Hybrid organic–inorganic structured materials as single-site heterogeneous catalysts

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Catalyst selectivity is associated with well-defined homogeneous active sites. Transition metal complexes and organocatalysts are highly active and selective in the homogeneous phase, and their heterogenization by incorporating them into inorganic solid materials allows combining their excellent catalytic activity with improved separation, recovering and recycling properties. In this article, we present the structural characteristics and catalytic properties of hybrid organic–inorganic materials in which the molecular catalysts are part of the inorganic structure, emphasizing the possibilities of periodic mesoporous hybrid materials and coordination polymers as single-site solid catalysts.

Keywords: selectivity; single-site catalysts; hybrid organic–inorganic; periodic mesoporous materials; coordination polymers; grafting

1. Introduction

The most important feature in catalysis is selectivity. Catalyst selectivity can be maximized when the nature of the selective active sites is known and a catalyst that only contains these sites is synthesized. Well-defined homogeneous active sites exist in the case of molecular catalysts such as those formed, for instance, by cations and anions in solution, transition metal complexes and organocatalysts, which are successfully used as homogeneous catalysts. However, it is difficult to prepare solid catalysts, but not impossible, with a system of unique and well-defined homogeneous active sites (Thomas 1997; Thomas et al. 2005). Generally, the synthesis of solid catalysts results in surface site heterogeneity with the corresponding negative impact on selectivity.

Since well-defined single sites can be achieved with transition metal complexes and organocatalysts, one can envisage the preparation of hybrid organic–inorganic solid materials in which the molecular catalysts would be part of the structure. This type of material should couple the advantages of homogeneous and heterogeneous catalysts, offering the possibility of preparing single-site heterogeneous catalysts (de Vos et al. 2002; Song & Lee 2002; Valkenberg & Hölderich 2002; Corma 2004; Madhavan et al. 2008).
In this article, we present the characteristics and catalytic properties of hybrid organic–inorganic materials, emphasizing the possibilities of periodic mesoporous hybrid materials and coordination polymers as single-site solid catalysts.

2. Hybrid organic–inorganic catalysts prepared by grafting molecular catalysts on solids

Heterogenization of homogeneous single-site catalysts on mesoporous inorganic solids allows combining the superior activity and selectivity of homogeneous catalysts with the easy separation, recovering and recycling of heterogeneous catalysts, and with the possibility of using continuous flow operations (Corma 2004). In this sense, MCM-41 and related mesoporous silicas have been widely used to prepare organic–inorganic hybrid catalysts (Kresge et al. 1992). MCM-41 combines very large surface areas (greater than 1000 m² g⁻¹) with regular pores of approximately 5 nm that allow the inclusion of molecular catalysts inside the hexagonally ordered parallel channels (Maschmeyer et al. 1995; Liu et al. 1997; Zhou et al. 1998). Active centres are immobilized on the walls by direct grafting. Thus, an adequately functionalized metal complex reacts with the Si-OH groups present at the surface or, otherwise, the ligands are firstly grafted to the surface and then reacted with the metal component (Corma et al. 1991, 1992, 1996 and references therein). However, it is not unusual to find that metal complexes decrease their activity and/or selectivity when supported, mainly because of inefficient interfacial mass transfer between the liquid phase and the solid, or because undesired interactions between the ligands of the metal complex and silanol groups present on the solid surface occur. These problems can be overcome by selecting a linker with the appropriate length, by removing the free silanol groups from the surface by silylation or by using the most adequate solvent. For instance, the highest activity values ever reported for the Friedel–Crafts enantioselective hydroalkylation of 1,3-dimethoxybenzene with 3,3,3-trifluoropyruvate using heterogenized metallic complexes were obtained with copper(II) bisoxazolines covalently anchored to silica (Corma et al. 2002).

To achieve this, the anchoring procedure was chosen to minimize the presence of uncomplexed copper on the surface and the free surface silanol groups, which were not used to anchor the metal complex, were silylated to avoid interactions with the complex or substrates (scheme 1). A similar strategy was used to improve the enantioselectivity of a chiral vanadyl Schiff base complex anchored on silica for the reaction of benzaldehyde with trimethylsilyl cyanide. The interaction of the complex with the solid was minimized by increasing the length of the linker to a chain with 11 carbon atoms, and by masking the presence of residual silanol groups with trimethylsilyl groups (Baleizao et al. 2003a,b).

In recent years, different types of metal complexes have been successfully anchored to MCM-41 and related mesoporous materials, resulting in highly efficient immobilized catalysts that can duplicate the activity of the homogeneous analogues while maintaining selectivity. In particular, great advances have been made in the field of asymmetric catalysis, which is one of the most challenging areas in heterogeneous catalysis. A classical approach to create an asymmetric environment around a metallic centre able to induce enantioselectivity in catalytic processes is the use of enantiomerically pure ligands containing donor atoms.
(mainly nitrogen and phosphorus) with a defined symmetry (Ojima & Nozaki 2000). In this sense, multidentate ligands containing N-heterocyclic carbene moieties (NHCs) are becoming increasingly popular (César et al. 2004) because (i) their electron donor properties can be enhanced, (ii) they tend to be more sterically demanding than phosphine ligands with the same substituents, and (iii) they are more stable towards molecular oxygen and moisture (Diez-González & Nolan 2007; Enders et al. 2007; de Fremont et al. 2009). Moreover, in catalytic systems, NHCs have been shown to prevent metal leaching, a problem often associated with weak ligand–metal interactions (Collman et al. 1987).

(NHC)NN–pincer ligands can be synthesized by reacting 2,6-dibromomethylpyridine with sub-stoichiometric amounts of 1-substituted imidazole, yielding the corresponding pyridine imidazolium salts that are finally converted into the chelating ligands (figure 1a) (Boronat et al. 2010a,b; del Pozo et al. 2010). Then, chiral chelating (NHC)NN–pincer ruthenium complexes were prepared by transmetalation from intermediate silver(I) complexes (figure 1b) and finally grafted onto MCM-41 (figure 1c). The introduction of the organometallic moieties did not induce drastic changes in the long-range hexagonal symmetry of host material, but induced a decrease in $S_{\text{BET}}$ area from 1030 to 842 m$^2$ g$^{-1}$, in agreement with observations in other systems after post-synthesis treatments.

The efficiency of the immobilized ruthenium complexes for the asymmetric hydrogenation of different alkenes and imines was studied and compared with that of the homogeneous counterpart. In the hydrogenation of (E)-diethyl 2-benzylidensuccinate, between 98 and 99 per cent ee was obtained with all catalysts tested, and higher turnover frequencies (TOFs) were observed for
the heterogenized catalysts (del Pozo et al. 2011). The effect of the co-ligand was studied by comparing the reactivity and enantioselectivity of the hydrid complexes with those derived from $p$-cymene and, as shown in figure 2, the hydride complexes either homogeneous (3aRu) or heterogenized (3bRuMCM-41, 4bRuMCM-41 and 4cRuMCM-41) are considerably more active than those
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derived from p-cymene. The grafted (NHC)NN–pincer ruthenium complexes were recovered from the reaction mixture by simple centrifugation and washing, and reused for several consecutive experiments with no appreciable loss of activity or selectivity.

The ease of functionalization of the imidazolium salt proligands allows the incorporation of NHCs in polydentate ligand structures, such as chiral di-NHC ligands and complexes (Lowry et al. 2008). Recently, the synthesis of stable C2-symmetric diimidazolidinylidene ligands bridged by a trans-2,2-dimethyl-1,3-dioxalane backbone and their use in catalytic asymmetric transformations have been reported. Different chelated gold, rhodium and palladium complexes were prepared and screened for catalytic activity in the hydrogenation of prochiral alkenes (Arnanz et al. 2010). The manipulation of L-tartaric acid gave access to (4R,5R)-bis(iodomethyl)-2,2-dimethyl-1,3-dioxolane (2 in figure 3a), which, when heated with 1-arylimidazoles 1a,b, produced quantitative yields of the salts [3a]I, [3b]I as light yellow solids. The treatment of these imidazolium iodide salts with Ag2O yielded the silver complexes (4S,5S)-3a, 3bAg (figure 3b), which were used as carbene transfer reagents to gold, palladium and rhodium (Lin et al. 2009). The reaction of the silver complexes with AuCl(tht) (tht = tetrahydrothiophene), [RhCl(cod)]2 and [PdCl2(cod)] (cod = 2,5-cyclooctadiene) yielded the corresponding (4S,5S)-3aAu, 3bAu, 3aRh, 3aPd complexes (figure 3b) in greater than 80 per cent yield with the formation of AgI precipitate.

The problem with (NHC)M-catalysed hydrogenations is the tendency of NHC to suffer a reductive elimination of the imidazolium salt [NHC-H]+, but bis-NHC ligands are expected to be resistant to this process. The efficiency of the synthesized gold, palladium and rhodium complexes in the asymmetric hydrogenation of several (E)-diethyl 2-R-succinates was investigated, and all complexes showed significant activities. In the hydrogenation of (E)-diethyl 2-benzylidenesuccinate, up to 99 per cent ee was obtained with the rhodium catalyst, while palladium and gold complexes yielded activities and selectivities comparable to those obtained with diphosphine ligands. Moreover, the bis-NHC complexes maintain their activity for at least three months, while the activity of the diphosphine [Rh(cod)(DIOP)]+ complex decreases after a week (Arnanz et al. 2010).

New hybrid bidentate ligands in which a chiral dioxalane is functionalized by using a powerful σ-donor NHC and a basic amine group have been synthesized with the aim of obtaining highly enantioselective catalysts (Villaverde et al. 2011). These ligands are believed to be well suited for asymmetric catalysis because of the closeness of the chiral information to the metal centre, the bulky substituents and the electronic differentiation. The hybrid chiral (NHC)-dioxolane-amines (S,S)-4a,4b were prepared following the procedure described in figure 4. Heating of (4R,5R)-bis(iodomethyl)-2,2-dimethyl-1,3-dioxolane (2) with one equivalent of 1-arylimidazole 1a or 1b produced quantitative yields of the respective mono-salts 3a and 3b as light yellow solids. These solids were heated in a microwave reactor with an excess of amine to afford the functionalized ligands (S,S)-4a,4b as light yellow oils. As previously described (Lin et al. 2009; Arnanz et al. 2010; Villaverde et al. 2011), the treatment of these imidazolium salts with Ag2O gave the corresponding silver complexes that were used as carbene transfer reagents to gold, palladium and rhodium.
(a) synthesis of ligand precursors

\[
\begin{align*}
\text{Ar} & \quad \text{N} \quad \text{Ar} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

1a,b → \[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

3a[I, 3b[I

a: \text{Ar} = 2,4,6-trimethylphenyl, b: \text{Ar} = 2,6-diisopropylphenyl

(b) synthesis of bis-NHC-complexes

\[
\begin{align*}
\text{[3a]+, [3b]+} \\
\text{Ag}_2\text{O} \\
\text{AuCl(tht)} \\
\text{PdCl}_2(\text{cod}) \\
\text{RhCl(cod)}_2
\end{align*}
\]

3aAu, 3bAu, 3aRh, 3bRh, 3aPd, 3bPd

a: \text{Ar} = 2,4,6-trimethylphenyl, b: \text{Ar} = 2,6-diisopropylphenyl

Figure 3. Synthesis of Au, Pd and Rh bis-NHC complexes (Arnanz et al. 2010).

(figure 4b). In a second step, the silyloxy complexes \((S,S)-[4aAu, 4bAu, 4aRh, 4bRh, 4aPd, 4bPd]\) were supported on MCM-41 by addition of the corresponding solution to a dispersion of MCM-41 in toluene and heating for 24 h. The efficiency of the gold-, palladium- and rhodium-supported complexes in the asymmetric hydrogenation of diethyl itaconate and \((E)-\)diethyl 2-benzylidenesuccinate was investigated and compared with that recorded using the

(a) synthesis of chiral mono-NHC ligand precursors

(a) synthesis of chiral mono-NHC ligand precursors

(b) synthesis of chiral mono-NHC-complexes

Figure 4. Representation of the synthetic route to obtain chiral NHC complexes with dioxolane backbone (Villaverde et al. 2011).
homogeneous catalysts. The best results were achieved with gold and palladium complexes derived from ligand 4b, and with palladium complexes derived from ligand 4a, all of them showing significant activities for the hydrogenation of (E)-diethyl 2-benzylidenesuccinate with 99 per cent ee. Recycling studies showed that Rh- and Pd-MCM-41 materials displayed very similar activities and enantioselectivities after the initial runs, while a fractional loss of active gold species with each successive cycle was observed with Au-MCM-41 material. However, this problem was minimized by treatment of the recovered material with an excess of benzonitrile at 50°C for 2h before washing, making this catalyst recyclable.

3. Hybrid organic–inorganic catalysts: periodic mesoporous materials

We have seen above the possibility of forming hybrid organic–inorganic catalysts by functionalization of preformed ordered inorganic mesoporous materials with specific organosilanes. However, these organic-functionalized mesoporous materials exhibit a separated heterogeneous bi-phase structure composed of an inorganic main framework with an external grafted layer that contains the specific active sites (Corma 2004; Margelefsky et al. 2008).

According to these characteristics, further investigations were undertaken to obtain novel crystalline porous materials, with a homogeneous distribution of functional groups within the framework of the structured mesoporous catalysts. This was achieved by preparing periodic mesoporous materials (PMOs) whose polymeric framework is composed of both inorganic and organic fragments. Following this, silsesquioxanes, which are organic–inorganic precursors, \((R'O)SiRSi(OR')_3\), were used as a silica source for the synthesis of hybrid materials that incorporate functional and active organic groups directly into the framework, instead of grafting the organic species onto the wall surface of the pores (Asefa et al. 1999; Inagaki et al. 1999; Melde et al. 1999). Figure 5 shows the general methodology employed to synthesize PMOs (Hoffmann et al. 2006), using a self-assembling route in the presence of surfactants that act as structure-directing agents to form structured mesoporous materials.

The advantages of these PMO hybrid porous materials rely on the highly ordered structures with very uniform pores, homogeneous distributions of active functional sites throughout the whole framework, high loadings of functional groups and the absence of any severe pore blocking (Inagaki et al. 2002). Within the field of catalysis, the possibility to introduce into the organic builders different organocatalysts with well-defined single-site acid, basic, chiral organocatalysts or even a combination of the above could be useful to generate organic–inorganic catalysts with heterogeneized functionalities stabilized into the mesoporous framework.

(a) Periodic mesoporous materials containing acid single sites

Acid sites can be introduced into the structure of PMOs by condensation of mercaptosilanes with different bridged silsesquioxanes by one-pot self-assembling methods in the presence of surfactants (Yang et al. 2002; Kapoor et al. 2003). A post-synthesis oxidation of the mercapto groups allows the preparation of
organic–inorganic mesoporous catalysts with acid sulphonic groups and marked hydrophobicity owing to the presence of one or more organic builders (Yuan et al. 2003). Inagaki and co-workers performed the preparation of this type of catalyst in the presence of triblock copolymer Pluronic P123 surfactants, and inorganic salts as additives. The results obtained showed unambiguously the formation of hybrid well-ordered hexagonal mesoscopic structures, working in a wide range of alkyl linkers inserted into the mesoporous framework. The role of the bridged organic groups was associated with an enhancement of the hydrothermal stability, which favours the catalytic activity of $-\text{SO}_3\text{H}$ functionalized mesoporous hybrid materials for the esterification of ethanol with acetic acid (Liu et al. 2005a,b).

Alternatively, interesting routes have been described to generate sulphonic periodic mesoporous organosilicas by the consecutive reduction and oxidation of sulphide builder groups introduced into the framework during the synthesis process (figure 6) (Liu et al. 2005a,b). The use of only one silsesquioxane precursor bis[3-(triethoxysilyl)propyl]disulphide together with non-ionic block copolymer surfactants as template facilitates the introduction of a great number of homogeneously distributed sulphide moieties within the network. The final oxidative post-treatment implies the complete transformation of sulphide builders to sulphonic groups without any significative structural alteration. These hybrid organic–inorganic acid catalysts were used for the esterification of aliphatic acids and ethanol, showing higher yield than zeolites and sulphonic acid resins. This fact is associated with the large pore diameter and low surface hydrophilicity exhibited by these PMOs (Li et al. 2008).

PMOs containing ethane builder groups were also functionalized by grafting with perfluoroalkylsulphonic acid units by reacting the porous hybrid, previously formed, with 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulphonic acid $\beta$-sultone (figure 7). The synthesized solid retains the surface area and porosity, with a high acid site density (around 1.30 mmolH$^+$ g$^{-1}$) and an exceptional proton

Figure 5. The self-assembling procedure to obtain PMOs in the presence of surfactants. The images are an artistic representation of PMOs (Hoffmann et al. 2006). (Online version in colour.)
Figure 6. Representation of synthesis methodology to obtain first the PMO containing disulphide moieties and finally the sulphonic hybrid PMO by oxidative treatment (Liu et al. 2005a, b). (Online version in colour.)

Figure 7. Preparation of perfluoroalkylsulphonic functionalized ethane-PMO by the grafting method (Shen et al. 2008).

d conductivity (up to $1.0 \times 10^{-1} \text{ S cm}^{-1}$). The post-functionalized ethane-PMO showed higher catalytic activity for the alkylation of isobutene with 1-butene than perfluoroalkylsulphonic acid in SBA-15, alkylsulphonic acid integrated into PMO and zeolite (Shen et al. 2008). The same PMO material was also successfully employed as a strong acidic heterogeneous catalyst in liquid phase self-condensation of heptanal, and acetalization of heptanal with 1-butanol, though water was formed in both reactions (Dube et al. 2009).

Within single-acid-site PMO materials, Polarz et al. have introduced benzoic and phenylphosphonic acid structural groups into a novel family of PMOs, named UKON by the authors, using 1,3-bis-(trialkoxyisilyl)-5-bromobenzene as
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Figure 8. Mesoporous UKON hybrid materials containing benzoic and phenylphosphonic acids as organic builders (Kuschel et al. 2008).

the silsesquioxane precursor. The halogenated aromatic builder compounds allow the functionalization of hybrid mesoporous materials by different derivatization reactions, generating interesting hybrid materials with acidic properties (figure 8) (Kuschel et al. 2008).

(b) PMOs containing base single sites

It is possible to generate effective basic PMO catalysts based on the combination of bridged silsesquioxanes and functionalized monosilanes. This has allowed the synthesis of ordered periodic mesoporous organosilicas with different organic moieties that act as builders while introducing basic single sites. The molecules containing the base sites are, normally, organic molecules

with amino groups which hang from the walls to the free channels in the synthesized PMO material (Burleigh et al. 2001a,b; Kapoor et al. 2006; Zhu et al. 2007). Amination post-treatments were also carried out on phenylene moieties structurally integrated into crystalline PMOs by Inagaki et al. The amine modification was achieved in approximately 28 per cent of total organic linkers, following two consecutive transformation steps based on the use of strong acid solutions of HNO₃–H₂SO₄ and SnCl₂–HCl (figure 9). The chemical modification of phenylene groups did not imply any substantial structural change, preserving both the ordered and crystal-like molecular scale periodicity of the starting material. The resultant NH₂-Ph-PMO hybrid successfully catalysed the Knöevenagel condensation reaction, acting as solid base catalyst (Ohashi et al. 2008).

Basic sites can also be included into the bridged silsesquioxanes which act as both builders and active sites conforming the structure of the mesoporous material. In those cases, the presence of additional functionalized monosilanes is not required because the disilane can facilitate the organic–inorganic structuration and the additional base activity useful for catalytic processes. Related to this approach, recently Corma et al. have prepared different base-single-site PMOs by the integration of Tröger base or protonic sponges as functional builders from the respective bridged silsesquioxane precursors (figure 10). These hybrids showed high activity as base catalysts for the Knoevenagel catalytic process and can be recycled without activity loss (Gianotti et al. 2011; Poli et al. 2001). The activity of the basic sites in the hybrid catalysts for condensation reactions can be increased if a mild acid is introduced to the adequate distance of the basic site in the organic component (Boronat et al. 2010a,b; Corma et al. 2011).

(c) PMOs containing chiral single sites

The concept of single-site PMOs can be expanded to obtain a new type of ordered hybrid materials with chirality that can be used as asymmetric catalysts. This emergent topic has been explored from different approaches, the most usual being the use of bridged silsesquioxane precursors that contain chiral organic linkers that are structurally integrated into the specific PMOs. In this way, Corma and co-workers prepared the first family of well-ordered chiral mesoporous organosilicas (ChiMOs) by introducing, in a one-pot synthesis, chiral vanadyl salen complexes into the walls of hybrid materials with M41S periodicity (figure 11). This specific ChiMO catalyst induced 30 per cent enantioselectivity in the cyanosilylation of benzaldehyde (Baleizao et al. 2003a,b, 2004).

Following this approach, García and co-workers prepared other attractive chiral periodic mesoporous organosilica, ChiMO, using as the organic–inorganic precursor bis-silylated tartramide derived from L-(-)-dimethyl tartrate
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Figure 10. (a) Synthesis of the di-iodo Tröger base derivative (1) and di-silylated precursor (2) from iodoaniline; (b) synthesis of 1,8-bis(dimethylamino)naphthalene (DMAN) bis-silylated precursor (Gianotti et al. 2011; Poli et al. 2001).

Figure 11. Bridged silsesquioxane containing vanadyl salen complex linker employed as the precursor of ChiMO (Baleizao et al. 2003a,b, 2004).
PNM0s that contain bridged benzoic acids as builders along the pore walls (UKONs) were used to incorporate, by post-synthesis treatments, amino acids such as, for instance, alanine. This synthetic route allows the preparation of organized mesoporous chiral hybrid materials with large surface (greater than 600 m$^2$/g; figure 13). The chirality of the surfaces was effectively probed by adsorption of chiral gases on the mesoporous solids (Kuschel et al. 2008).

Also within the UKON family materials, a novel ChIMO was prepared starting from (S)-1,3-bis-tri-iso-propoxysilyl-5-phenylethanol bridged silsesquioxane precursor (figure 14a). A final post-synthesis modification to attach Al(III) as Lewis acid centre to the chiral building blocks allows the usage of the hybrid material as an enantioselective catalyst for the asymmetric carbonylene reaction (figure 14b), showing that the surface-bound Al(III) active site exhibits higher enantiomeric excesses than analogous molecular homogeneous catalysts. Moreover, the presence of secondary surface groups, such as propyl or methyl groups, introduced by silylation of silanol groups, improves the catalytic performance when bulkier groups are incorporated to the pore walls, with a beneficial cooperative effect between the structural catalytic sites and the close surface groups (Kuschel & Polarz 2010).

Interesting approaches to directly generate chiral PDM0s during the synthesis process by the use of optimal precursors was proposed by CRUDDEN et al., who employed axially chiral biphenyl monomers as starting disilanes. This route
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permitted, for the first time, the transmission of chirality into the solid PMO material, being possible the detection of chiral aggregates within the hybrid material, by means of circular dichroism techniques (figure 15) (MacQuarrie et al. 2008).

Innovative approaches to obtain chiral periodic organosilicas would be the synthesis of well-structured PMOs conformed by chiral channels. In this case, the morphology of solids and their spatial conformation are essential to prepare PMOs with intrinsic chirality. Tatsumi et al. synthesized new chiral PMOs using an achiral fluorinated surfactant (FC-4911), generating ordered mesoporous hybrids which contain chiral channels (Meng et al. 2007). The chiral solids were conformed by twisted hexagonal or spiral hexagonal rods when 1,2-bis(triethoxysilyl)ethene or 1,4-bis(triethoxysilyl)benzene (BTEB) were used as hybrid silica precursors. It is remarkable that the spiral samples obtained with BTEB exhibited high structural periodicity, showing a spacing of 0.85 nm in the crystalline mesoporous wall (figure 16). However, few reports have been published up to now following this approach, though it could be of interest to obtain chiral PMOs catalysts for enantioselective reactions.

4. Coordination polymers or metal–organic frameworks

Metal–organic frameworks (MOFs), built up from gathering both metallic ionic units and bridged organic builders, emerge as an attractive group of ordered porous hybrids, featuring unique structural and functional characteristics. Indeed, the potential applications of these materials received particular attention mainly for adsorption and separation, as well as for sensors (Harbuzaru et al. 2008, 2009), and to a certain extent in catalysis acting as stable single-site active materials (Li

Figure 14. (a) Synthesis of mesoporous organosilica containing chiral pore walls; (b) the asymmetric carbonylene scheme reaction (Kuschel & Polarz 2010).

et al. 1999; Lebedev et al. 2005; Corma et al. 2010a,b). Depending on whether the active sites in the MOFs are part of the structural nodes or linkers, or they are generated by post-synthesis modifications in the MOFs, it is possible to classify MOF catalysts into three principal groups: (i) MOFs directly used as catalysts where the metal nodes or organic bridges exhibit catalytic activity, (ii) MOFs in which active organic molecules or metallic nanoclusters are occluded or supported in the channels or cavities, and (iii) chemically modified MOFs by post-synthesis treatments by grafting a homogeneous catalyst counterpart onto the MOFs, or by covalent post-modification of organic builders.

(a) MOFs used directly as single-site catalysts

Because most of the MOFs are built up by self-assembly of transition metals as structural nodes and organic linkers with binding centres, each builder unit constitutes a potential Lewis acid or Lewis basic site, respectively. The structural ionic metallic nanoclusters of different conventional MOFs have been successfully applied as Lewis acid catalysts in processes such as cyanosilylations (Fujita et al. 1994; Schlichte et al. 2004; Horike et al. 2008), acetalizations (Llabrés et al. 2007; Gándara et al. 2008; Lu et al. 2008), oxidations (Llabrés et al. 2008), hydrogenations and oxidative self-couplings (Xiao et al. 2007), isomerizations and cyclizations (Alaerts et al. 2006), aldolizations (Fujita et al. 1994) or Friedel–Crafts alkylations (Ravon et al. 2008). In those cases, metallic nodes based on Cd, Co, Cu, In, Mn, Pd or Zn nanoclusters act as active Lewis acid sites.
Metallic nanocluster builders inserted into mono-dimensional MOFs could perform as Lewis acid catalysts, as evidenced by Brown and co-workers who hydrothermally synthesized a new extended infinite MOF \([\text{Cu(H}_2\text{btec})(\text{bipy})]\) (\(\text{H}_4\text{btec} = 1, 2, 4, 5\)-benzenetetracarboxylic acid, bipy = 2, 2’-bipyridine; figure 17). In this hybrid material, each Cu(II) centre has a distorted square planar environment, completed by two N atoms from one bipy ligand and two O atoms belonging to two dihydrogen benzene-1,2,4,5-tetracarboxylate anions (\(\text{H}_2\text{btec}^{2-}\)).
The \([\text{Cu(bipy)}]^2+\) moieties are bridged by \(\text{H}_2\text{btec}^2-\) anions to form an infinite one-dimensional coordination polymer with a zig-zag chain structure along the \(c\)-axis, forming a double-chain structure by H bonds between adjacent sinusoidal chains. The MOF was tested as catalyst for the oxidation of cyclohexene and styrene, with tert-butyl hydroperoxide as oxidant. \([\text{Cu(H}_2\text{btec})(\text{bipy})]\) demonstrated higher TOFs for cyclohexene conversion than for styrene, but with high selectivity towards epoxidation in both cases (Brown et al. 2009).

Following with the catalytic activity of Cu-MOFs, recently Corma et al. have described the preparation of copper-containing MOF as catalysts, such as \([\text{Cu(2-pymo)}]_2\), \([\text{Cu(im)}]_2\), \([\text{Cu}_3(\text{BTC})]_2\) and \([\text{Cu(BDC)}]\) (2-pymo, 2-hydroxypyrimidinolate, im: imidazolate, BTC: benzene tricarboxylate, BDC: benzene dicarboxylate), and their use as active and regioselective catalysts for click reactions such as the 1,3-dipolar cycloaddition, being the performance of these MOF catalysts comparable to homogeneous Cu catalysts. Specifically, it was found that the activity of Cu changes with the organic linker in the MOF, with those containing CuN₄ being more active than those containing CuO₄ centres. Remarkably, these Cu-MOF catalysts allowed performing a one-pot two-step process in which the azide is formed \textit{in situ} and reacted immediately with phenylacetylene to form the 1,4-triazole (figure 18) (Luz et al. 2010).

Novel MOFs featuring both Lewis acidity and shape selectivity properties have been recently presented (Gándara et al. 2009). Specifically, a scandium MOF conformed by octadecasil zeolitic cages has been synthesized. In contrast, zeolitic cages of the AST type were found in the scandium-squarate MOF (Sc(C₄O₄)₃). However, in comparison with the zeolitic AST net, in which cages are connected through the 6-rings, the Sc atoms are the only shared knots between the cages, resulting in a binodal network with unique topology (figure 19). The thermal stability of these Sc-MOFs was close to 400°C, and it was an efficient heterogeneous Lewis acid catalyst for cyanosilylation and acetalization of carbonyl compounds.

Now, it will be illustrated how MOFs could also be used directly as catalysts taking advantage of the intrinsic Lewis basic properties featured by the organic groups acting as linkers in the crystalline structure (Kitagawa et al. 2012).
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Figure 18. Formation of triazole compounds, from azide intermediates, using Cu-MOF catalysts (Luz et al. 2010).

Figure 19. Polyhedral representation of the new Sc2(C4O4)3 MOF viewed along the c-axis (Gándara et al. 2009). (Online version in colour.)

Recently, MOFs have been prepared with non-coordinated amino groups, IRMOF-3 (isoreticular MOF), and amino-functionalized MIL-53, which are stable solid basic catalysts for the Knoevenagel condensation of ethyl cyanoacetate and ethyl acetoacetate with benzaldehyde (figure 20). IRMOF-3 exhibits activities that are at least as high as the most active solid basic catalysts reported for this reaction, with 100 per cent selectivity to the condensation product. In the case of the amino-MIL-53 MOF, its poor performance for Knoevenagel condensations is attributed to strong adsorption and diffusion limitations in the one-dimensional pore structure. The performance of the IRMOF-3 catalysts demonstrates that the activity of the amino group in aniline increases by interaction with the carboxylic groups when it is incorporated in the MOF structure. This interaction is claimed to be responsible for an increase in the pKa of the basic catalyst, showing a higher activity than their homogeneous counterparts. The IRMOF-3...
catalysts are stable under the reaction conditions, and could be reused without loss of activity. The catalytic performance of IRMOF-3 is closer to that of the organocatalysts based on the same basic moieties owing to the particular environment of the catalytic site and the accessibility through the pores of the IRMOF-3. The higher activity can be explained from DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) results that demonstrated the occurrence of benzaldimine intermediates in the reaction mechanism (Gascón et al. 2009). Moreover, leaching of the active sites was observed, being an intrinsic part of the organic linker.

(b) Active catalytic counterpart occluded into metal–organic frameworks

Another possibility to design single-site MOF catalysts comes from embedding active organic moieties into the well-defined cavities for their stabilization into the chemical metal–organic environment. This method is currently used to heterogenize different organocatalysts to avoid the major drawbacks of homogeneous catalysts in terms of catalyst separation and recycling. Within this approach, quaternary alkylammonium salts such as Me₄NCl, Me₄NBr, Et₄NBr, Pr₄NBr, Bu₄NBr were occluded inside MOF-5 (Zn₄O(BDC)₃, BDC = benzene-1,4-dicarboxylate) and the resulting materials revealed excellent catalytic performance for the coupling reaction of CO₂ with propylene oxide to produce propylene carbonate. The reasons for the high catalytic activity of the MOF-5/nBu₄NBr is the high surface area and accessibility to the active site, and the synergic effect of the couple MOF-5 and n-Bu₄NBr to catalyse the reaction even at low CO₂ pressure. After easy separation, the catalyst can be reused without a noticeable decrease in activity and selectivity after being used three times. The MOF-5/Bu₄NBr catalytic system also revealed high activity and selectivity for the cycloaddition of CO₂ with other epoxides, such as glycidyl phenyl ether, epichlorohydrin and styrene oxide (Song et al. 2009).

Hybrid structured materials as catalysts

Interestingly, other catalytic systems such as polyoxometalates have been occluded and stabilized into the supercavities of different MOFs. Different series of crystalline hybrids, such as \([\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_2][\text{H}_n\text{XM}_{12}\text{O}_{40}] \cdot (\text{C}_4\text{H}_{12}\text{N})_2\) (X = Si, Ge, P, As; M = W, Mo), were obtained by one-step hydrothermal synthesis of copper nitrate, BTC and different Keggin polyoxometalates (POMs). In these compounds, the catalytically active Keggin polyanions were alternately distributed as non-coordinating guests into the cuboctahedral cages of a Cu-BTC-based MOF host (figure 21). These materials demonstrated high stability for thermal and acid–base conditions. No POM leaching or framework decomposition was detected. The catalytic activity of these MOFs, containing occluded PW_{12} species, was tested for the hydrolysis of esters in excess of water, showing high catalytic activity and being used in repeated cycles without activity loss (Sun et al. 2009).

Finally, additional post-synthesis treatments of MOFs have been carried out in order to covalently anchor different homogeneous organocatalysts onto the organic builders that are hence perfectly stabilized and integrated into the MOF. This methodology opens the doors to obtain novel modified single-site catalytic MOFs based on active groups grafted on their surface. Moreover, the presence of accessible functional groups (for instance, amino, sulphonylic or vinyl groups) from the modified organic linkers would facilitate additional covalent anchoring of other organic or organometallic complexes in successive post-synthesis steps to obtain more specific catalysts. In this regard, Farrusseng et al. have modified by post-synthesis treatment zinc carboxylate (IRMOF-3) and triazolate (ZnF(Am₂TAZ), Am = amino, TAZ = triazolate) (Savonnet et al. 2009), which were prepared from aminoterephthalic acid (Huang et al. 2003; Goforth et al. 2005), both with amino groups pointing to the channels (figure 22). The modification consisted in the
acylation of NH₂ with nictinoyl chloride with the objective of increasing the surface hydrophobicity while maintaining the basicity, the pKa of the attached pyridine group being similar to that of aniline as precursor.

The catalytic performance of these modified MOFs was superior to the non-modified MOFs analogues for the aza-Michael reaction, probably owing to the higher hydrophilicity of the former. The resultant catalysts were also more active than their homogeneous counterparts owing to the stronger adsorption in the micropores of the organic compounds.

The validity of the post-synthesis modification approach was also demonstrated by Corma et al., who incorporate covalently Au(III) Schiff base complexes onto type-IRMOF-3 MOFs previously grafted with salicylaldehyde molecules (figure 23a). The Au(III)-containing MOF was highly active and selective for three-dimensional coupling and cyclization reactions in the liquid phase. Importantly, the catalyst was fully recyclable, without leaching or modification during the reaction. More specifically, the latter was the multi-reaction coupling of N-protected ethynylaniline, amine and aldehyde catalysed by IRMOF-3-SI-Au in dioxane (figure 23b). This catalyst gave higher activity than homogeneous and any gold-supported catalysts reported up to now (Zhang et al. 2009). The well-defined Au(III) sites were active for H₂ dissociation and proved to be active for the gas-phase selective hydrogenation of 1,3-butadiene into the butenes. Recently, this type of gold MOF, IRMOF-3-SI-Au, has been successfully used as catalyst for the cyclopropanation of alkenes with high chemo- and diastereoselectivities, bridging the gap between homogeneous and heterogeneous catalysis (Corma et al. 2010a,b).

5. Conclusions

Different single-site catalysts based on PMOs, MOFs and supported silica materials have been presented. They show that the integration of homogeneous active compounds into the defined and structurated matrixes can increase the performance of molecular catalysts. Indeed, the presence of single-site heterogenized active phases in organized solids allows us to obtain highly specific catalysts, with the advantages of recyclability and separation associated with heterogeneous catalysis. Definitively, the presence of single isolated sites in the framework of hybrid organic–inorganic structured materials bridges the gap between homogeneous and heterogeneous catalysts, and opens the possibilities for preparing well-defined multisite catalysts for performing cascade-type reactions with solid catalysts (Climent et al. 2011).

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