate Framework) was used as precursor. The group of Zhang used MIL-101(Fe) material as precursor for the magnetic nanoparticles for highly efficient visible-light-driven hydrogen evolution [45].

Supercapacitors

The importance of long- and short-term storage of electrical energy boosted the battery and supercapacitor technologies in the last years. Since MOFs are substantially considered as insulators and there are only few exceptions reported yet, there are only few reports claiming the potential of MOFs for batteries and supercapacitors. In most cases the MOFs are used as precursors for the synthesis of corresponding metal oxides, which cannot be considered as a direct MOF application [46–52]. The exhaustive review article precisely describes the application of MOFs and their derivatives in batteries and supercaps [53]. At the same time, there are several recent reports, in which MOFs are directly involved in the supercapacitors. The group of Liu successfully tested nickel-based, pillared DABCO-MOFs (DMOFs) as electrode materials [54]. Ni-DMOF-ADC (ADC - 9,10-anthracenedicarboxylic acid electrode) showed specific capacitances of 552 and 438 F g^{-1} at current densities of 1 and 20 A g^{-1} with capacity retention of 98%. Co–LMOF, used as an electrode material by Wang et al., shows even maximum specific capacitance of 2474 F g^{-1} at 1 A g^{-1} in 1 M KOH. Very recently Dincă and co-workers used conductive ($Ni_3(HITP)_2$) MOFs as an active electrode material for supercapacitor, reach a very high surface area normalized capacitance of ~18 μF cm^{-2} and with that constructed first electrochemical double layer capacitor based on non-carbon active materials [55**].

Conclusions

The growing number of publications on energy-related applications of MOFs in the recent two years indicates a great progress in this field. New materials with record working capacity for methane storage were synthesized. Advantage of flexible MOFs for increasing the working capacity was highlighted. New chemically stable MOFs for adsorption heat transformations were tested. The advantages of MOF composites for solar cells and hydrogen evolution reaction were pointed out. Finally, the design and synthesis of conductive MOFs made a breakthrough in the emergent application fields like fuel cells and supercapacitors.

Acknowledgements

This work is supported by German Federal Ministry of Science and Education (BMBF Project No 05K16OD3).

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