



Metal Organic Frameworks for Advanced Applications

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1. Introduction

Metal organic frameworks (MOFs) are a class of porous materials with a modular structure. This allows for a very wide structural diversity and the possibility of synthesizing materials with tailored properties for advanced applications [1,2]. Thus, MOF materials are the subject of intense research, with strong relevance to both science and technology. MOFs are formed by the assembly of two components—cluster or metal ion nodes—which are also called secondary building units (SBUs), and organic linkers between the SBUs, usually giving rise to crystalline structures with an open framework and significant porous texture development. The main aim of this Special Issue of *Catalysts* is to present the most relevant and recent insights in the field of synthesis and characterization of MOFs and MOF-based materials for advanced applications, including adsorption, gas storage/capture, drug delivery, catalysis, photocatalysis, and/or chemical sensing.

2. Metal–Organic Frameworks for Advanced Applications

This Special Issue includes outstanding studies focused on the synthesis of new MOF-based materials with enhanced properties in terms of behavior and/or stability for adsorption and catalytic applications. In this sense, Khraisheh et al. [3] analyzed the potential application of two MOFs (SIFSIX-3-Ni and NbOFFIVE-1-Ni) for the separation of prime olefins from gas streams at different temperatures and pressures. Dynamic adsorption breakthrough tests were also conducted, and the stability and regeneration ability of the MOFs were established after eight consecutive cycles. The results revealed that SIFSIX-3-Ni can be considered an effective adsorbent for the separation of 10/90 v/v $C_{3}H_{4}/C_{3}H_{6}$ under the range of experimental conditions analyzed. The separated $C_{3}H_{6}$ was obtained with a 99.98% purity. Following with the stream purification applications, Mirante et al. [4] researched the catalytic efficiency of a layered coordination polymer to remove simultaneous sulfur and nitrogen compounds from fuels. An ionic lamellar coordination polymer based on a flexible triphosphonic acid linker achieved complete desulfurization and denitrogenation after 2 h using single model diesels, an ionic liquid as extraction solvent ($[BMIM]PF_6$) and H_2O_2 as oxidant. The lamellar catalyst showed a high recycle capacity for desulfurization. The reusability of the diesel/H₂O₂/[BMIM]PF₆ system catalyzed by a lamellar catalyst was more efficient for denitrogenation than for the desulfurization process when using a multicomponent model diesel. This behavior was not associated with the catalyst performance, but mainly due to the saturation of S/N compounds in the extraction phase. Salahuddin et al. [5] studied the use of MnO₂-doped ZIF-67 MOF for the electrocatalytic oxygen reduction reaction. The material showed an improved performance due to the incorporation of MnO₂ not only by enhancing the surface area, but also the conductivity. Chen et al. [6] reported photocatalytic CO_2 reduction with MIL-100(Fe)-CsPbBr₃ composites. The composites, with a high specific surface area, displayed an enhanced solar light response, and an improved charge carrier separation, resulted in an improved photocatalytic performance. Optimization of the relative composition, with the formation of a dual-phase CsPbBr₃ to CsPb2Br₅ perovskite composite, showed an excellent photocatalytic performance with 20.4 µmol CO produced per gram



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of photocatalyst during one hour under visible light irradiation. Palani et al. [7] explored the practical advantages and limitations of applying a UiO-66-based MOF catalyst in a flow microreactor for the catalytic hydrolysis of ethyl paraoxon, an organophosphorus chemical agent. It was concluded that tableting and sieving were viable methods to obtain MOF particles of a suitable size to be successfully screened under flow conditions in a microreactor, the optimal condition being catalyst particles with a sieved fraction between 125 and 250 µm. The synthesis of new materials was also addressed in this Special Issue. Li et al. [8] used tetracaboxylic acid, 3-(20,40-dicarboxylphenoxy)phthalic acid (H4dpa), as a multifunctional linker for the hydrothermal synthesis of new coordination polymers. Hence, a simple synthetic procedure led to the formation of a series of copper(II), manganese(II), and zinc(II) coordination polymers, whose catalytic activity was also explored in the mild cyanosilylation of benzaldehyde substrates with trimethylsilyl cyanide. The zinc(II)-based one functions as an effective and reusable heterogeneous catalyst to produce cyanohydrin products in up to 93% yields. Santibáñez et al. [9] described the aerobic oxidation of cyclohexene using heterometallic MOFs as catalysts in solvent-free conditions with oxydiacetic acid. It was concluded that the Langmuir surface area and the redox potentials were more important than the acid strength and acid sites of the studied MOFs, in terms of the referred catalytic performance. In addition, the reaction conditions were also shown to play an important role in the catalytic performance of the studied systems. In particular, the type of oxidant and the way to supply it to the reaction medium influenced the catalytic results. Jiao et al. [10] described the fast immobilization of human carbonic anhydrase II on Ni-based MOF nanorods with high catalytic performance. These results showed that the Ni-MOFs have great potential and high efficiency for the specific binding of immobilized enzymes. Pertiwi et al. [11] used MIL-101(Cr) MOF as a solid-acid catalyst for the solution conversion of biomass-derived glucose to 5-hydroxymethyl furfural (5-HMF). The substitution of Cr^{3+} by Fe^{3+} and Sc^{3+} in the MIL-101 structure resulted in more environmentally benign catalysts. It was observed that MIL-101(Fe) could be prepared, and the inclusion of Sc was possible at low levels (10% of Fe replaced). During extended synthesis times, the polymorphic MIL-88B structure was formed instead. The optimum material was a bimetallic (Fe,Sc) form of MIL-88B, which provides ~70% conversion of glucose with 35% selectivity towards 5-HMF after 3 h at 140 °C, which was a higher conversion compared to other heterogeneous catalysts reported in the same solvent. Padmanaban and Yoon [12] studied the surface modification of an MOF-based catalyst with Lewis metal salts for improved catalytic activity in the fixation of CO₂ into polymers.

The stability of MOFs is a crucial aspect only scarcely analyzed in the literature. In this sense, Gomez-Avilés et al. [13] reported a quantitative study of the water stability of NH₂-MIL-125(Ti), analyzing the ligand release along the contact time in water. This study demonstrates that NH₂-MIL-125(Ti) easily leached out over time while maintaining its structure. The effect of different thermal treatments applied to the MOF was investigated in order to enhance its water stability. Similarly, Wang et al. [14] synthesized Mn-MOF-74, which was further modified via two paths for enhanced water resistance. The results of selective catalytic reduction (SCR) performance tests showed that polyethylene oxide-polypropylene-polyethylene oxide (P123)-modified Mn-MOF-74 exhibited outstanding NO conversion of up to 92.1% in the presence of 5 vol.% water at 250 °C, compared to 52% for Mn-MOF-74 under the same conditions. It was concluded that the water resistance of Mn-MOF-74 was significantly promoted after the introduction of P123 and that the unmodified P123-Mn-MOF-74 was proven to be a potential low-temperature SCR catalyst.

This Special Issue contains several reviews, which analyzed promising approaches for the synthesis and advanced applications of MOFs. The combination of MOFs with other materials constitutes a promising methodology to synthesize materials with tunable and optimized characteristics for specific applications. Thus, Sun et al. [15] analyzed the synthesis of hybrid materials by supporting or incorporating polyoxometalates (POMs) into/onto MOFs. These hybrid materials combine the strong acidity, oxygen-rich surface, and redox capability of POMs while overcoming their drawbacks, such as difficult handling, a low surface area, and a high solubility. MOFs are ideal hosts due to their high surface area, long-range ordered structure, and high tunability in terms of the pore size and channels. In some cases, MOFs add an extra dimension to the functionality of hybrids. A study discussed their synthesis strategies, together with their major applications, such as their use in different catalytic applications. Jang et al. [16] described the use of MOFs as catalysts for air and water pollution environmental remediation, including an interesting approach focused on the synthesis of MOF-based filtering membranes by electrospinning using an eco-friendly polymer. Elhenawy et al. [17] reviewed the applications of MOFs in the carbon capture, focused on the applications of MOFs in the adsorption, membrane separation, catalytic conversion, and electrochemical reduction of CO₂ to provide new practical and efficient techniques for CO_2 mitigation. Finally, Liu et al. [18] described the recent advances in MOF-based nanocatalysts for photo-promoted CO₂ reduction applications. This review described the unique advantages of MOF-based materials for the photocatalytic reduction of CO_2 . The catalytic reaction process, conversion efficiency, as well as the product selectivity of photocatalytic CO₂ reduction while using MOF-based materials was thoroughly discussed, with a special focus to the catalytic mechanism of CO₂ reduction with the aid of electronic structure investigations.

It can be concluded that MOFs have undiscovered potential for multiple advanced applications. We will probably witness an explosion of different applications of these versatile and attractive materials in the coming years. It is likely that their use in real applications will be the key for their further development.

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