Single-atom active sites on metal-organic frameworks

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Single-site heterogeneous catalysis has been recently accepted as a novel branch of heterogeneous catalysis. Catalysts with single-atom active sites (SAHCs) allow the design and fine-tuning of the active moiety, and can potentially combine the advantages of heterogeneous and homogeneous catalysis. This study illustrates how porous metal-organic frameworks (MOFs) can be synthesized with homogeneous distribution of SAHCs. The catalytic potential of MIXMOFs is shown. A short overview of catalysis with mesoporous silica materials is described to demonstrate their importance in SAHC.

Keywords: metal-organic frameworks; catalysis; post-synthetic modification; single-atom active site; MIXMOF

1. Introduction

Most heterogeneous industrial catalysts are nanodispersed metal particles on a support, but despite their enormous employment, the study of their behaviour under catalytic conditions—which would help the optimization and rationalization of the various catalytic processes—is difficult. For many years density functional theory (DFT) calculations, kinetics and vibrational spectroscopy have been the main ways to comprehend the behaviour of heterogeneous catalysts, and, in recent years, much progress has been made towards in situ and operando measurements, especially with the advent of atom-selective techniques available at synchrotron facilities, such as X-ray scattering, and absorption and emission spectroscopies (van Bokhoven 2010). However, theoretical calculations are strongly limited by band theory. Generally, only a few atoms at the surface contribute to activity, and low-coordinated, unsaturated atoms or ensembles thereof often function as active sites (Judai et al. 2004; Remediakis et al. 2005; Herzing et al. 2008; Turner et al. 2008; Vajda et al. 2009; Lei et al. 2010). Having catalysts either with homogeneously distributed active sites (single-site heterogeneous catalysis; Thomas et al. 2005; Thomas & Raja 2010) or with species downsized to single atoms (single-atom active site

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heterogeneous catalysis (SAHC); Thomas et al. 2011) is highly desirable for performing catalytic reactions. The production of single-atom or sub-nanometre particles is, however, rather difficult, although various examples in the literature demonstrate its successful application (Lee et al. 2004; Yoon 2005; Qiao et al. 2011). One main problem is the stability of such species, whose high reactivity might facilitate sintering, and thus deactivation, under reaction conditions.

On the other hand, homogeneous catalysts are usually well-defined and generally provide single-atom transition metal sites stabilized by ligands (Leeuwen 2004). Their characterization can be accurate nowadays thanks to techniques that allow their fine-structure determination at atomic level, such as single-crystal X-ray diffraction (SC-XRD) and nuclear magnetic resonance (NMR) spectroscopy. In addition to the techniques available in heterogeneous catalysis, such as vibration spectroscopy and DFT calculation, in situ measurements are largely performed by NMR spectroscopy, although only available mostly to diamagnetic systems. X-ray absorption and emission spectroscopies are being applied to homogeneous systems to an increasing extent (Tromp et al. 2003). The understanding of catalytic behaviour is also highly facilitated by the existence of extensive molecular orbital (MO) theory supported by many decades of experimental organometallic chemistry, which demonstrates the discrete energies of the MO. Moreover, homogeneous catalysts are usually more active and selective than heterogeneous ones. Despite such advantages, industry is still reluctant to use homogeneous catalysis owing to difficulties in catalysis separation and limited implementation to fixed-bed continuous flow reactor systems. Still, their application in relatively big scale processes, such as hydroformylation, hydrogenation, oligomerization, polymerization and metathesis is known (Leeuwen 2004). Nowadays, the main application of homogeneous catalysts is in the fine chemical industry, especially for the synthesis of enantiomeric molecules, where high selectivity is desired. Therefore, the high cost of the end products can afford high metal loading and non-recycling catalysts.

Theoretically, the ‘perfect’ catalytic system combines the high activity, selectivity and flexibility of homogeneous catalysis with the recycling of the heterogeneous ones. Many efforts have been made in this direction. Inspired by the success of homogeneous catalysis, heterogeneous catalysts based on species with single sites are continuously sought, but the control of particle size remains challenging (Lee et al. 2004; Qiao et al. 2011). Heterogeneous active sites similar to those of homogeneous ones are easier to produce. For this reason, SAHC has been a continuously growing field in the past decades. Materials that are good candidates as supports for this purpose must feature big pores to accommodate the sterically demanding metal complex and to allow adsorption, diffusion and desorption of reactants and products. For many years, mesoporous silica, such as MCMs and SBAs, seemed to be the way to go (Wight & Davis 2002; Taguchi & Schuth 2005). Many examples show the success of such materials in the heterogenization of known homogeneous processes. Still, such mesoporous materials lack crystallinity, which means that there is no knowledge of the fine structure at a molecular level. Using crystalline materials as backbones to anchor sites enables the knowledge of the active sites and of the environment around them.

With the development of metal-organic frameworks (MOFs), a relatively novel class of crystalline materials, catalysts with big pores and that are also crystalline
became available (Kitagawa et al. 2004; Rowsell & Yaghi 2004; Férey 2008). MOFs are produced by combining multi-dentate organic building blocks with inorganic units to give rigid structures, whose chemical composition can often be measured by SC-XRD. Besides crystallinity, one great advantage of MOFs is that, given a starting framework geometry (figure 1a), it is possible to build frameworks that have the same topology, but that differ by the presence of functional groups (figure 1b) and by the size of the organic building block (figure 1c). This concept, called isoreticularity (Eddaoudi et al. 2002; Cavka et al. 2008; Garibay & Cohen 2010), allows one to tune the pore size of the material and adds the possibility of introducing functional groups within the framework. Moreover, if two or more isoreticular organic linkers are employed, frameworks bearing different functionalities that are randomly and homogeneously distributed within the framework are produced (figure 1d) by exploiting the concept of multi-variable or mixed MOFs (MTV-MOFs or MIXMOFs; Burrows et al. 2008; Kleist et al. 2009; Deng et al. 2010). In general, functionalization can further be obtained via post-synthetic modification (PSM) to give a large variety of materials with different chemical and physical properties (Wang et al. 2009; Cohen 2011; Tanabe & Cohen 2011). The properties described above— isoreticularity, MIXMOFs and PSM—combined with the fact that MOFs are constituted by organic compounds...
Figure 2. Formation of the active titanium site on the TS-1 used for the synthesis of propeneoxide.

make such materials particularly versatile from a chemical point of view, and chemical versatility is essential to design active sites inspired by homogeneous and enzymatic catalysts.

In this study, we will describe the progress of mesoporous silica in the heterogenization of known homogeneous systems. Thereafter, we will describe our recent advances towards the creation of single-atom heterogeneous catalysts in MOFs. We will focus our attention on the production of materials with homogeneous distribution of active sites throughout the crystals.

2. Other materials in single-atom active site heterogeneous catalysis

In this part of the section, we will discuss other strategies/materials which found application to realize SAHC. The most prominent method to generate single-site catalysts is certainly the use of silica as support. Because of the high amount of independent contributions from different groups in this field of research, we will discuss the general concepts and give some selected examples (Barbaro 2010). The designation silica means the more or less crystalline aggregates of silicic acid anhydrides, which, depending on the synthesis process, appear as nanoparticles or as mesoporous materials, such as MCM-41 (Beck et al. 1992; Kresge et al. 1992; Lin et al. 1999; Widenmeyer & Anwander 2002), SBA-15 (Wang et al. 2001) or periodic mesoporous organosilicas (PMOs; Hoffmann et al. 2006). Apart from these supports, there exists the class of aluminosilicates or zeolites (Cundy et al. 2003). Enchanted by the chemical elegance and the structural features, many researchers in the world are dealing with zeolites and their application in catalysis and material science. Although zeolites play a prominent role in science and industry, we will describe only a very short example, because a detailed discussion exceeds the scope of this study. One of the most fascinating approaches on SAHC with zeolites is the use of TS-1 as catalysts in the epoxidation of propene. In contrast to the epoxidation of ethene, which can be accomplished by reaction of ethene with oxygen in presence of a silver catalyst at temperatures between 200°C and 300°C, it is highly complicated to generate propeneoxide (PO) with high selectivity from propene. Facing this problem, Haruta and co-workers developed an elegant process for the formation of PO with high selectivity (Chowdhury et al. 2006). TS-1, developed in the early 1980s by researchers at ENICHEM, shows the implementation of titanium in the ZSM-5 structure, leading to the formation of single-site redox-active centres, which are inert to catalyst deactivation by leaching (Hoft et al. 1996). Haruta combined the use of these redox-active centres with the in situ generation of hydrogen peroxide by gold nanoparticles (figure 2).
The interplay of the gold nanoparticles and the titanium atoms in the TS-1 leads to the formation of activated peroxide for the synthesis of PO. The high importance of titanium silicalites is also reflected in a process conjointly developed by BASF and DOW for industrial synthesis of PO on a 300,000-t/a scale. In this process, a titanium silicalite is used as catalyst and hydrogen peroxide is directly used as oxidant.

In the example given, the active site is incorporated in the structure of the material. The use of non-zeolite materials, such as MCM-41 and silica nanoparticles for SAHC is mainly characterized by the quest for SMs, allowing the anchoring of the active sites on (not in) the material. Furthermore, the anchoring and the SMs can be divided into covalent or ionic anchoring, respectively. Covalent grafting either means that the support is modified by groups specially designed for the reaction with the suitable counterpart, e.g. the reaction of an amine with an isocyanate or a sulphide with a benzylbromide (figure 3a), or means that the catalyst/ligand is chemically modified suitable for anchoring on the support (figure 3b; Piestert et al. 2005; Blümel 2008; Maishal et al. 2008; Lei et al. 2010).

A third method includes the incorporation of surface hydroxyl groups in the coordination sphere of the metal complexes (figure 3c; Schnellbach et al. 1996; Jarupatrakorn & Don Tilley 2002; Copéret et al. 2003). In this field of research, especially the groups of Don Tilley, Christophe Copéret, Didier Astruc and Janet Blümel have to be mentioned. A different strategy for the immobilization of catalysts is the use of electrostatic interactions. This might either happen by modification of the ligand, allowing a strong interaction with a support of opposite charge or by direct metal support interactions (figure 4a,b). The advantage of immobilization by the ligand is that the method can be applied to catalysts neutral on the ligand and that leaching might be diminished, as the catalyst can change oxidation state or charge during catalysis (Yang et al. 2008).

In one very last example, we will show that SAHC is not only restricted to metal catalysis. In 2010, Werner Thiel and co-workers reported the synthesis of PMOs modified by amino groups and sulphonic acid groups at the same time, two functionalities which cannot coexist in solution (and in homogeneous catalysis; Shylesh et al. 2010). They used the materials for consecutive deacetalization/Henry reaction of acetals with nitromethane (figure 5).
Figure 4. The principles of ionic anchoring. L denotes ligand; M denotes metal.

Figure 5. Consecutive deacetalization/Henry reaction according to Thiel and co-workers.

The work was highly inspired by biological systems taking advantage of different reaction centres closely arranged, showing opposite and sometimes even incompatible catalytic activity.

All in all, we gave a short overview about different strategies for the implementation of single-site catalytic centres on silica supports. Our examples show that SAHC is a powerful tool for straightforward organic transformations and even industrial applications, and we are sure that the concept will be expanded to new and revolutionary processes.

3. Single-atom active sites within metal-organic frameworks

There are numerous MOF catalysts and, as previously described in our perspective (Ranocchiari & van Bokhoven 2011), they can be divided into three types: (i) those with active site on the framework, (ii) those with encapsulated active species, and (iii) those with active sites attached through PSM. Catalysts with intrinsic activity at the inorganic nodes or at the organic linker belong to group 1. Some examples are $[\text{Cd(bpy)}]_n(\text{NO}_3)_2$ (Fujita et al. 1994) (bpy, bipyridine) and $[\text{Cr}_3\text{F(H}_2\text{O)}_2\text{O(tpa)}_3]_n$ (MIL-101, tpa, terephthalic acid) in which the inorganic group acts as catalytically active acid site (Hwang et al. 2008), and IRMOF-3, an amino MOF-5, which is an active basic catalyst for the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (Gascon et al. 2009). The second category includes all catalysts in which the active site is positioned in the pores of the MOF structure via non-covalent interactions. Metal particles, complexes and clusters supported throughout a MOF fall into this category, and some examples are Pd@MOF-5, Cu@MOF-5 (Hermes et al. 2005), $[\text{PW}_{11}\text{TiO}_{40}]@\text{MIL}101$ (Maksimchuk et al. 2010), which are catalysts for the hydrogenation of cyclooctene, the synthesis of methanol from syngas and the oxidation of $\alpha$-pynene. The third and last group is made of catalysts in which the
active site is attached to the MOF by covalent interaction built for example via PSM. IRMOF-3 with vanadyl–iminophenol moieties, active in the oxidation of cyclohexane (Ingleson et al. 2008), and IRMOF-3 with Au–iminophenols (Zhang et al. 2009), active in the selective hydrogenation of 1,3-butadiene, are readily obtained from the amino MOF-5 through PSM and are examples of this kind of catalyst.

In principle, one can have single-site and SAHCs with all the categories described earlier, but catalysts belonging only to the third type enable fully exploiting the exceptional chemical versatility of MOFs and allow designing, optimizing and rationalizing the structure of heterogeneous catalysts. For this reason, we will focus our attention on how to obtain heterogeneous catalysts with SAHCs produced by PSM.

4. Design of single-atom active sites by post-synthetic modification

MOFs feature high crystallinity do not have theoretical pore-size limitations and provide unique opportunities. This means that it is possible to have a homogeneous distribution of one or more active sites owing to the high crystallinity of the material and, at the same time, to overcome diffusion and pore-size limitations. Also, their chemical versatility gives the possibility of flexibly designing catalysts at the atomic scale. The higher the flexibility, the higher the possibility to perform fine-tuning of catalysts and thus control reactivity and selectivity according to the application needs. However, at the present time, this is still at an early development stage, especially for catalysts produced by PSM.

Standard PSM methods consist of suspending a functionalized MOF with an organic or inorganic reactant for several days in an organic solvent, usually chlorinated. Afterwards, the non-reacted and the excess of reactant are washed out, and the product analysed. In rare cases, SC-XRD is performed and the post-functionalization proved. Commonly, solid-state characterization such as IR and UV spectroscopy together with NMR spectroscopy in the solid and liquid phases after digestion of the material can elucidate the conversion of PSM, whose success should also be confirmed by powder X-ray diffraction and Brunauer Emmett Teller surface area to verify the framework integrity. PSM is extensively used and can be considered nowadays as a fundamental tool to modify MOFs to tune their physical and chemical properties. Functionalized materials with different topologies that undergo PSM are most commonly those with amino and alcohol groups. Some examples are IRMOF-3 (an amino MOF-5), NH$_2$-DMOF, NH$_2$-UiO-66 and NH$_2$-UMCM-1. PSM to build organic covalent bonds with anhydrides, isocyanates and aldehydes is relatively common (Wang & Cohen 2007, 2009; Dugan et al. 2008), but also that to introduce bonds with transition metals is known (Kaye & Long 2008).

From a catalytic point of view, the combination of PSM with organic and inorganic compounds is a very versatile way to introduce a catalytically active metal centre to the material, and one of the best protocols to ensure the coordination of a transition metal to the support is to produce chelating moieties (Doonan et al. 2009; Tanabe & Cohen 2009), although examples where this is not necessary are known (Kitaura et al. 2004; Wu et al. 2005). Chelating groups can be introduced more easily by post- than by pre-synthetic functionalization in
MOFs because they may compete in the coordination to inorganic nodes. Still, the examples in the literature are relatively few, and their application in catalysis is sometimes proved. NH$_2$-UMCM-1, a MOF with big pores of 17 Å and 29 Å, has been subjected to PSM to produce chelating groups with both aldehydes and anhydrides. Reaction with 2-pyridinecarboxyaldehyde followed by coordination with Pd$^{2+}$ led to a Pd-functionalized MOF, whose characterization was performed by extended X-ray absorption fine structure. No catalytic application of such material has been published, though. The same MOF undergoes PSM with anhydrides to produce chelates that coordinate Cu$^{2+}$ and Fe$^{3+}$. The resulting materials are active catalysts for the Mukaiyama aldol reaction. IRMOF-3, an amino-functionalized MOF-5, was reacted with salicylaldehyde to form the iminophenol moiety with conversion up to 13 per cent. PSM with Au$^{3+}$, respectively, V$^{5+}$ complexes led to active catalysts in the hydrogenation of butadiene and in the oxidation of cyclohexene.

These examples illustrate that the synthesis of chelates by PSM is a successful method to produce unique catalytic materials, but show also its limitation. The required reaction times are long in the range of 1–5 days and the yield of PSM under standard conditions strongly depends on the pore size of the starting materials and is generally low. Whereas NH$_2$-UMCM-1 gives relatively high conversions ranging from 35 per cent to more than 99 per cent, IRMOF-3 gives only up to 13 per cent. When moderate or low conversion of PSM to produce chelates is obtained, the material cannot be fully considered a heterogeneous analogue of a homogeneous ligand because of the concomitant presence of significant amounts of non-reacted functional groups. This means that, after PSM with transition metal complexes, it is more difficult to have homogeneous distribution of active sites. At this point, one has a material that does not fully exploit the unique features of MOFs. Such heterogeneous catalysts, although they can be efficient for a certain catalytic reaction, may not be well defined.

Novel methods to perform PSM with organic compounds are required to obtain quantitative conversion (and yield), which is highly desired to get high-quality catalytic materials and to optimally use the accessible surface area to feature SAHCs homogeneously distributed throughout the framework. Our group has recently developed a new method that enables (near) quantitative introduction of functional groups in the pores of MOFs at fast rates (Servalli et al. 2012). This novel methodology, called vapour phase PSM (VP-PSM), is a general, efficient and versatile route that overcomes the limitation of standard PSM methods. The concept of VP-PSM is based on that of chemical vapour deposition (CVD; Zhang et al. 1998; Serp et al. 2002). Organic substances, instead of volatile metal complexes, such as in CVD, are diffused through the pores of the MOFs in static vacuum and moderate temperature to create organic covalent bonds. In this way, only the reactant is in contact with the microporous surface of the material and with the functional groups, there is no competitive adsorption of the reagent with the solvent—which is present in large amount in standard PSM—and higher yields of PSM can be obtained.

To show the power of VP-PSM, we took as an example the reaction of salicylaldehyde with IRMOF-3, an amino-functionalized material isoreticular to MOF-5. The group of Rosseinsky has extensively studied this reaction to maximize PSM yields and obtain good material with chelating moieties for V-catalysed oxidation of cyclohexene (see above). Their conditions consisted of
suspending IRMOF-3 with salicylaldehyde in toluene at room temperature for 7 days and gave up to 13 per cent yield, calculated by elemental analysis. When we applied our VP-PSM method to the same reaction, in a first experiment, the MOF was dried in vacuum overnight at 100°C. The material was placed into a paper filter in an argon-flushed Schlenk tube containing salicylaldehyde (1.5 equiv) according to the set-up in figure 6. In this way, the MOF is not in direct contact with the reactant in the VP at ambient pressure and room temperature.

The Schlenk tube was subsequently left in static vacuum and heated at 100°C for 16 h to allow phase change of the reactant to vapour. The resulting solid was washed with toluene and dichloromethane to remove the physisorbed excess of substrate/by-products, dried and analysed. Because the fully evacuated material lost crystallinity as observed by powder XRD, we pre-activated IRMOF-3 just by drying it for 30 min at room temperature under a flux of argon without removing toluene from the pores. Under these conditions, the red-coloured product SI-IRMOF-3 was obtained in more than 99 per cent yield, as measured by 1H-NMR spectroscopy after digestion, and without loss of framework integrity (figure 7). This result clearly shows that VP-PSM overcome time and yield limitations of PSM under standard conditions because the reaction is performed in 16 h to give quantitative yield.

However, such quantitative yield of post-functionalization came with a price. SI-IRMOF-3 showed a BET surface area of 360 m² g⁻¹. Because the BET surface area of the starting material was 2314 m² g⁻¹, the loss of microporosity upon VP-PSM was 85 per cent. This occurs because several iminophenol moieties are present in each cage, which decrease pore size and volume. Although the sorption data clearly show that, with VP-PSM, we reach the limit of PSM in terms of yield, the low surface area of the resulting salicylimino material might limit its further functionalization with metal complexes and catalytic application. For this reason, we designed a material that would keep similar sorption properties before and after PSM, and with homogeneous distribution of chelating moieties by applying the concept of MIXMOFs.

We synthesized NH₂-MIXMOF-5 with 12 per cent amino groups by a modified literature procedure. Thereafter, we performed VP-PSM analogously to IRMOF-3 and obtained SI-MIXMOF-5 in more than 99 per cent yield (figure 8). The BET surface area of NH₂-MIXMOF-5 was 3120 m² g⁻¹, whereas that of SI-MIXMOF-5 was 2820 m² g⁻¹, only 10 per cent lower than the starting amino MIXMOF. Therefore, we were able to produce a material with (i) homogeneous distribution of chelating groups, (ii) with ‘diluted’ chelates, and (iii) with sorption properties similar to those of the starting material. So far, MIXMOFs have found a limited application in catalysis and none of them is related to catalysis via PSM. Besides the fact that this is the first example of PSM by an MIXMOF, this result shows that material with ‘diluted’ functionalities might open new perspectives in catalysis where diffusion limitations are dominant, such as catalytic transformations of relatively big substrates by supported large metal complexes.

Intrigued by the possibility of using MIXMOFs to produce catalysts with diluted active sites, we explored the field further on by performing an in depth microscopic investigation to understand other differences between IRMOFs and

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**Figure 7.** Standard post-synthetic modification (PSM) versus vapour phase (VP)-PSM of IRMOF-3 with salicylaldehyde. (Online version in colour.)

**Figure 8.** Vapour phase post-synthetic modification (VP-PSM) of IRMOF-3 with salicylaldehyde. (Online version in colour.)
MIXMOFs. As model systems, we took IRMOF-3 and NH$_2$-MIXMOF-5 with 12 per cent amino groups. SCs of such materials were modified with a rhodium complex that is known to react with monodentate amino functionalities, such as [Rh(COD)$_2$]OTf (COD = 1,5-cyclooctadiene; Liu et al. 2011). By reaction under standard PSM in degassed dichloromethane for 7 days at 50°C, the crystals featured a brownish hue indicating the presence of rhodium. Rh elemental analysis showed a 1.94 wt$_{Rh}$% for IRMOF-3, and 1.91 wt$_{Rh}$% for NH$_2$-MIXMOF-5.

Crystals of approximately 200 μm size of both rhodium MOFs were analysed by synchrotron-based, X-ray spectro-micro-tomography (Tomcat beamline, Swiss Light Source). For each crystal, tomograms were recorded employing X-ray beam energies below and above the Rh K-edge. Consequently, in addition to microscopic information about the physical structure of each MOF crystals, the resulting spectroscopic contrast of the two tomograms reveals the spatial distribution of Rh concentration. Interestingly, both materials feature comparable Rh content, but, whereas the IRMOF features a gradient of Rh from the surface to the inner part of the crystal, the MIXMOF has a more homogeneous distribution of Rh throughout the whole crystal (figure 9), although a rim of few micrometres with higher Rh content can be distinguished owing to macrofractures on the surface of the crystal. These results are explained by examining the differences in density...
of functionalizations in the two materials. IRMOF-3 features amino groups in each edge of the cubic-shaped cavity of the MOF. In such material, \([\text{Rh(COD)}_2]^+\) reacts first at the surface of the crystal, and, by sticking to the many amino groups reduces dramatically the volume in the cavity, which then decreases the space to allow diffusion of the complex into the inner part of the crystal. On the other hand, an MIXMOF has amino groups that are randomly distributed throughout the crystal and there is only around one functionalization per nine edges. Under these circumstances, the Rh complex is free to diffuse within the crystal and attach to the few functionalizations available.

To conclude this section, we demonstrated how PSM is a valuable tool to produce SAHCs. Our new VP-PSM method enhances the flexibility of PSM and allows one to obtain post-modified materials with only one type of functional group homogeneously distributed within the framework. Also, we rationalized and investigated some basic properties of post-functionalized MIXMOFs, which have the potential of creating diluted active sites to solve issues concerning diffusion-limited catalysis.

5. Conclusion

In this study, we showed how SAHCs can be designed and synthesized in MOFs via VP-PSM to obtain chelates that are readily available for metal coordination and that are homogeneously distributed throughout IRMOF materials. We also showed interesting features of MIXMOFs as potential catalysts for reactions with diffusion limitations and where a homogenous distribution of metal centres is needed. Such findings will have an impact on the design of catalytic MOFs.

Heterogeneous catalysts with single sites and SAHCs offer advantages that will make their employment more decisive in processes that combine selectivity under mild conditions with sustainability. MOFs and mesoporous silica are both suitable materials for this purpose. MOFs are more indicated for the design of active sites and the environment around it, which makes them ideal for very selective processes, fine chemical production and enzyme-like catalysis. On the other hand, mesoporous silica tends to fit more for reactions under harsher conditions and with strong diffusion limitations. Still, the research in this direction is at an early stage and needs to be further developed also in the discovery of new tools that are unique for each specific material. We are sure that the industrial and academic importance of such materials will grow enormously in the following years.

References


Single-atom active sites


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