

MOFs as chemical nano-reactors: synthesis and stabilization of catalytically active metal species in confined spaces

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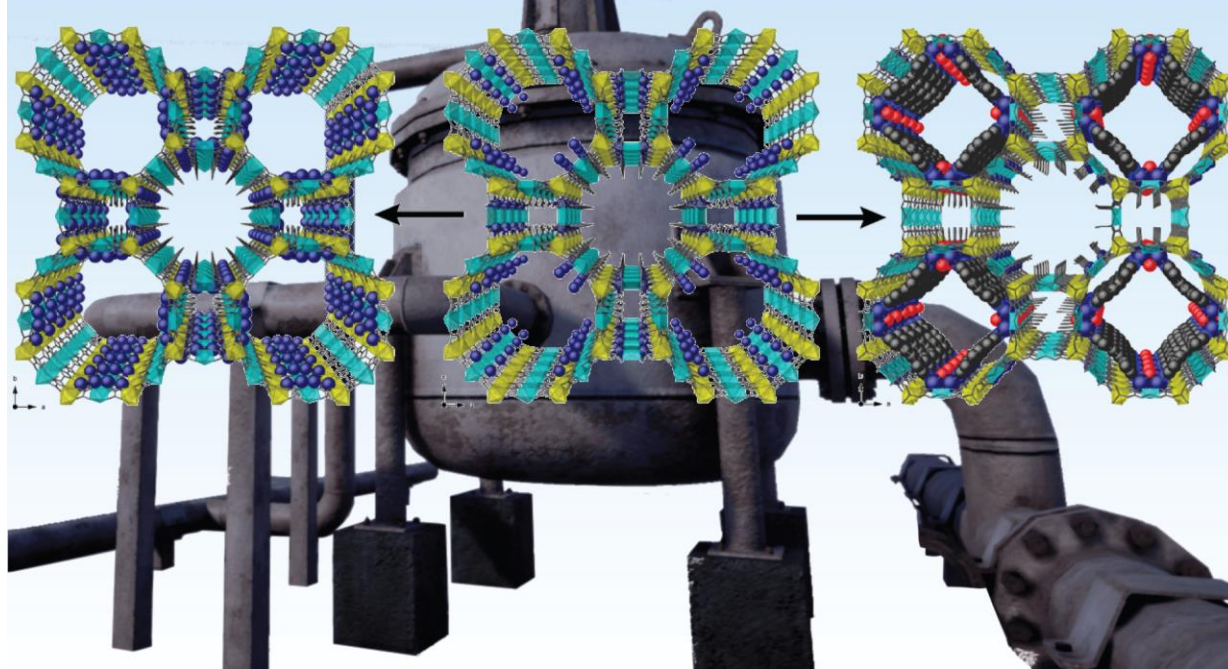
CONSPECTUS. Since the advent of the first metal-organic frameworks (MOFs), we have witnessed an explosion of captivating architectures with exciting physicochemical properties and applications in a wide range of fields. This, in part, can be understood under the light of their rich host-guest chemistry and the possibility to use single-crystal X-ray diffraction (SC-XRD) as basic characterization tool. Moreover, chemistry on preformed MOFs, applying recent developments in template-directed synthesis and post-synthetic methodologies (PSMs), has shown as a powerful synthetic tool to (i) tailor MOFs channels of known topology *via* single-crystal to single-crystal (SC-SC) processes, (ii) impart higher degrees of complexity and heterogeneity within them, and most importantly, (iii) improve their capabilities towards applications respect the parent MOFs. However, the unique properties of MOFs have been, somehow, limited and underestimated. This is clearly reflected on the use of MOFs as chemical nano-reactors, which have been barely uncovered. In this Accounts, we bring together our recent advances on the construction of MOFs with appealing properties, to act as chemical nano-reactors and be used to synthesise and stabilize –within their channels– catalytically-active species that otherwise could be hardly accessible. Firstly, through two relevant examples, we present the potential of the metalloligand approach to build highly robust and crystalline oxamato- and oxamidato-MOFs with tailored channels, in terms of size, charge and functionality. These are initial requisites to have a playground where we can develop and fully take advantage of singular properties of MOFs, as well as visualize/understand the processes that take place within MOFs pores, and somehow make structure-functionalities correlations and develop more performant MOFs nano-reactors. Then, we describe how to exploit the unique and singular features that offer each of these MOFs confined space for (i) the incorporation and stabilization of metals salts and complexes, (ii) the *in-situ* stepwise synthesis of sub-nanometric metal clusters (SNMCs) and (iii) the confined-space self-assembly of

supramolecular coordination complexes (SCCs), by means of PSMs and underpinned by SC-XRD. The strategy outlined here has led to unique rewards such as the highly challenging gram-scale preparation of stable and well-defined ligand-free SNMCs, exhibiting outstanding catalytic activities and the preparation of unique SCCs –different to those assembled in solution– with enhanced stabilities, catalytic activities, recyclabilities and selectivities. The results presented in this Accounts are just few recent exponents, but highly encouraging, of the large potential way of MOFs as chemical nano-reactors. More work is needed to found the boundaries and fully understand the chemistry in the confined space. In this sense, mastering the synthetic chemistry of discrete organic molecules and inorganic complexes have basically changed our way of live. Thus, achieving the same degree of control on extended hybrid networks will open new frontiers of knowledge with unforeseen possibilities. We aim to stimulate the interest of researchers working abroad different fields to fully unleash the host-guest chemistry in MOFs as chemical nano-reactors with exclusive functional species.

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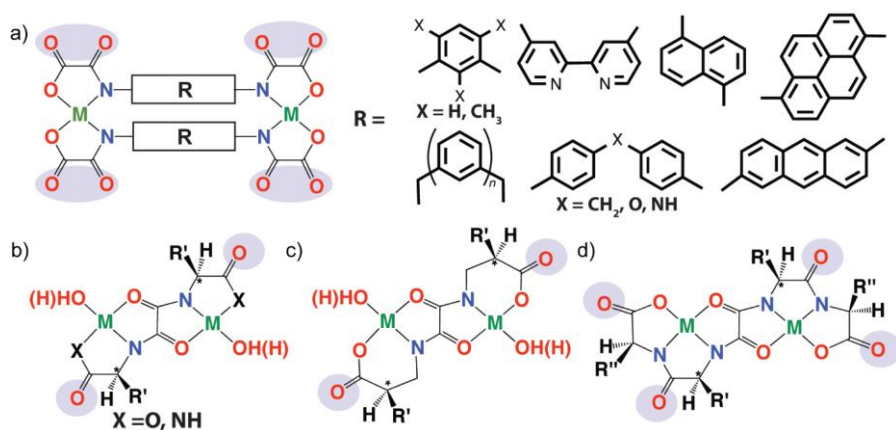


Introduction

Metal–organic frameworks (MOFs)^{1–4} are porous crystalline materials displaying unique remarkable features that translate into a large number of applications⁵ such as gas storage and separation,⁶ transport,⁷ catalysis,⁸ chemical sensing,⁹ light-harvesting/solar-energy conversion,¹⁰ water remediation,¹¹ or drug delivery.¹² MOFs stand out for high and tunable surface areas and pore sizes, as well as for dispersed active sites and functionalities within such porosity. These factors lead to a very rich host-guest chemistry,¹ where the interactions established between guest molecules and the functional empty space of MOFs originate most of these thrilling applications. In this sense, pre- or post-synthetic¹³ fine-tuning of the MOF's empty space results in a modulation of the affinity with guest molecules.¹⁴ Overall, guest molecules can be either inserted¹⁵ “as a whole” –including both the *ship-in-a-bottle* and the *bottle-around-ship* strategies– or constructed within the channels of the MOFs, acting as chemical nano-reactors,¹⁶ using the so-called post-synthetic methods (PSMs).¹³ In this respect, the vast majority of work have been devoted to the insertion approach.¹⁵ Conversely, few examples have been published about the step-by-step preparation of complex molecules within the tunable functional channels of MOFs.¹⁴ Thus, more examples are mandatory to validate this strategy and to overcome several remaining challenges such as the gram-scale preparation of these host-guest materials and their proper characterization by fully exploiting the possibility to use single-crystal X-ray diffraction.^{17–19}

Among the wide diversity of possible functional entities that can be inserted/synthesized within MOFs, catalytically active species are particularly suited considering the intrinsic features of these porous materials. MOFs have become complementary to traditional heterogeneous catalysts, *i.e.* zeolites.^{20,21} The catalytic activity of MOFs⁸ can be originated from the constituting building blocks –open metal sites and organic linkers– of the coordination network or from the guests

embedded into their pores. With regard to guest species –the central topic of this manuscript– MOFs offer advantages to support catalytically-active metal cations,²² complexes,²³ small clusters²⁴ and nanoparticles.^{25,26} Despite MOFs –as compared to other solid catalysts such as zeolites and other microporous silicoaluminos materials with embedded metal species^{27–29}– present thermal and chemical stability limitations, they offset these limitations with a rich structural variety –due to the large number of known metal centers/secondary building units (SBUs) and organic linkers– and high tunable porosity, which ease the accessibility of active sites for catalysis, facilitate the transport of substrates and products and offer size- and shape-selective catalysis. Furthermore, the crystalline nature of MOFs allows an uniform distribution of identical catalytic species, which, unlike other porous materials, can be, theoretically, also characterized by single-crystal X-ray diffraction^{19,30} (SC-XRD), thus facilitating the identification of active catalysts and the study of reaction mechanisms.¹⁸ However, despite these remarkable advantages, SC-XRD has been scarcely used to elucidate the crystal structures of the host-guest catalytically-active materials. In a similar way, the use of MOFs as chemical reactors for the step-by-step *in-situ* synthesis and stabilization of catalytically active species has been only barely explored,³¹ since many MOFs break down after the use of PSMs.



SCHEME 1 Selected examples of oxamato- (a) and oxamidato-based ligands (b-d) derived from aromatic diamines (a), α - (b) and β -amino acids (c) and oligopeptides (d). Shading areas highlight their free carbonyl-oxygen atoms.

Preparation of Robust and Crystalline Metal-Organic Frameworks

In this context, and aiming to unveiling the potential of MOFs as nano-reactors, we have developed a strategy based on the use of highly robust and crystalline MOFs that allow a fine-tuning of their porous empty space in size, shape, charge and functionality. In particular, we have focused on oxamato- and oxamidato-based MOFs³² as suitable candidates, as they have demonstrated to be resistant in a wide variety of solvents and conditions,³³ and thus, to resist PSMs maintaining their structure and crystallinity.³⁴ The preparation of oxamato-based MOFs follows a metalloligand design strategy,³² which allows –to a certain extent– a better control of the final structure of the porous framework^{32,33} and a proper functionalization of the MOF channels.^{30,35–37} The synthetic strategy relies on the initial preparation of preformed stable oxamato- and oxamidato-based metal complexes that can be employed, ultimately, as robust building blocks to form highly-stable and crystalline heterobimetallic MOFs, exploiting their free carbonyl-oxygen atoms (Scheme 1). The modularity of this design strategy enables that the oxamate/oxamidate ligands –and ultimately the MOF channels– can be directly functionalized by choosing the suitable amine-derivative precursor (Scheme 1). The outstanding features of these MOFs makes them ideal candidates for the straight insertion and stabilization of highly reactive catalytic species^{38–40} and their use as chemical nano-reactors for the step-by-step preparation of functional catalytically active species within the confined functional space (Figure 1).

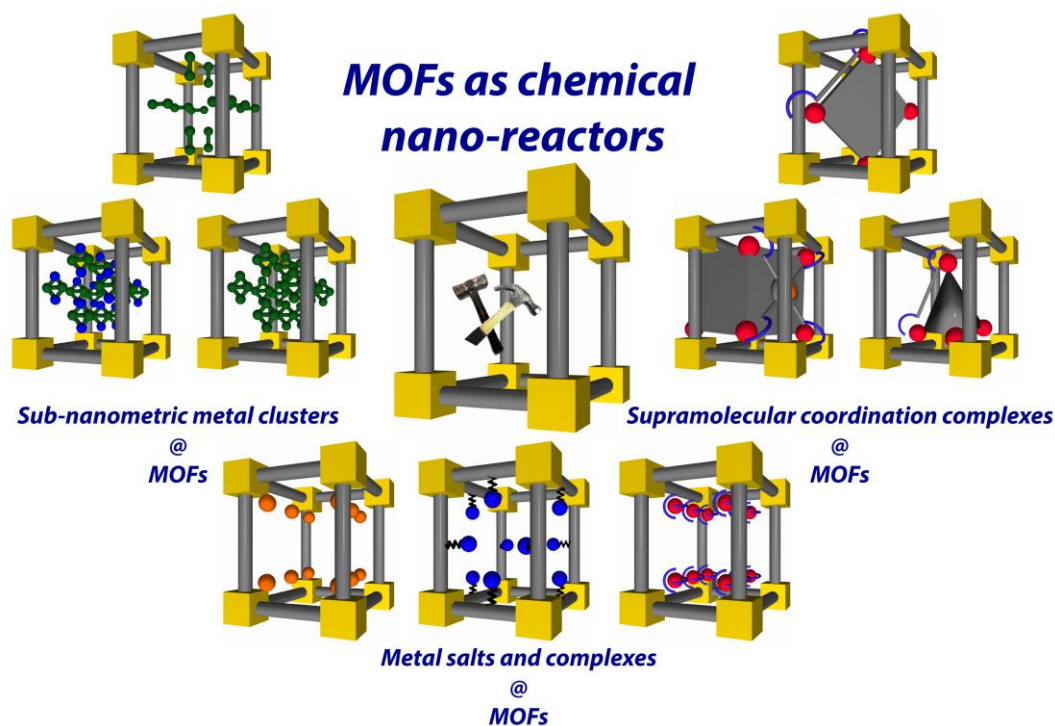


FIGURE 1. Overview of the three main blocks presented in this account where MOFs support catalytically-active species.

In this Account, we describe our advances related to (i) the insertion and stabilization of catalytically-active metal salts and complexes, (ii) the *in-situ* step-by-step chemical synthesis of subnanometer metal clusters and single atoms within their confined functional space and (iii) the MOF-driven self-assembly of catalytically active supramolecular assemblies, using different types of PSMs. To this end, we have selected an anionic oxamato-based MOF, of formula $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\} \cdot 54\text{H}_2\text{O}^{34}$ [where $\text{Me}_3\text{mpba}^{4-} = N, N'$ -2,4,6-trimethyl-1,3-phenylenebis(oxamate)] (Figure 2a) and a neutral oxamidato-based MOF of formula $\{\text{Ca}^{\text{II}}\text{Cu}^{\text{II}}_6[(S,S)\text{-methox}]_3(\text{OH})_2(\text{H}_2\text{O})\}^{37,38}$ [where methox = bis(*S*)-methionine oxalyl diamide] (Figure 2b). These two MOFs present, as common remarkable features, high structural stability and crystallinity with the appropriate empty space to host and stabilize different catalytically-active species. The combination of these characteristics allows these porous materials to resist the successive PSMs used to insert or synthesize the different catalytically species within the channels,

while retaining their crystallinity, which permits the use of SC-XRD for the proper characterization of these host-guest species.

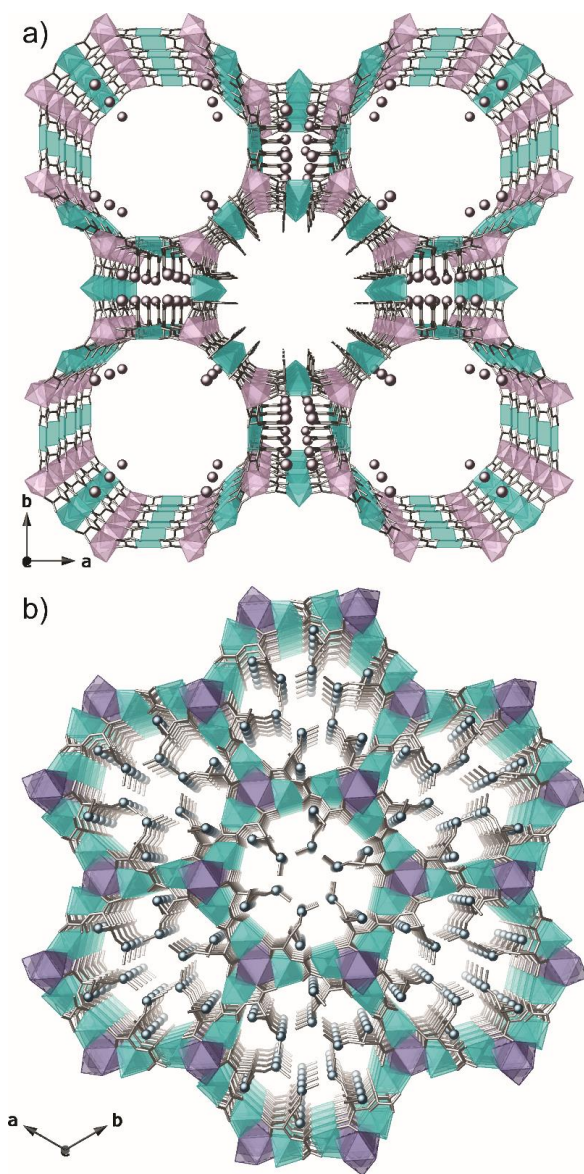


FIGURE 2. SC-XRD structures of the $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\}\cdot 54\text{H}_2\text{O}$ (a) and the $\{\text{Ca}^{\text{II}}\text{Cu}^{\text{II}}_6[(\text{S,S})\text{-methox}]_3(\text{OH})_2(\text{H}_2\text{O})\}$ (b) 3D networks. Copper, nickel and calcium atoms from the coordination networks are represented by cyan, pink and dark blue polyhedral whereas nickel cations and sulphur atoms within the pores are depicted by pink and blue spheres.

Insertion and Stabilization of Catalytically-Active Metal Salts and Complexes

Homogeneous catalysis⁴¹ provides, as the most characteristic feature, that both catalyst and reactants are present in the same phase and exhibit, consequently, high catalytic activities. However, very often, these catalytically-active species present different drawbacks such as difficulty to separate them from the resulting products and lower recyclability.⁴¹ A good manner to overcome these limitations is to support these species in porous solids,^{42,43} thus constituting an heterogeneization process. Among porous solids, MOFs are particularly suitable for the encapsulation and stabilization of these catalytically active species, on the basis of the mentioned fascinating host-guest chemistry and the possibility to characterize the host-guest materials by using SCXRD. In this context –depending on the physical and chemical features of MOFs channels–, catalytically-active species can be retained within the MOF pores either electrostatically –when the framework and the inserted molecules exhibit opposite charge– or by anchoring them to the MOF walls taking advantage of binding affinity with functional groups decorating the channels.

The first illustrative example is the efficient insertion and immobilization of catalytically-active gold salts within the *L*-methionine-derived MOF $\{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\}$.³⁸ Aiming at evaluating the efficiency of this porous material –exhibiting functional channels densely decorated with thio-ether groups derived from the natural amino acid *L*-methionine (Figure 2a)– in the selective capture of AuCl and AuCl₃ salts from electronic wastes, two novel host-guest adsorbates with formulas $(AuCl_3)_3@ \{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\} \cdot 9H_2O$ (**Au^{III}@1**) and $(AuCl)_2@ \{Ca^{II}Cu^{II}_6[(S,S)\text{-methox}]_3(OH)_2(H_2O)\} \cdot 3H_2O \cdot 3CH_3OH$ (**Au^I@1**) were obtained (Figure 3). The high robustness, crystallinity and proper functionalization of the channels of this MOF did not only allowed that the MOF resisted the PS insertion of gold salts in very high loadings (15-20 wt%), but also permitted the use of SC-XRD to unveil the crystal structures of both host-guest

adsorbates (Figure 3). A careful analysis of the crystal structure of $\text{Au}^{\text{III}}@1$ and $\text{Au}^{\text{I}}@1$, reveals that each gold atom is anchored to the channels by interacting, as expected, with sulphur atoms from the amino acid residue. This is of two-fold relevance from a catalytically application viewpoint, as it enables to have a precise control of the MOF loading and reduces the risk of leaching during catalysis. In addition, the crystal structures of $\text{Au}^{\text{III}}@1$ and $\text{Au}^{\text{I}}@1$ also showed high flexibility for the thio-alkyl residues, that are able to adapt to the different oxidation state of the inserted guest molecule, which is a remarkable feature also thinking of catalysis. Notice that the relative weight of Au(I) and Au(III) in the MOF is up to 15%, exceptionally high for a solid and not far from the Au wt% in classical organometallic complexes with widespread use in catalysis (i.e. AuPPh_3Cl and $\text{AuPPh}_3\text{NTf}_2$).

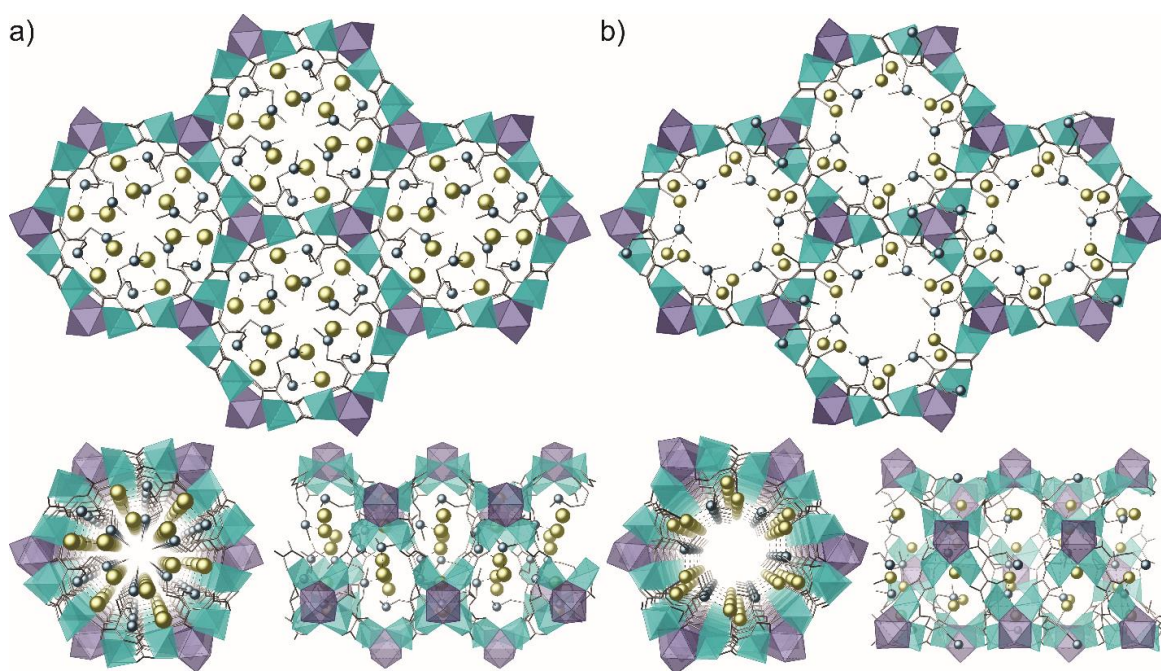


FIGURE 3. Perspective views of the porous structures of $\text{Au}^{\text{I}}@1$ (a) and $\text{Au}^{\text{III}}@1$ (b) determined by single-crystal X-ray diffraction. Colour codes idem to Figure 2 with the inclusion of gold spheres for gold metal atoms. Adapted with permission from ref. 38. Copyright 2016 ACS.

The hydroalkoxylation of alkynes can be efficiently catalyzed by a plethora of gold salts in solution. However, they usually agglomerate under reaction conditions to form inactive NPs. We tested **Au^{III}@1** and **Au^I@1** in the cyclization/ketalization of 4-pentyn-1-ol observing high yields and selectivities, and higher reusability –at least 5 catalytic cycles without apparent loss of catalytic activity– due to the strong Au-S interactions that prevented any leaching of gold without poisoning the catalyst.

Broadening the applicability to anionic frameworks, the Ni^{II}₂{Ni^{II}₄[Cu^{II}₂(Me₃mpba)₂]₃}·54H₂O MOF³⁴ was also used as a vessel to encapsulated cationic Ru(III) and Fe(III) hexaaquo-complexes by using a solid–state PS cation exchange. In so doing, two novel host-guest adsorbates with formulas $[\text{Ru}^{\text{III}}(\text{H}_2\text{O})_6]_{0.83}[\text{Ru}^{\text{III}}_2(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_{10}]_{0.25}\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\}\cdot 61\text{H}_2\text{O}^{40}$ (**[Ru(H₂O)₆]³⁺–MOF**) and $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6][\text{Fe}_2^{\text{III}}(\mu\text{-O})_2(\text{H}_2\text{O})_6]_{1/2}\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\}\cdot 72\text{H}_2\text{O}^{39}$ (**[Fe(H₂O)₆]³⁺–MOF**) (Figure 4a) were obtained. SC-XRD showed that, apart from electrostatic interactions, [M^{III}(H₂O)₆]³⁺ molecules are also retained, within larger octagonal channels of the MOF (*ca.* 2.2 nm), by arrays of H–bonds – between the water molecules surrounding M^{III} ions and the oxygen atoms of the channels– ensuring fixation and stabilization of these catalytically-active entities within the channels (Figures 4a right, 4b and 4c). Interestingly, the simplicity of the synthetic soft procedure used –consisting basically on suspending the preformed MOF in Ru(III) or Fe(III) aqueous solutions– allows the gram-scale preparation of these host-guest compounds.

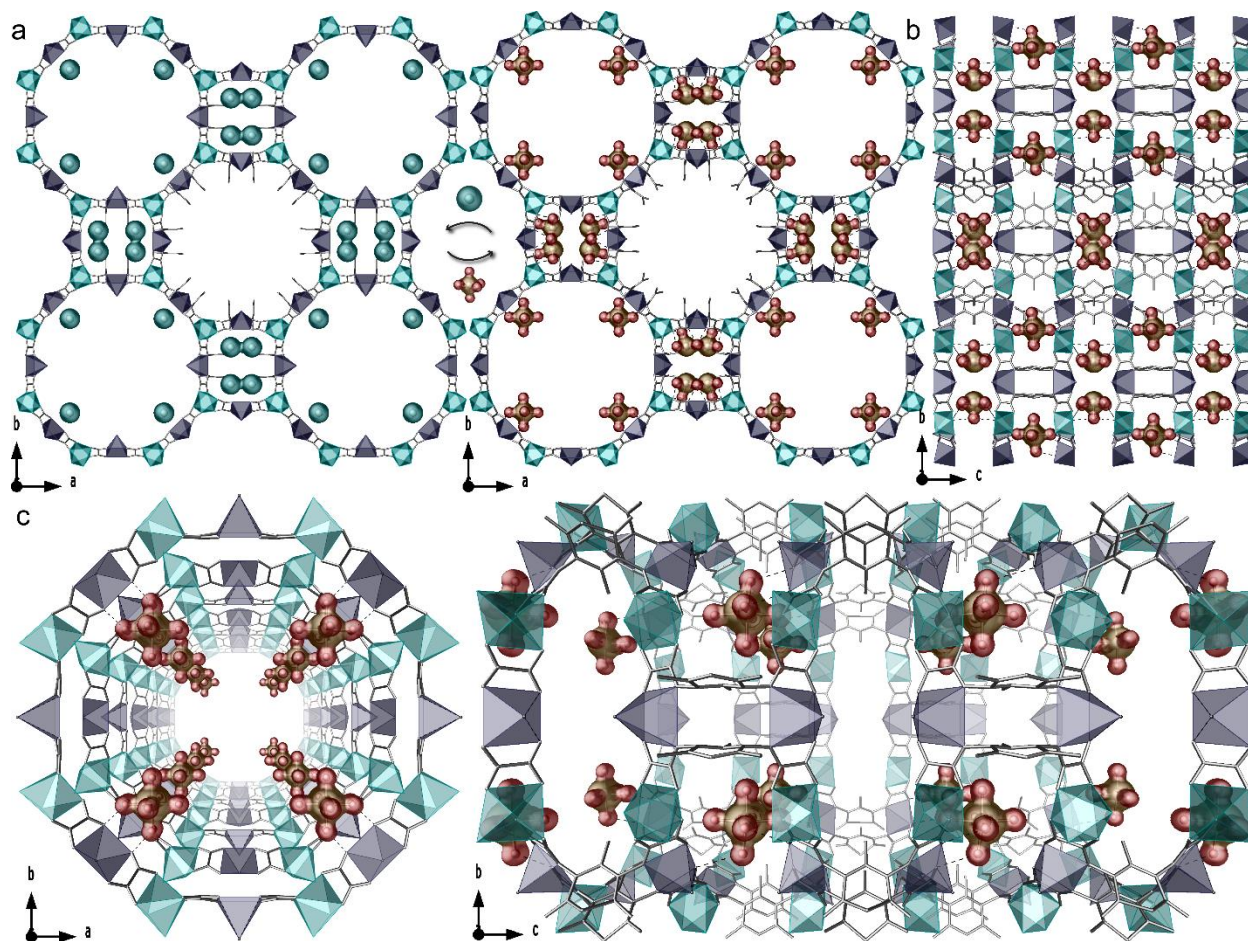


FIGURE 4. (a) Views of the crystal structures of $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\} \cdot 54\text{H}_2\text{O}$ (left) and the resulting $[\text{M}(\text{H}_2\text{O})_6]^{3+}\text{-MOF}$ ($\text{M} = \text{Fe}$ and Ru) after the cation exchange. (b and c) Views of one channel of $[\text{M}(\text{H}_2\text{O})_6]^{3+}\text{-MOF}$ emphasizing the stabilizing interactions (dotted lines). Copper(II) and nickel(II) cations from the coordination network are represented by cyan and blue polyhedra, respectively, whereas the ligands are depicted as gray sticks. M^{3+} cations and water molecules hosted in the channels are represented by gold and red spheres with surface, respectively. Adapted with permission from refs. 39 and 40. Copyright 2018 ACS.

Aiming at confirming the enhanced catalytic activity and reusability of these supported complexes, different experiments were carried out. Ruthenium compounds are known to perform well in different alcohol dehydrogenation reactions.⁴⁴ However, their implementation is still weak in dehydrogenating imination reactions,⁴⁵ as the H_2 produced during the reaction tends to further

reduce the imine to amine. In fact, among the wide variety of Ru compounds that were tested in solution, only $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ in HBF_4 aqueous solution showed catalytic activity for imine formation, most-likely due to its acidity, accessibility and water-stability. However, such hexa-aquocomplex in homogeneous phase suffered a rapid degradation under reaction conditions. In order to overcome such limitation, $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ was firstly supported in alumina, silica, titania and magnesia, but no real catalytic and stability improvement took place. The degradation was only attenuated by encapsulating the $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ complex in anionic faujasite-type zeolites, and much improved when supported in the $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\} \cdot 54\text{H}_2\text{O}$ MOF (Figure 4a). Indeed, the resulting $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}\text{-MOF}$ catalyst gave high yields (*ca.* 90%) for the imination of 4-vinylbenzyl alcohol and 3,4-dimethylaniline, which is the highest among all Ru catalysts tested. No leaching processes and/or degradation of the catalyst were observed in toluene as solvent and, consequently, much better recyclability (at least 5 cycles without loss of catalytic activity) was observed. Here, it must be underlined the key role played by SC-XRD to unveil both, the crystal structures of the host-guest material and also to follow the cation exchange process (Figure 4a).

Dealing with $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}\text{-MOF}$, the resolution of its crystal structure proved invaluable not just to characterize the material but also to choose the most appropriate catalytic reaction. Indeed, the resulting stabilized $\text{Fe}^{\text{III}}\text{-O}$ sites were capable to catalyze efficiently and chemoselectively the acetylene hydrogenation in ethylene flows under simulating front-end industrial conditions⁴⁶ (Figure 5). These results confirm that acetylene is efficiently and selectively hydrogenated by such active $\text{Fe}^{\text{III}}\text{-O}$ entities.

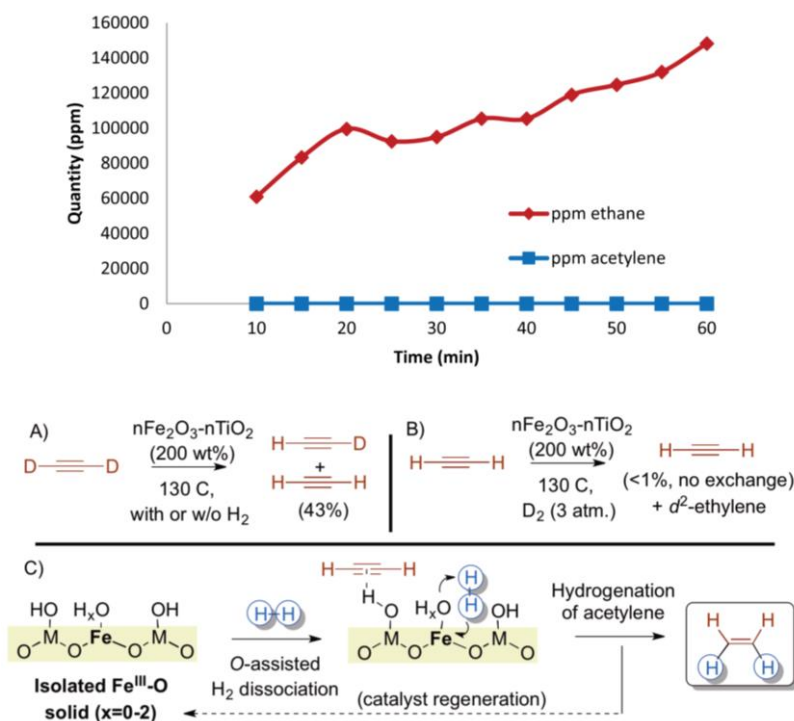


FIGURE 5. (Top) Acetylene (blue squares) and ethane (red rhombuses) amounts in ppm during the continuous hydrogenation of acetylene (1.2%) in an ethylene flow catalyzed by $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}\text{-MOF}$ at 150 °C. (Bottom) Reaction scheme for the hydrogenation of acetylene (A and B) with a plausible mechanism (C). Adapted with permission from ref. 39. Copyright 2018 ACS.

Overall, the presented strategy illustrates a very straightforward way to obtain, in multigram-scale, largely accessible and stabilized within MOFs channels catalytically-active metal complexes and salts. In addition, the possibility to unveil the crystal structure of these host-guest materials goes beyond providing cutting-edge characterizations of such host-guest systems, which is of fundamental importance to select the most appropriate catalytic reactions and to unveil their mechanisms.

Step-by-step Chemical Synthesis of Subnanometer Metal Clusters and Single Atoms within MOFs

The emergence of metal nanoparticles⁴⁷ (MNPs) at the end of last century, resulted, into a paradigmatic shift in science. More recently, a series of works have unveiled exceptional properties –such as luminescence, biocompatibility and antitumoral and superlative catalytic activities– for small aggregations of metal atoms, so-called sub-nanometer metal clusters^{48,49} (SNMCs), and single metal atom catalysts (SACs).⁵⁰ However, the characterization and the gram-scale preparation of stable and well-defined ligand-free SNMCs and/or SACs is still highly challenging. This, in part, is consequence of their tendency to agglomerate into larger MNPs due to the lack of stabilizing/blocking ligands, whose presence, in turn, decreases greatly their catalytic activity. In this context, a variety of selected MOFs with tailored properties such as high robustness, crystallinity and appropriate porosity, might be the perfect platforms –owing to the previously described host-guest chemistry– to synthesize, stabilize and characterize SNMCs within their pores. Our synthetic strategy is divided in two main blocks: *(i)* The preparation of highly robust and crystalline MOFs with appropriate functional empty space and *(ii)* the application of PSMs for the assembly of such unique ultrasmall SMNCs or the reduction and stabilization of SACs, which are very difficult to be obtained and, especially, stabilized, outside the channels.

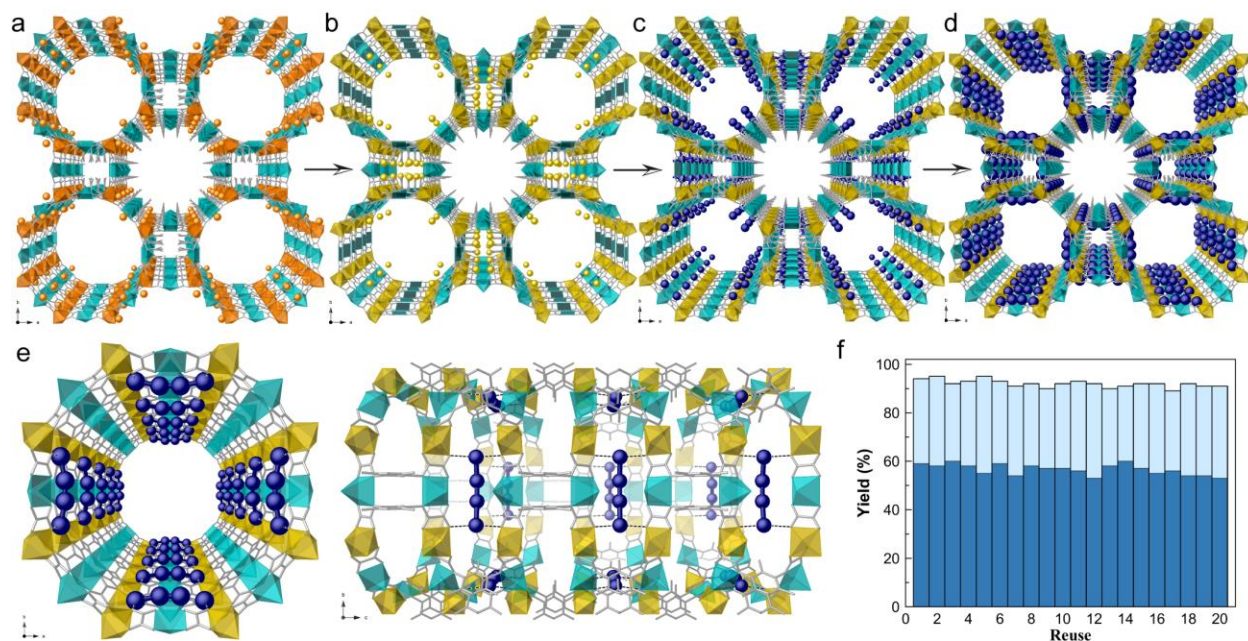


FIGURE 6. (a-d) Three-step synthesis of **Pd₄@MOF**. (e) Perspective views of a channel of **Pd₄@MOF** emphasising the stabilising interactions. (f) shows the reuses of **Pd₄@MOF** for the Buchner ring expansion reaction with “at once” (dark blue) and pump (light blue) additions. Adapted with permission from ref. 51. Copyright 2017 Springer Nature.

The first example reported was the clean multigram-scale preparation of well-defined ligand-free Pd₄ clusters within the channels of the previously described anionic Ni^{II}₂{Ni^{II}₄[Cu^{II}₂(Me₃mpba)₂]₃}·54H₂O MOF.⁵¹ The process involved three consecutive PS steps: (i) A transmetallation and cation exchange processes involving the replacement of all magnesium(II) cations in an ancestor MOF of formula Mg^{II}₂{Mg^{II}₄[Cu^{II}₂(Me₃mpba)₂]₃}·54H₂O MOF to give the CuNi MOF (Figures 6a and 6b). (ii) The exchange of the nickel(II) cations within the pores by palladium(II) ones (Figure 6c). (iii) The controlled insertion of the reducing agent (NaBH₄) to synthesize *in-situ* the naked Pd₄ NCs (Figure 6d). Here, SC-XRD played a two-fold fundamental role, elucidating the crystal structure in every step and endowing us with key insights on two structural factors that seem to be at the origin of such controlled formation of SMNCs –*i.e.* number of inserted cations and their organization in the confined space. Figure 6c allows the observation of a very homogeneous distribution of Pd²⁺ cations along the channels, which are

situated in specific positions interacting with the carboxylate-oxygen atoms from the network and limited in number by the anionic charge of the MOF. As a result, the palladium atoms have restrained movement capacity which favours the formation of SMNCs and prevents their aggregation into larger MNPs. The Pd₄ NCs are also stabilised by different weak supramolecular interactions (Figure 6e) which impose such uncommon linear structure and prevent their leaching during catalytic processes.

The resulting [Pd₄]²⁺@MOF exhibits outstanding catalytic behaviour in different carbene-insertion reactions, with TONs at least one order of magnitude higher than those of the *state-of-the-art* catalysts. In addition, the MOF-supported Pd₄ NCs exhibited great recyclability (at least 20 catalytic cycles without apparent loss of catalytic activity, Figure 6f) and they could be also used in-flow, simulating the conditions of a continuous reactor, thus opening the window for their potential real application.

The same strategy was used to stabilise Pt₁¹⁺ SACs,⁵² within the same anionic MOF used for the growth of Pd₄ NCs. In this case, following a two-step PS process –consisting first on the insertion of Pt²⁺ cations within MOF channels and second, their *in-situ* reduction with NaBH₄– the gram-scale synthesis of structurally and electronically well-defined Pt₁¹⁺ SACs was achieved (Figure 7a). SC-XRD gave us precious insights of how water molecules surrounding Pt₁¹⁺ atoms play a two-fold role by stabilizing and isolating the Pt(I) SACs, and also by regulating such uncommon charge for the Pt atoms as well as the adsorption of reactants (*vide infra*). Indeed, all these points have important implications in the catalytic activity of the Pt₁¹⁺@MOF. This hybrid material is capable to catalyze, very efficiently, the low-temperature WGS (water-gas shift reaction): CO + H₂O → CO₂ + H₂ (Figure 7b). Remarkably, the combination of experimental results and theoretical calculations –based on the real crystal structure of the final Pt₁¹⁺@MOF–

allowed to unveil the plausible mechanism governing such catalytic reaction. Thus, at least two water molecules surrounding the Pt_1^{1+} SAC participate in the reaction attacking CO, and ultimately, both oxygen atoms in CO_2 come from these water molecules (Figure 7c).

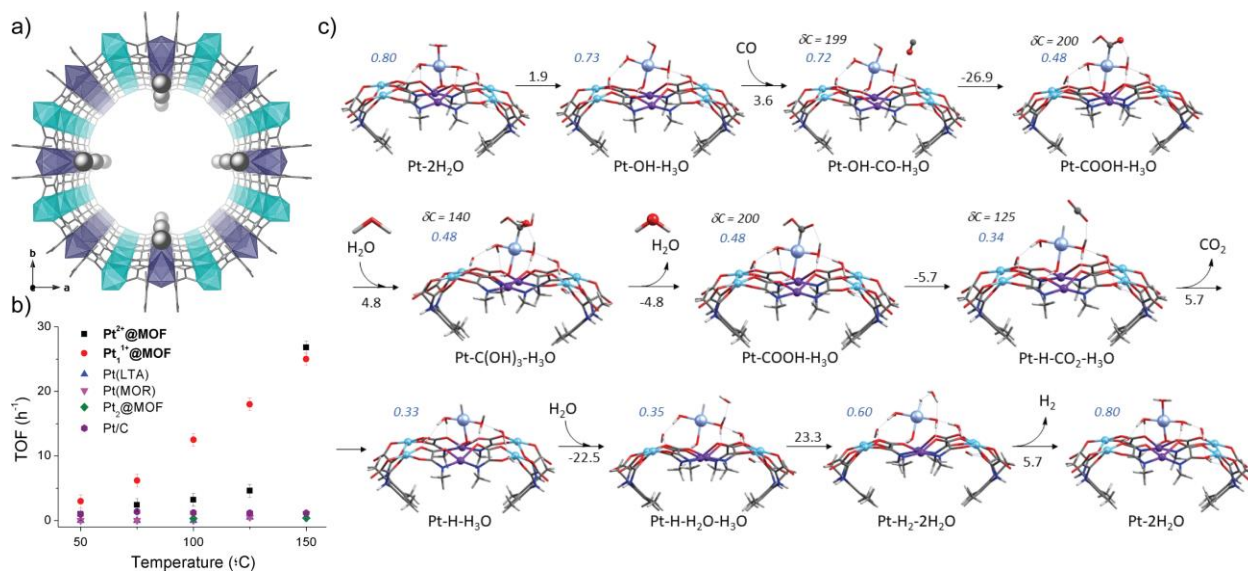


FIGURE 7. a) View of a single channel of $\text{Pt}_1^{1+}@MOF$. Pt atoms are represented as grey spheres. b) Temperature-programmed WGS catalyzed by $\text{Pt}_1^{1+}@MOF$ (red dots) compared to other Pt-supported catalysts. (c) Plausible mechanism of the WGS catalyzed by $\text{Pt}_1^{1+}@MOF$. Adapted with permission from ref. 52. Copyright 2018 John Wiley and Sons.

A very similar strategy, was also carried out with the *L*-methionine-derived MOF of formula $\{\text{Ca}^{\text{II}}\text{Cu}^{\text{II}}_6[(\text{S},\text{S})\text{-methox}]_3(\text{OH})_2(\text{H}_2\text{O})\}$ (Figure 2b). In so doing, the gram-scale synthesis and stabilization of Pt_2^0 NCs,⁵³ homogeneously distributed and densely-packaged within the channels of the MOF, was achieved (Figure 8). The synthetic approach consisted on the application of a two-step PS process. Firstly, the selected MOF was soaked within $\text{K}_2[\text{PtCl}_4]$ solutions. In agreement with the well-known affinity of sulphur atoms for platinum ions, it was observed a very efficient capture and homogeneous distribution of Pt^{2+} salts along the channels (Figure 8, left). The homogeneous distribution and limited number of metal atoms –by the number of sulphur containing groups– together with the confined space offered by these channels and the restrained

movement of these metal salts –effectively anchored to the functionalities of the walls– allowed the formation of ligand-free ultrasmall SNMCs instead of larger MNPs. Indeed, after the introduction of the reducing agent (NaBH_4) in the second PS step, well-defined Pt_2^0 clusters units were obtained in the final host-guest material $\text{Pt}_2^0@MOF$ (Figure 8, right). Again, the resolution of the crystal structures of these host-guest materials allowed to propose a plausible formation mechanism for such tiny Pt_2^0 NCs, where the flexibility of thio–alkyl groups play a key role approaching two neighboring Pt^{2+} –S units to build the Pt_2^0 ones.

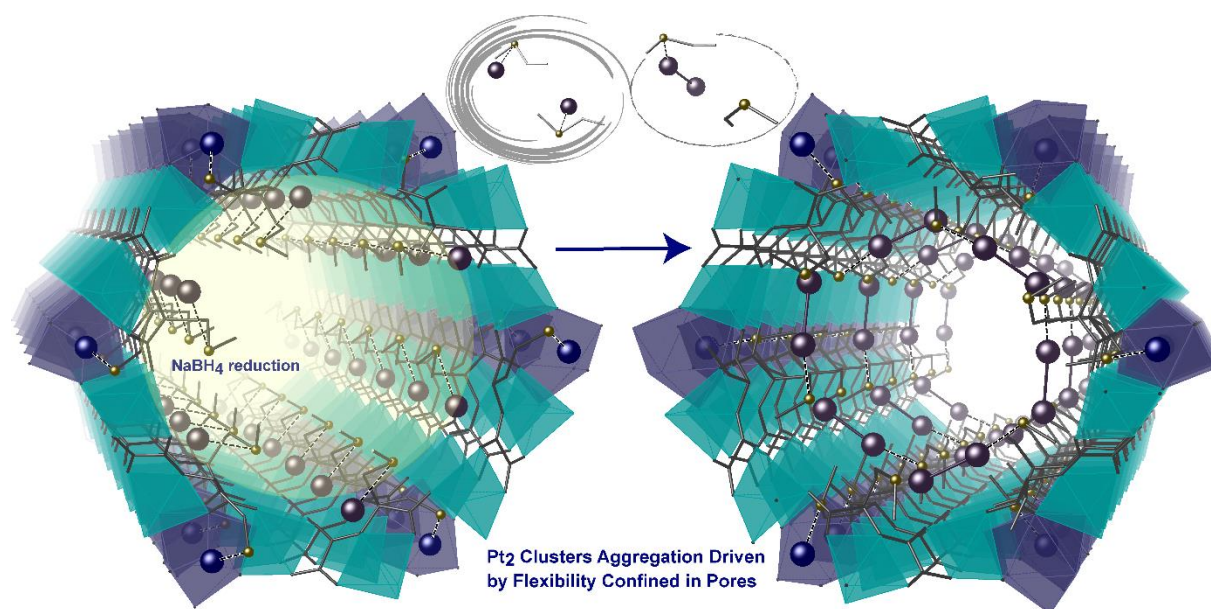


FIGURE 8. Views of one single channel of $\text{Pt}^{2+}@MOF$ (left) and $\text{Pt}_2^0@MOF$ (right) underlining the proposed aggregation of Pt^{2+} atoms during the reduction process to generate the Pt_2 clusters in $\text{Pt}_2^0@MOF$ (right). Color codes idem to Figure 2 with the inclusion of blue spheres for platinum metal atoms. Dashed lines represent the $\text{Pt}\cdots\text{S}$ interactions. Adapted with permission from ref. 53. Copyright 2018 John Wiley and Sons.

The catalytic activity of $\text{Pt}_2^0@MOF$ was evaluated for three energetically–costly industrial gas-phase reactions such as the hydrogen cyanide (HCN) production, alkene hydrogenations and CO_2 methanation. $\text{Pt}_2^0@MOF$ was capable to catalyze efficiently the three processes at low-temperatures (25 to 140 °C), confirming the great capacity of these SNMCs to activate such

refractory molecules. For instance, **Pt₂⁰@MOF** exhibited outstanding catalytic activity for the room temperature formation of NH₄CN from NH₃ and CO, revealing the largest catalytic activity among the wide variety of Pt catalysts tested (including Pt salts, complexes and supported NPs). On the other hand, **Pt₂⁰@MOF** also catalyzes very efficiently the Sabatier reaction (CO₂ methanation: CO₂ + 4H₂ ⇌ CH₄ + 2H₂O) at temperatures lower than 150 °C. This remarkable high activity of Pt₂⁰ in the low-temperature region agrees with their low calculated energy of activation (E_a = 35 KJ mol⁻¹), which is about one half of that shown by commercial catalysts (E_a ≈ 65 KJ mol⁻¹). Finally, **Pt₂⁰@MOF** was also capable to catalyze, efficiently, the ethylene hydrogenation in flow with a low calculated activation energy (E_a ≈ 32 KJ mol⁻¹), which allows a reaction temperature of 60 °C, below that used by catalysts such as MNPs (200–400 °C).

These results validate the proposed strategy for the MOF-driven gram-scale preparation and stabilization of well-defined ligand-free SNMCs and/or SACs with outstanding catalytic activity for different reactions of interest. The synthetic approach relies on the use of highly crystalline and robust MOFs that allow both the use of PSMs and SC-XRD. A fine control of the porous empty space is mandatory to control the growth of SNMCs and/or SACs, since it regulates the number of metal atoms inserted and its homogeneous distribution within MOFs channels.

MOF-Driven Self-Assembly of Catalytically Active Supramolecular Assemblies

Supramolecular Chemistry⁵⁴ has offered many examples of Supramolecular Coordination Complexes (SCCs), which exhibit fascinating architectures and thrilling functionalities. However, the application of SCCs in catalysis has been somehow hampered because of a lack of spatial three-dimensional organization and limited structural robustness under reaction conditions. In addition, the self-assembly of SCCs have been always limited to homogenous chemistry in solution. This,

inherently, have led to the construction of supramolecular architectures where the pivotal metal ions of the assembly are fully-coordinated, which have mitigated its catalytic application.

In such a context, our group faced the two-fold challenge of obtaining more structurally robust and spatially well-organized SCCs, and exploiting the potential of the pivotal metal atoms building the SCCs. In so doing, we have taken advantage of the microenvironment of oxamato- and oxamidato-based MOFs channels and its exceptional features for the stepwise fabrication and characterization of complex functional SCCs, otherwise hardly accessible, within their large pores and showing enhanced robustness and catalytic properties.

The synthetic strategy –similar to that used for the synthesis of SNMCs and SACs– relies on the use of selected crystalline and robust MOFs as chemical reactors for the *in-situ* self-assembly of these SCCs. Once appropriate MOFs are prepared/selected, a two-step PS methodology is used to construct these supramolecular assemblies. The first step consists on the controlled insertion of the metal cations (Figure 9). In this point, the resolution of the crystal structure of this intermediate phase becomes crucial, as it allows to observe metal atom positions and distances. On the basis of these parameters, appropriate ligands can be selected and inserted in the second PS step to self-assemble SCCs within MOFs channels (Figure 9).

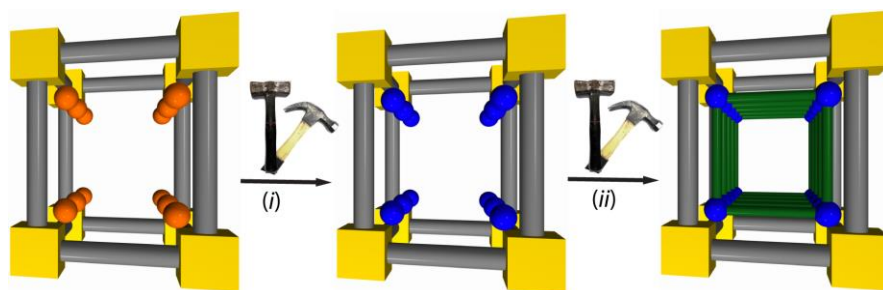


FIGURE 9. Schematic representation of the two-consecutive synthetic steps to build SCCs@MOFs.

Applying this approach, we recently reported the preparation of two mechanically-bonded *in-situ* self-assembled catalytically-active SCCs@MOFs.⁵⁵ Starting from the anionic $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}^{\text{II}}_2(\text{Me}_3\text{mpba})_2]_3\}\cdot 54\text{H}_2\text{O}$ MOF (Figure 2a), the first PS step consisted of replacing Ni^{2+} cations hosted in the pores (Figure 2a) by Pd^{2+} ones (Figure 10). The crystal structure of this intermediate phase allowed the direct visualization of the position and distances between Pd^{2+} units –which situate in the larger octagonal pores of the MOF forming dinuclear cationic entities– the number of Pd atoms and the available empty space. After a careful analysis, two aromatic dipyridine ligands (L_1 and L_2 where $\text{L}_1 = 1,2\text{-di(pyridin-4-yl)ethyne}$ and $\text{L}_2 = \text{methyl } 3,5\text{-bis(pyridine-4-ylethynyl)benzoate}$), were selected and the $\text{Pd}^{2+}\text{@MOF}$ was soaked in CH_3CN solutions of L_1 and L_2 . As a result, two novel unique palladium supramolecular assemblies were found within the channels of the MOF. In particular, a new Pd^{II}_8 ($\text{Pd}^{\text{II}}_8\text{@MOF}$) square metal-organic polygon when using the linear ligand L_1 (Figure 10), whereas a $\text{Pd}^{\text{II}}_{16}$ supramolecular assembly ($\text{Pd}^{\text{II}}_{16}\text{@MOF}$) with the tripodal bended ligand L_2 (Figure 10), were observed. Remarkably, the crystal structure of both supramolecular constructs could be ascertained with atomic precision –for the first time in a MOF as far as we know– by SC-XRD (Figure 10). The Pd^{II}_8 metal-organic polygons –assembled by covalent bonds– exhibit a square structure where the dipalladium(II) units situate at the corners of each square, whereas the $\text{Pd}^{\text{II}}_{16}$ supramolecular assemblies combine covalent bonds and strong H-bonds involving also water molecules. In addition, both supramolecular assemblies are further stabilised by mechanical-bonds with the walls of the MOF channels (Figure 11), which undoubtedly contributes to enhance the robustness of such assembled metal complexes and, thus, their stability under catalytic reaction conditions.

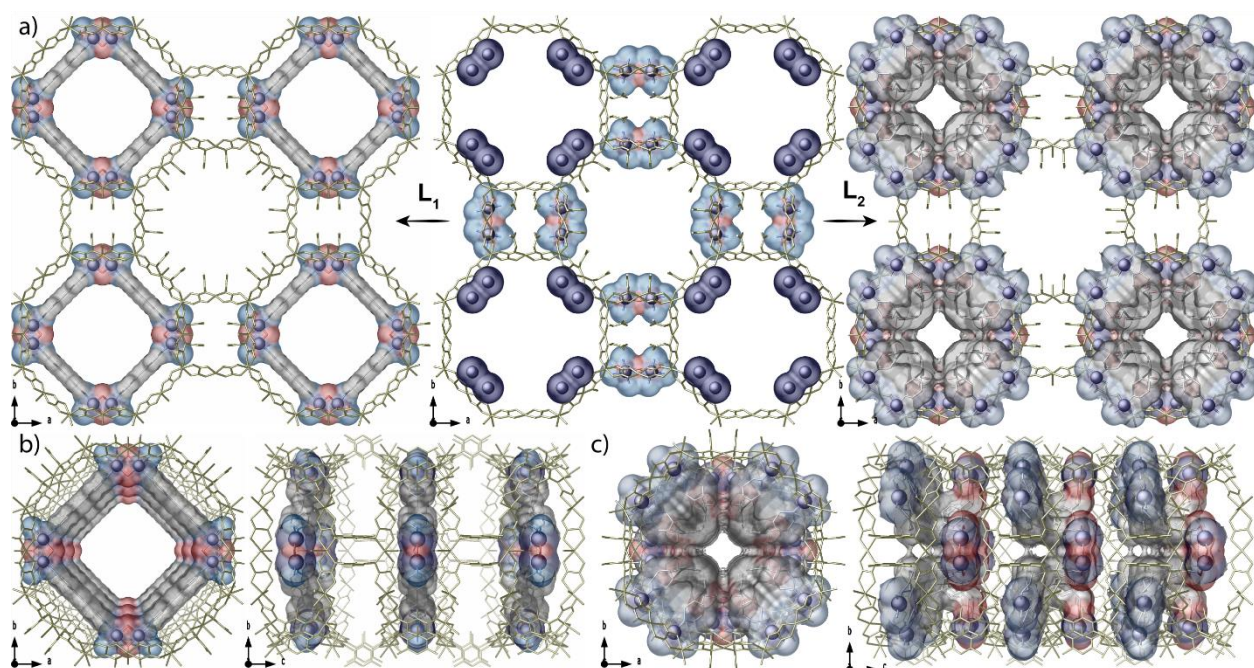


FIGURE 10. Views of the experimental XRD structures of $\text{Pd}^{2+}@\text{MOF}$ (center), $\text{Pd}^{\text{II}}_8@\text{MOF}$ (left) and $\text{Pd}^{\text{II}}_{16}@\text{MOF}$ (right). Views of one single channel of $\text{Pd}^{\text{II}}_8@\text{MOF}$ (b) and $\text{Pd}^{\text{II}}_{16}@\text{MOF}$ (c). The heterobimetallic CuNi 3D anionic network is depicted as gold sticks. Pd(II) cations and ligands forming the squares and cages are represented by blue spheres and sticks, respectively. Surfaces are used to highlight the SMCs. Reproduced with permission from ref. 55. Copyright 2019 ACS.

Aiming at confirming the proposed hypothesis, the catalytic performance in metal-based reactions of both materials was studied. In particular, for the coupling of different boronic acids and alkynes, they showed improved catalytic activity in comparison with $\text{Pd}^{2+}@\text{MOF}$ and other Pd^{II} complexes and traditional metal-organic cages –which tend to decompose– and a good recyclability. In addition, the confined limited space within the Pd^{II}_8 and $\text{Pd}^{\text{II}}_{16}$ compounds leads to enhanced selectivity in comparison with the other tested Pd^{II} species. Finally, a third heterometallic PdAu supramolecular construct was also assembled within this MOF and reported in this work as a preliminary result. This compound exhibits interesting catalytic properties, but further studies are still necessary to fully characterise its structure.

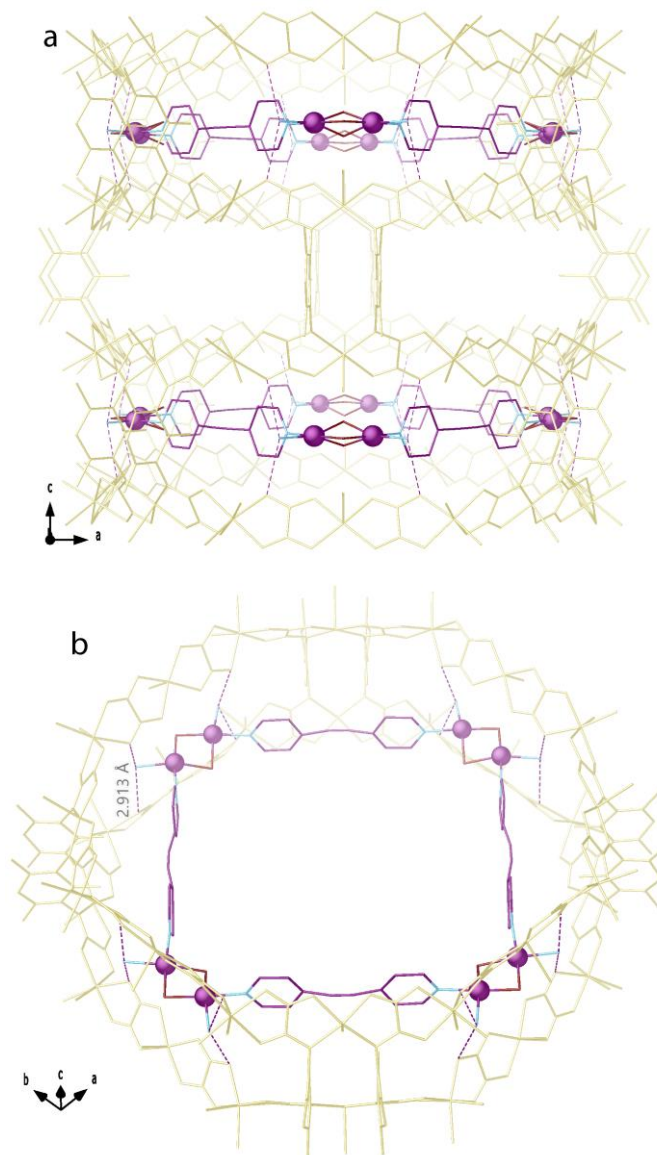


FIGURE 11. Perspective views of a fragment of $\text{Pd}^{\text{II}}_8\text{@MOF}$ along the b axis and the $[111]$ direction (a and b) emphasizing the symmetric $\text{NH}_3 \cdots \text{O}$ interactions [$\text{H}_3\text{N} \cdots \text{Ooxamate}$ of $2.913(9) \text{ \AA}$]. Reproduced with permission from ref. 55. Copyright 2019 ACS.

Conclusions

Through these lines we have described our last advances on the use of the unique host-guest chemistry and high robustness and cristallinity of oxamato- and oxamidato-based MOFs to start unveiling the great potential of MOFs as chemical nano-reactors. The particular examples shown

above are simple exponents of the singular and unprecedented opportunities that offer the empty space of MOFs. Thus, having in mind the vast number of reported MOFs, it is tempting to think that a new dimension in the field is waiting to be uncovered. However, this would not be an easy task and several challenges have to be overcome. In this sense, it would be necessary to make stronger efforts to develop materials with both the needed crystallinity and structural robustness, to resist the PSMs and to take advantage of SC-XRD, and try to achieve materials with enhanced thermal stability, as close as possible to other microporous materials with embedded metal species.²⁷⁻²⁹ MOFs with remarkable stability in different media have been thoroughly developed, but most frequently it has not been coupled with appealing crystals. The strengthening of this point will boost not only this emerging application of MOFs as chemical nanoreactors, but also all the entire field through cross-fertilization.

MOFs field have been started to install in a fierce competition to develop the most performant material in different applications. In particular, the present strategy has led to the preparation of unique catalytically-active MOF-driven metal species that, in some cases, may compete with the state-of-the-art industrial catalysts. Moreover, besides the positive advances that this has enabled, we consider that basic research and deeper comprehension of the singular possibilities of MOFs channels should be more intensively evaluated. This, in a first stage could be implemented with the validation of the design principles shown above to MOFs with other organic and inorganic constituents, and then, to MOFs with higher degree of complexity and heterogeneity within their channels, such as multivariate- MOFs (MTV-MOFs).⁵⁶ This would help us to gain precious insights on the key parameters that rule the synthesis and self-assembly of functional species within MOFs channels. We believe that this is an appealing way to start mastering this type of

chemistry in confined space as it has been done with covalent chemistry of small molecules in homogenous phase.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- (1) Kitagawa, S.; Matsuda, R. Chemistry of Coordination Space of Porous Coordination Polymers. *Coord. Chem. Rev.* **2007**, *251*, 2490–2509.
- (2) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37*, 191–214.

- (3) Long, J. R.; Yaghi, O. M. The Pervasive Chemistry of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214.
- (4) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 974.
- (5) Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G. Metal–Organic Frameworks as Platforms for Functional Materials. *Acc. Chem. Res.* **2016**, *49*, 483–493.
- (6) Lin, R.-B.; Xiang, S.; Xing, H.; Zhou, W.; Chen, B. Exploration of Porous Metal–Organic Frameworks for Gas Separation and Purification. *Coord. Chem. Rev.* **2019**, *378*, 87–103.
- (7) Shimizu, G. K. H.; Taylor, J. M.; Kim, S. Proton Conduction with Metal-Organic Frameworks. *Science* **2013**, *341*, 354–355.
- (8) Dhakshinamoorthy, A.; Li, Z.; Garcia, H. Catalysis and Photocatalysis by Metal Organic Frameworks. *Chem. Soc. Rev.* **2018**, *47* 8134–8172.
- (9) Hu, Z.; Deibert, B. J.; Li, J. Luminescent Metal–Organic Frameworks for Chemical Sensing and Explosive Detection. *Chem. Soc. Rev.* **2014**, *43*, 5815–5840.
- (10) So, M. C.; Wiederrecht, G. P.; Mondloch, J. E.; Hupp, J. T.; Farha, O. K. Metal–Organic Framework Materials for Light-Harvesting and Energy Transfer. *Chem. Commun.* **2015**, *51*, 3501–3510.
- (11) Mon, M.; Bruno, R.; Ferrando-Soria, J.; Armentano, D.; Pardo, E. Metal–Organic Framework Technologies for Water Remediation: Towards a Sustainable Ecosystem. *J. Mater. Chem. A* **2018**, *6*, 4912–4947.
- (12) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. Metal–Organic Frameworks in Biomedicine. *Chem. Rev.* **2012**, *112*, 1232–1268.

- (13) Cohen, S. M. The Postsynthetic Renaissance in Porous Solids. *J. Am. Chem. Soc.* **2017**, *139*, 2855–2863.
- (14) Fracaroli, A. M.; Siman, P.; Nagib, D. A.; Suzuki, M.; Furukawa, H.; Toste, F. D.; Yaghi, O. M. Seven Post-Synthetic Covalent Reactions in Tandem Leading to Enzyme-like Complexity within Metal–Organic Framework Crystals. *J. Am. Chem. Soc.* **2016**, *138*, 8352–8355.
- (15) Dhakshinamoorthy, A.; Garcia, H. Catalysis by Metal Nanoparticles Embedded on Metal–Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 5262.
- (16) Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Kapteijn, F.; Gascon, J. MOFs as Nano-reactors. In *Metal–Organic Frameworks as Heterogeneous Catalysts*; Editors: Llabres i Xamena, F. X. and Gascon, J.; Royal Society of Chemistry: Cambridge, U.K., 2013; Chapter 10, pp 310–343.
- (17) Rissanen, K. Crystallography of Encapsulated Molecules. *Chem. Soc. Rev.* **2017**, *46*, 2638–2648.
- (18) Burgun, A.; Coghlan, C. J.; Huang, D. M.; Chen, W.; Horike, S.; Kitagawa, S.; Alvino, J. F.; Metha, G. F.; Sumby, C. J.; Doonan, C. J. Mapping-Out Catalytic Processes in a Metal–Organic Framework with Single-Crystal X-Ray Crystallography. *Angew. Chemie Int. Ed.* **2017**, *56*, 8412–8416.
- (19) Bloch, W. M.; Champness, N. R.; Doonan, C. J. X-Ray Crystallography in Open-Framework Materials. *Angew. Chemie Int. Ed.* **2015**, *54*, 12860–12867.
- (20) Tao, Y.; Kanoh, H.; Abrams, L.; Kaneko, K. Mesopore-Modified Zeolites: Preparation, Characterization, and Applications. *Chem. Rev.* **2006**, *106*, 896–910.
- (21) Liu, L.; Lopez-Haro, M.; Lopes, C. W.; Li, C.; Concepcion, P.; Simonelli, L.; Calvino, J.

- J.; Corma, A. Regioselective Generation and Reactivity Control of Subnanometric Platinum Clusters in Zeolites for High-Temperature Catalysis. *Nat. Mater.* **2019**, *18*, 866–873.
- (22) Li, B.; Leng, K.; Zhang, Y.; Dynes, J. J.; Wang, J.; Hu, Y.; Ma, D.; Shi, Z.; Zhu, L.; Zhang, D.; Sun, Y.; Chrzanowski, M.; Ma, S. Metal–Organic Framework Based upon the Synergy of a Brønsted Acid Framework and Lewis Acid Centers as a Highly Efficient Heterogeneous Catalyst for Fixed-Bed Reactions. *J. Am. Chem. Soc.* **2015**, *137*, 4243–4248.
- (23) Pullen, S.; Fei, H.; Orthaber, A.; Cohen, S. M.; Ott, S. Enhanced Photochemical Hydrogen Production by a Molecular Diiron Catalyst Incorporated into a Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 16997–17003.
- (24) Wang, N.; Sun, Q.; Yu, J. Ultrasmall Metal Nanoparticles Confined within Crystalline Nanoporous Materials: A Fascinating Class of Nanocatalysts. *Adv. Mater.* **2019**, *31*, 1803966.
- (25) Li, G.; Zhao, S.; Zhang, Y.; Tang, Z. Metal-Organic Frameworks Encapsulating Active Nanoparticles as Emerging Composites for Catalysis: Recent Progress and Perspectives. *Adv. Mater.* **2018**, *30*, 1800702.
- (26) Wang, S.; McGuirk, C. M.; D’Aquino, A.; Mason, J. A.; Mirkin, C. A. Metal-Organic Framework Nanoparticles. *Adv. Mater.* **2018**, *30*, 1800202.
- (27) Zhai, Y.; Pierre, D.; Si, R.; Deng, W.; Ferrin, P.; Nilekar, A. U.; Peng, G.; Herron, J. A.; Bell, D. C.; Saltsburg, H.; Mavrikakis M.; Flytzani-Stephanopoulos, M. Alkali-Stabilized Pt-OH_x Species Catalyze Low-Temperature Water-Gas Shift Reactions. *Science* **2010**, *329*, 1633–1636.
- (28) Flytzani-Stephanopoulos, M.; Gates, B. C. Atomically Dispersed Supported Metal Catalysts. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 545–574.

- (29) Kistler, J. D.; Chotigkrai, N.; Xu, P.; Enderle, B.; Prasertdam, P.; Chen, C.-Y.; Browning, N. D.; Gates, B. C. A Single-Site Platinum CO Oxidation Catalyst in Zeolite KLTL: Microscopic and Spectroscopic Determination of the Locations of the Platinum Atoms. *Angew. Chemie Int. Ed.* **2014**, *53*, 8904–8907.
- (30) Mon, M.; Bruno, R.; Ferrando-Soria, J.; Bartella, L.; Di Donna, L.; Talia, M.; Lappano, R.; Maggiolini, M.; Armentano, D.; Pardo, E. Crystallographic Snapshots of Host–Guest Interactions in Drugs@metal–Organic Frameworks: Towards Mimicking Molecular Recognition Processes. *Mater. Horizons* **2018**, *5*, 683–690.
- (31) Liu, L.; Song, Y.; Chong, H.; Yang, S.; Xiang, J.; Jin, S.; Kang, X.; Zhang, J.; Yu, H.; Zhu, M. Size-Confined Growth of Atom-Precise Nanoclusters in Metal–Organic Frameworks and Their Catalytic Applications. *Nanoscale* **2016**, *8*, 1407–1412.
- (32) Grancha, T.; Ferrando-Soria, J.; Castellano, M.; Julve, M.; Pasán, J.; Armentano, D.; Pardo, E. Oxamato-Based Coordination Polymers: Recent Advances in Multifunctional Magnetic Materials. *Chem. Commun.* **2014**, *50*, 7569–7585.
- (33) Dul, M.-C.; Pardo, E.; Lescouëzec, R.; Journaux, Y.; Ferrando-Soria, J.; Ruiz-García, R.; Cano, J.; Julve, M.; Lloret, F.; Cangussu, D.; Pereira, C. L. M.; Stumpf, H.O.; Pasán, J.; Ruiz-Pérez, C. Supramolecular Coordination Chemistry of Aromatic Polyoxalamide Ligands: A Metallosupramolecular Approach toward Functional Magnetic Materials. *Coord. Chem. Rev.* **2010**, *254*, 2281–2296.
- (34) Grancha, T.; Ferrando-Soria, J.; Zhou, H.-C.; Gascon, J.; Seoane, B.; Pasán, J.; Fabelo, O.; Julve, M.; Pardo, E. Postsynthetic Improvement of the Physical Properties in a Metal–Organic Framework through a Single Crystal to Single Crystal Transmetallation. *Angew. Chemie Int. Ed.* **2015**, *54*, 6521–6525.

- (35) Mon, M.; Tiburcio, E.; Ferrando-Soria, J.; Gil San Millán, R.; Navarro, J. A. R.; Armentano, D.; Pardo, E. A Post-Synthetic Approach Triggers Selective and Reversible Sulphur Dioxide Adsorption on a Metal–Organic Framework. *Chem. Commun.* **2018**, *54*, 9063–9066.
- (36) Mon, M.; Qu, X.; Ferrando-Soria, J.; Pellicer-Carreño, I.; Sepúlveda-Escribano, A.; Ramos-Fernandez, E. V.; Jansen, J. C.; Armentano, D.; Pardo, E. Fine-Tuning of the Confined Space in Microporous Metal–Organic Frameworks for Efficient Mercury Removal. *J. Mater. Chem. A* **2017**, *5*, 20120–20125.
- (37) Mon, M.; Lloret, F.; Ferrando-Soria, J.; Martí-Gastaldo, C.; Armentano, D.; Pardo, E. Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF. *Angew. Chemie Int. Ed.* **2016**, *55*, 11167–11172.
- (38) Mon, M.; Ferrando-Soria, J.; Grancha, T.; Fortea-Pérez, F. R.; Gascon, J.; Leyva-Pérez, A.; Armentano, D.; Pardo, E. Selective Gold Recovery and Catalysis in a Highly Flexible Methionine-Decorated Metal–Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 7864–7867.
- (39) Tejada-Serrano, M.; Mon, M.; Ross, B.; Gonell, F.; Ferrando-Soria, J.; Corma, A.; Leyva-Pérez, A.; Armentano, D.; Pardo, E. Isolated Fe(III)–O Sites Catalyze the Hydrogenation of Acetylene in Ethylene Flows under Front-End Industrial Conditions. *J. Am. Chem. Soc.* **2018**, *140*, 8827–8832.
- (40) Mon, M.; Adam, R.; Ferrando-Soria, J.; Corma, A.; Armentano, D.; Pardo, E.; Leyva-Pérez, A. Stabilized Ru[(H₂O)₆]³⁺ in Confined Spaces (MOFs and Zeolites) Catalyzes the Imination of Primary Alcohols under Atmospheric Conditions with Wide Scope. *ACS Catal.* **2018**, *8*, 10401–10406.

- (41) Frisch, P. D. A Review of: "Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes. George W. Parshall, John Wiley & Sons, New York, N.Y., 1980. XI + 740 Pp., \$28.00." *Synth. React. Inorg. Met. Chem.* **1981**, *11*, 179–180.
- (42) White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. Supported Metal Nanoparticles on Porous Materials. Methods and Applications. *Chem. Soc. Rev.* **2009**, *38*, 481–494.
- (43) Liu, L.; Díaz, U.; Arenal, R.; Agostini, G.; Concepción, P.; Corma, A. Generation of Subnanometric Platinum with High Stability during Transformation of a 2D Zeolite into 3D. *Nat. Mater.* **2017**, *16*, 132–138.
- (44) Guillena, G.; Ramón, D. J.; Yus, M. Hydrogen Autotransfer in the N -Alkylation of Amines and Related Compounds Using Alcohols and Amines as Electrophiles. *Chem. Rev.* **2010**, *110*, 1611–1641.
- (45) Chen, B.; Wang, L.; Gao, S. Recent Advances in Aerobic Oxidation of Alcohols and Amines to Imines. *ACS Catal.* **2015**, *5*, 5851–5876.
- (46) *Cheung, P. T.-T.; Bergmeister, J.J. III, WO 03/106020, US Patent, Chevron Phillips Chem. Co., 2003 and US0137433, 2005.*
- (47) Grzelczak, M.; Pérez-Juste, J.; Mulvaney, P.; Liz-Marzán, L. M. Shape Control in Gold Nanoparticle Synthesis. *Chem. Soc. Rev.* **2008**, *37*, 1783.
- (48) Oliver-Meseguer, J.; Cabrero-Antonino, J. R.; Dominguez, I.; Leyva-Perez, A.; Corma, A. Small Gold Clusters Formed in Solution Give Reaction Turnover Numbers of 107 at Room Temperature. *Science* **2012**, *338*, 1452–1455.
- (49) Argo, A. M.; Odzak, J. F.; Lai, F. S.; Gates, B. C. Observation of Ligand Effects during

- Alkene Hydrogenation Catalysed by Supported Metal Clusters. *Nature* **2002**, *415*, 623–626.
- (50) Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–1748.
- (51) Fortea-Pérez, F. R.; Mon, M.; Ferrando-Soria, J.; Boronat, M.; Leyva-Pérez, A.; Corma, A.; Herrera, J. M.; Osadchii, D.; Gascon, J.; Armentano, D.; Pardo, E. The MOF-Driven Synthesis of Supported Palladium Clusters with Catalytic Activity for Carbene-Mediated Chemistry. *Nat. Mater.* **2017**, *16*, 760–766.
- (52) Rivero-Crespo, M. A.; Mon, M.; Ferrando-Soria, J.; Lopes, C. W.; Boronat, M.; Leyva-Pérez, A.; Corma, A.; Hernández-Garrido, J. C.; López-Haro, M.; Calvino, J. J.; Ramos-Fernandez, E. V.; Armentano, D.; Pardo, E. Confined Pt₁¹⁺ Water Clusters in a MOF Catalyze the Low-Temperature Water-Gas Shift Reaction with Both CO₂ Oxygen Atoms Coming from Water. *Angew. Chemie Int. Ed.* **2018**, *57*, 17094–17099.
- (53) Mon, M.; Rivero-Crespo, M. A.; Ferrando-Soria, J.; Vidal-Moya, A.; Boronat, M.; Leyva-Pérez, A.; Corma, A.; Hernández-Garrido, J. C.; López-Haro, M.; Calvino, J. J.; Ragazzon, G.; Credi, A.; Armentano, D.; Pardo, E. Synthesis of Densely Packaged, Ultrasmall Pt₂⁰ Clusters within a Thioether-Functionalized MOF: Catalytic Activity in Industrial Reactions at Low Temperature. *Angew. Chemie Int. Ed.* **2018**, *57*, 6186–6191.
- (54) Lehn, J. *Supramolecular Chemistry*; Wiley, 1995.
- (55) Adam, R.; Mon, M.; Greco, R.; Kalinke, L. H. G.; Vidal-Moya, A.; Fernandez, A.; Winpenny, R. E. P.; Doménech-Carbó, A.; Leyva-Pérez, A.; Armentano, D.; Pardo, E.; Ferrando-Soria, J. Self-Assembly of Catalytically Active Supramolecular Coordination Compounds within Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 10350–10360.

- (56) Mon, M.; Bruno, R.; Tiburcio, E.; Viciano-Chumillas, M.; Kalinke, L. H. G.; Ferrando-Soria, J.; Armentano, D.; Pardo, E. Multivariate Metal–Organic Frameworks for the Simultaneous Capture of Organic and Inorganic Contaminants from Water. *J. Am. Chem. Soc.* **2019**, *141*, 13601–13609.