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Additional Information

“Recent Advances in Single-site Heterogeneous Catalysis (SSHC)”

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

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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 sites heterogeneity with the corresponding negative impact on selectivity.

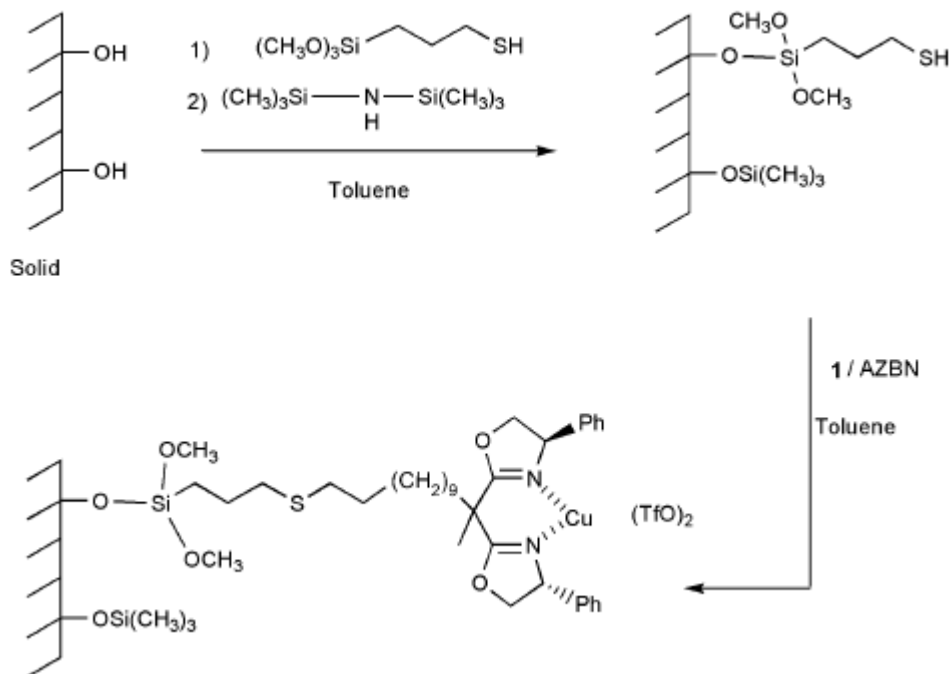
Since well defined single sites can be achieved with transition metal complexes and organocatalysts, one can envisage the preparation of hybrid organic-inorganic solid materials in where the molecular catalysts would be part of the structure. This type of materials should couple the advantages of the homogeneous and heterogeneous catalysts, offering the possibility of preparing single-site heterogeneous catalyst (Song *et al.* 2002; Valkenberg *et al.* 2002; De Vos *et al.* 2002; Madhavan *et al.* 2008; Corma 2004).

In this manuscript 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.

1. Hybrid organic-inorganic catalysts prepared by grafting molecular catalysts on solids

Heterogenization of homogeneous single-site catalysts on mesoporous inorganic solids allows to combine 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 ($> 1000 \text{ m}^2/\text{g}$) with regular pores of $\sim 5 \text{ nm}$ 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 centers 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). However, it is not unusual to find that metal complexes decrease their activity and/or selectivity when supported, mainly due to 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 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, that 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.* 2003).



Scheme 1. Anchoring of Cu(II) bisoxazoline complex **1** to silica (Corma *et al.* 2002).

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 which can duplicate the activity of the homogeneous analogues while maintaining selectivity. In particular, great advances have been done 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 2000; Jacobsen 1999). In this sense, multidentate ligands containing N-heterocyclic carbene moieties (NHCs) are becoming increasingly popular (Cesar *et al.* 2004) because: a) their electron donor properties can be enhanced, b) they tend to be more sterically demanding than phosphine ligands with the same substituents and c) they are more stable toward molecular oxygen and moisture (de Fremont *et al.* 2009; Enders *et al.* 2007; Diez-Gonzalez *et al.* 2007). 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.* 2010; 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_{BET} area from 1030 to 842 $\text{m}^2 \text{g}^{-1}$, in agreement with observations in other systems after post-synthesis treatments.

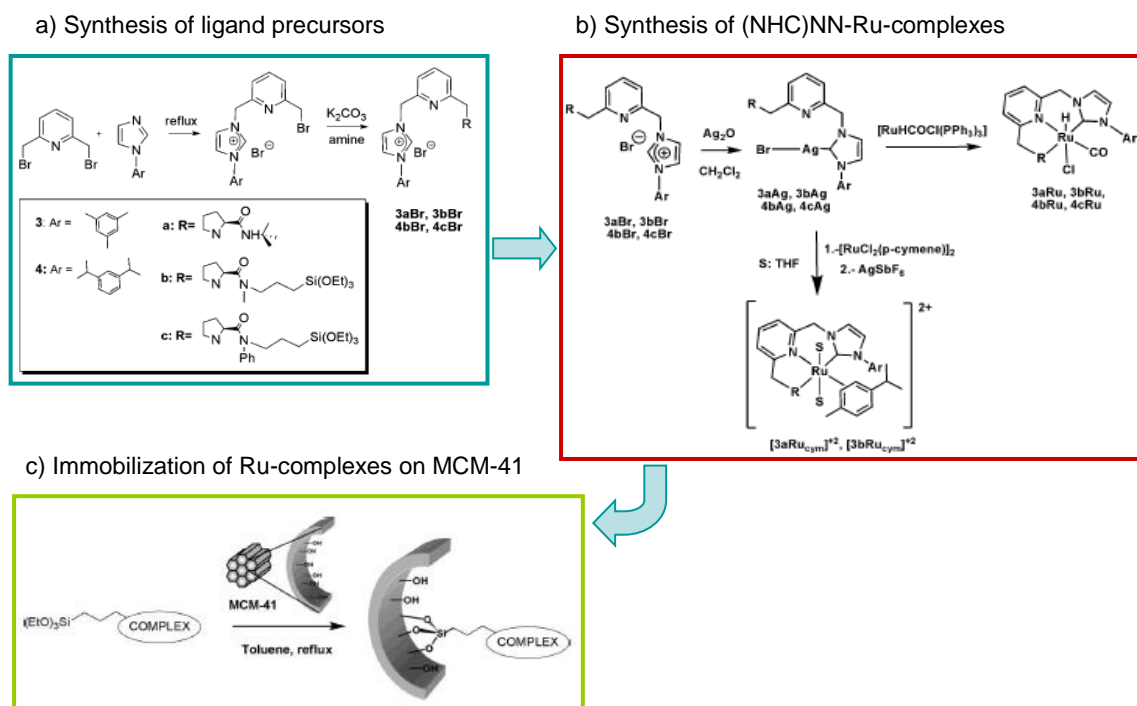


Figure 1. Representation of the synthetic route to obtain (NHC)NN-Ru-complexes immobilized on MCM-41 (del Pozo *et al.* 2011).

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% ee was obtained with all catalysts tested, and higher TOFs were observed for the heterogenised catalysts (del Pozo *et al.* 2011). The

effect of the co-ligand was studied by comparing the reactivity and enantioselectivity of the hydride complexes with those derived from *p*-cymene and, as shown in Figure 2, the hydride complexes either homogeneous (3aRu) or heterogenised (3bRuMCM-41, 4bRuMCM-41 and 4cRuMCM-41) are considerably more active than those 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.

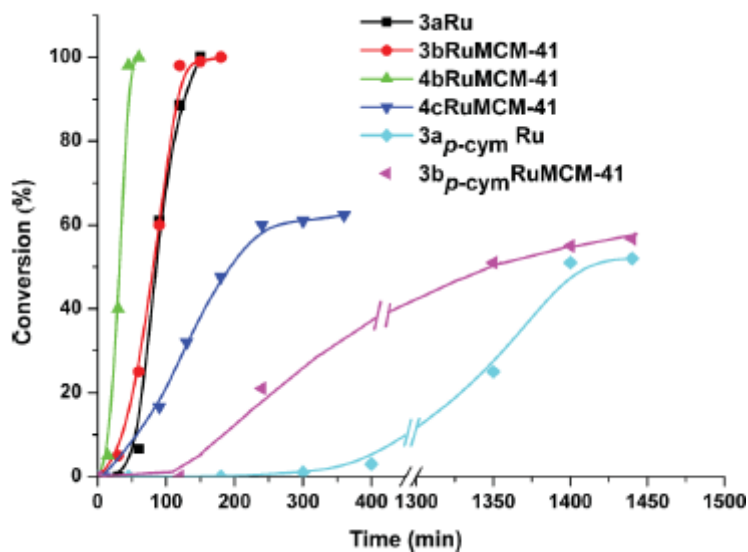
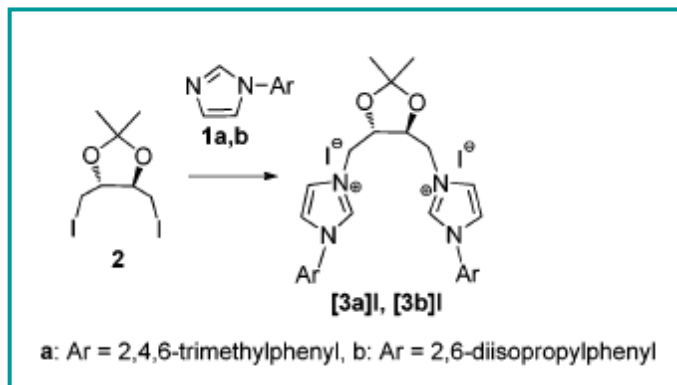


Figure 2. Kinetic profile of the Ru-catalysed hydrogenation of (E)-diethyl 2-benzylidensuccinate (del Pozo *et al.* 2011).

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 has 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 (4*R*,5*R*)-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 (4*S*,5*S*)-**3a**,**3b**Ag (Figure 3b), that 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 (**4*S*,5*S***)-**3aAu**, **3bAu**, **3aRh**, **3aPd** complexes (see Figure 3b) in > 80% yield with the formation of AgI precipitate.

a) Synthesis of ligand precursors



b) Synthesis of bis-NHC-complexes

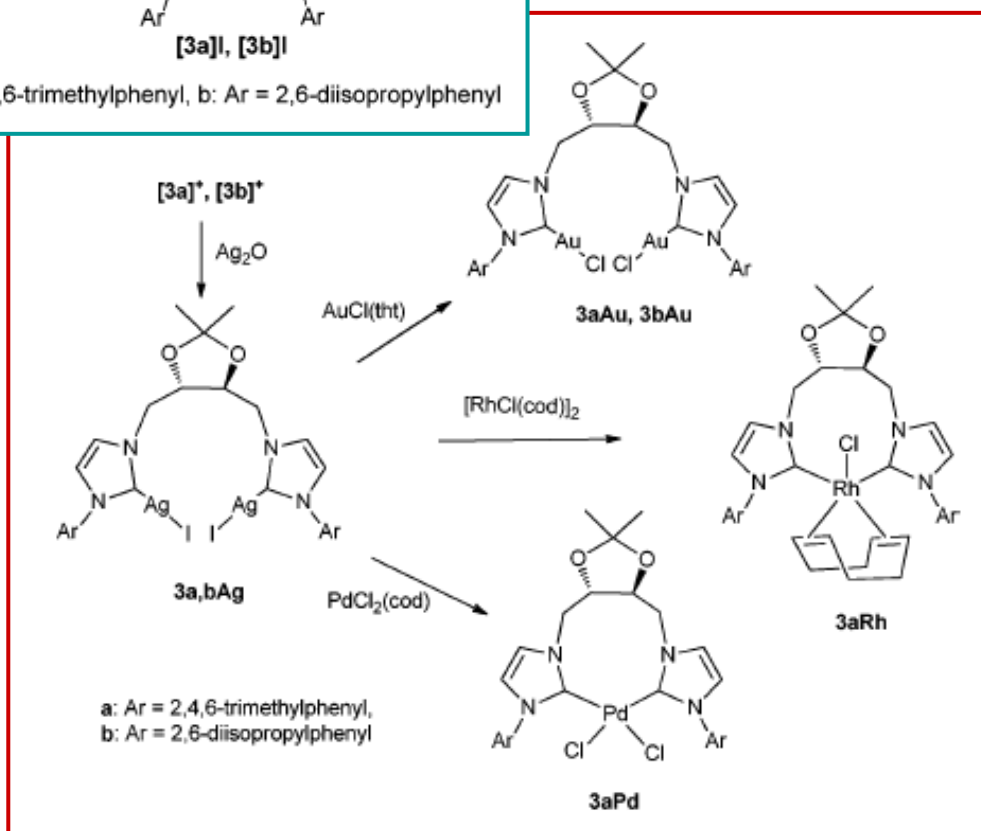


Figure 3. Synthesis of Au, Pd and Rh bis-NHC complexes (Arnanz *et al.* 2010).

The problem with (NHC)M-catalyzed hydrogenations is the tendency of NHC to suffer a reductive elimination to 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% 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 $[\text{Rh}(\text{cod})(\text{DIOP})]^+$ 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 center, 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 (Arnanz *et al.* 2010; Lin *et al.* 2009; Villaverde *et al.* 2011), the treatment of these imidazolium salts with Ag_2O gave the corresponding silver complexes that were used as carbene transfer reagents to gold, palladium and rhodium (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 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% 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° for 2h before washing, making this catalyst recyclable.

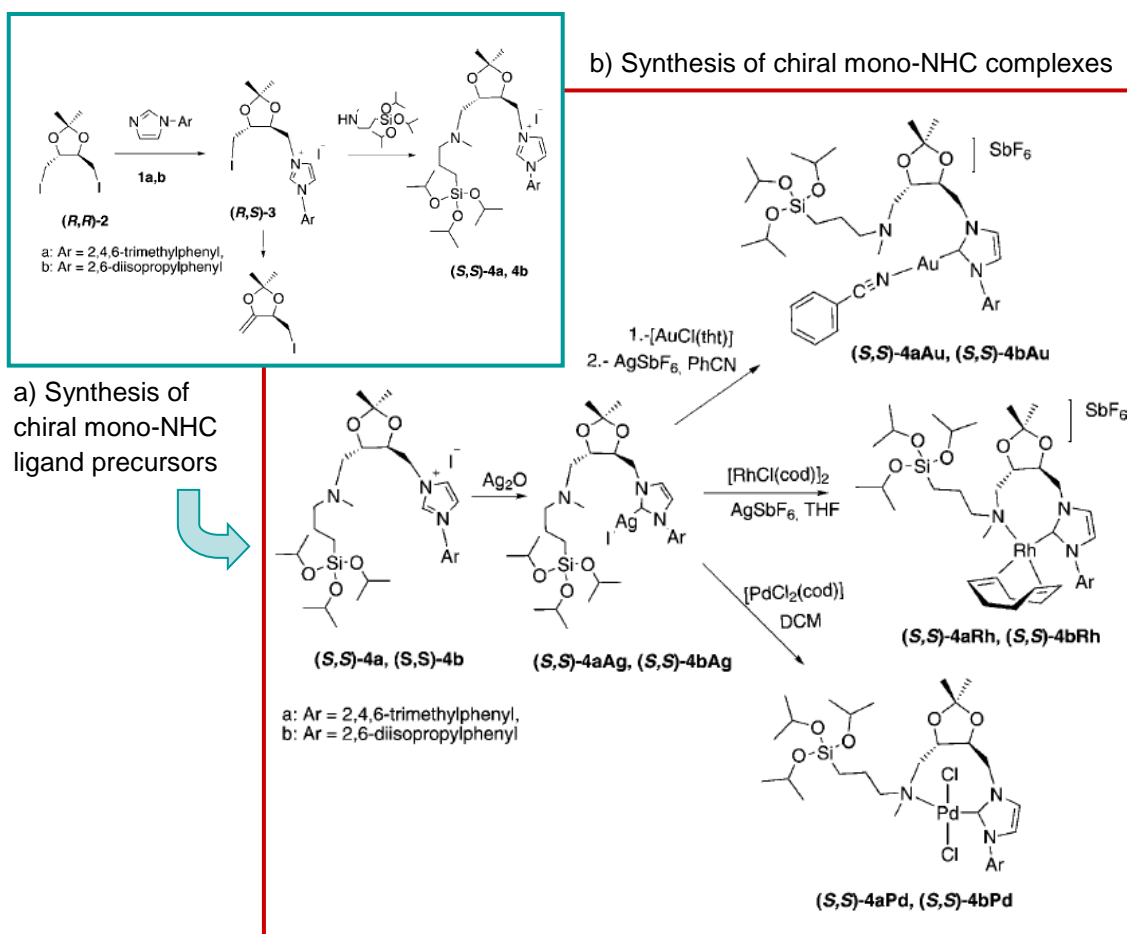


Figure 4. Representation of the synthetic route to obtain chiral NHC complexes with dioxolane backbone (Villaverde *et al.* 2011).

3. Hybrid Organic-Inorganic Catalysts: Periodic Mesoporous Materials (PMOs)

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 which 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, $3(R'O)SiRSi(OR')_3$, 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 (Inagaki *et al.* 1999; Asefa *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 presence of surfactants that act as structure directing agents to form structured mesoporous materials.

The advantages of these PMOs 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 combination of the above, could be useful to generate organic-inorganic catalysts with heterogeneized functionalities stabilized into the mesoporous framework.

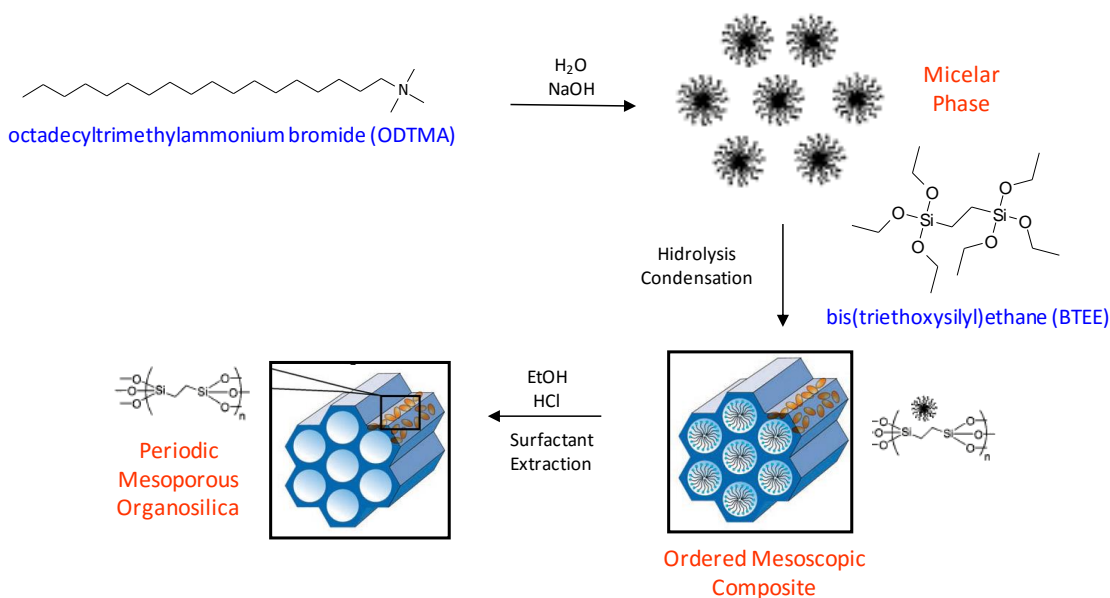


Figure 5. Self-assembling procedure to obtain PMOs in presence of surfactants. The images are artistic representation of PMOs (Hoffmann *et al.* 2006).

PMOs 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 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 sulfonic groups and marked hydrophobicity due to the presence of one or more organic builders (Yuan *et al.* 2003). Inagaki *et al.* performed the preparation of this type of catalysts in 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 favors the catalytic activity of $-\text{SO}_3\text{H}$ functionalized mesoporous hybrid materials for the esterification of ethanol with acetic acid (Liu *et al.* 2005).

Alternatively, interesting routes have been described to generate sulfonic periodic mesoporous organosilicas by the consecutive reduction and oxidation of sulfide builder groups introduced into the framework during the synthesis process (Figure 6) (Liu *et al.* 2005). The use of only one silsesquioxane precursor bis[3-(triethoxysilyl)propyl]disulfide (BTPDS) together with nonionic block copolymer surfactants as template, facilitates the introduction of a great number of homogeneously distributed sulfide moieties within the network. The final oxidative post-treatment implies the complete transformation of sulfide builders to sulfonic 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 sulfonic acid resins. This fact is associated with the large pore diameter and low surface hydrophilicity exhibited by these PMOs (Li *et al.* 2008).

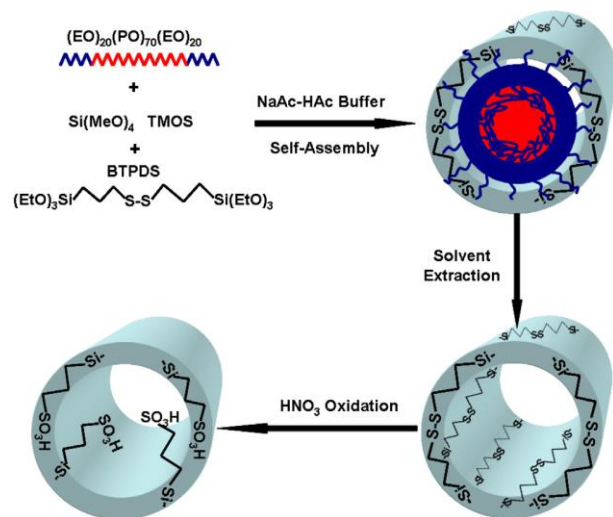


Figure 6. Representation of synthesis methodology to obtain first the PMO containing disulfide moieties and finally the sulfonic hybrid PMO by oxidative treatment (Liu *et al.* 2005).

PMOs containing ethane builder groups, were also functionalized by grafting with perfluoroalkylsulfonic acid units by reacting the porous hybrid, previously formed, with 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid β -sultone (Figure 7). The synthesized solid retains the surface area and porosity, with a high acid site density (around 1.30 mmolH⁺/g) and an exceptional proton conductivity (up to 1.0 x 10⁻¹ S/cm). The post-functionalized ethane-PMO showed higher catalytic activity for the alkylation of isobutene with 1-butene than perfluoroalkylsulfonic acid in SBA-15, alkylsulfonic acid integrated into PMO and zeolite (Shen *et al.* 2008). The same PMO material was also successfully employed as 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).

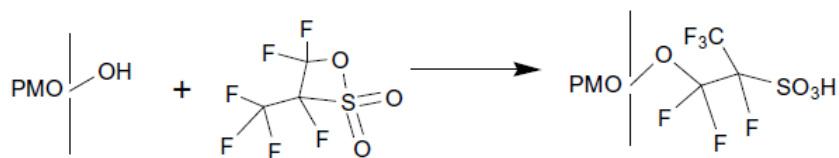


Figure 7. Preparation of perfluoroalkylsulfonic functionalized ethane-PMO by the grafting method (Shen *et al.* 2008).

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-(trialkoxysilyl)-5-bromobenzene as 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).

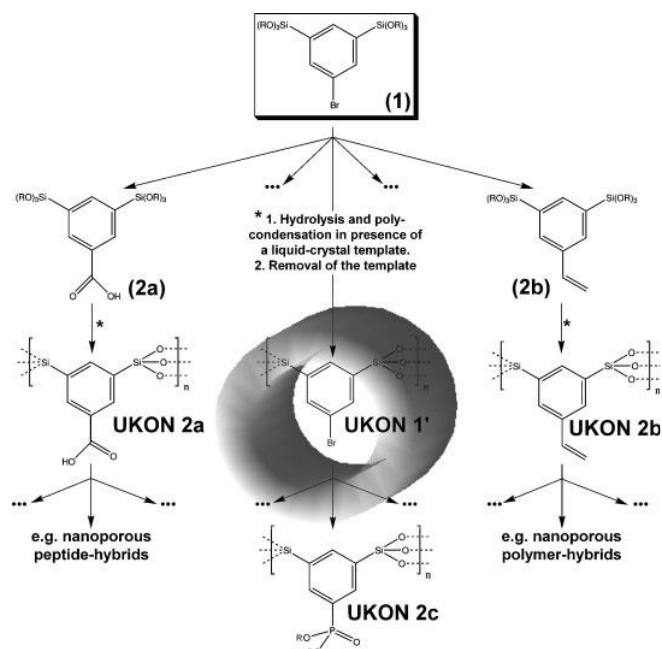


Figure 8. Mesoporous UKON hybrid materials containing benzoic and phenylphosphonic acids as organic builders (Kuschel *et al.* 2008).

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 which act as builders whilst introducing basic single sites. The molecules containing the base sites are, normally, organic molecules with amino groups that will hang from the walls to the free channels in the synthesized PMO material (Burleigh *et al.* 2001; Zhu *et al.* 2007; Kapoor *et al.* 2006). 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 ~28% of total organic linkers, following two consecutive transformation steps based on the use of strong acid solutions of $\text{HNO}_3\text{--H}_2\text{SO}_4$ and $\text{SnCl}_2\text{--HCl}$ (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 $\text{NH}_2\text{-Ph-PMO}$ hybrid,

successfully catalyzed the Knöevenagel condensation reaction, acting as solid base catalyst (Ohashi *et al.* 2008).

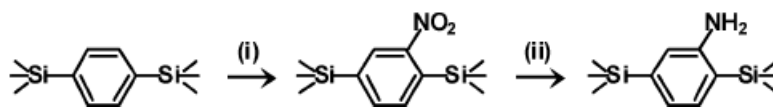
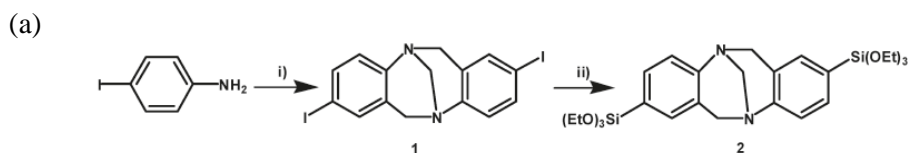


Figure 9. Amination of phenylene builder moieties in crystal-like Ph- PMOs: (i) HNO₃-H₂SO₄ and (ii) SnCl₂-HCl (Ohashi *et al.* 2008).

Basic sites can also be included into the bridged silsesquioxanes which act both, as 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 with 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.* 2011). 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.* 2010; Corma *et al.* 2011).



^a (i) $(\text{CH}_2\text{O})_m$, THF, -15°C to room temperature 48 h, NH_3 aq.; (ii) $[\text{Rh}(\text{CH}_3\text{CN})_2(\text{cod})]$ BF_4 , Et_3N , $(\text{EtO})_3\text{SiH}$, DMF anhydrous 7 h, 80°C .

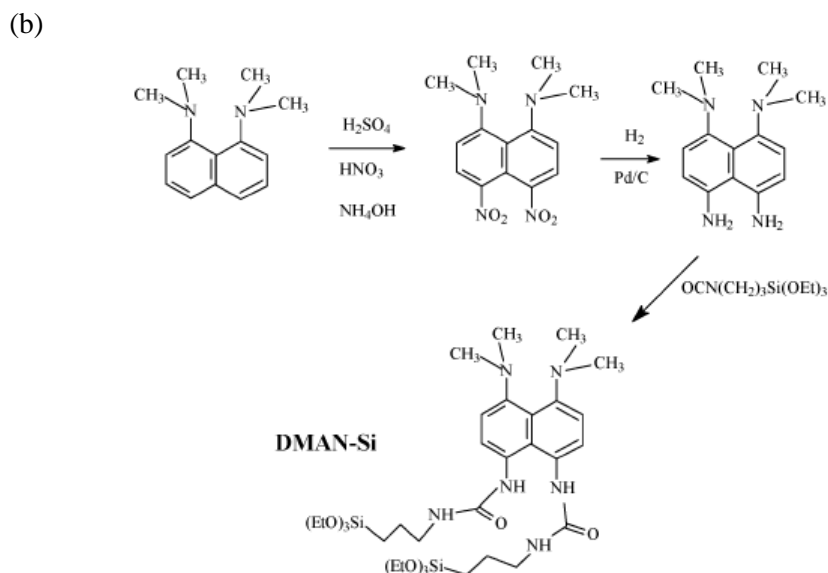


Figure 10. a) Synthesis of the di-iodo Tröger base derivative (1) and di-silylated precursor (2) from iodoaniline; b) synthesis of 1,8-bis(dimethylamino)naphthalene (DMAN) bis-silylated precursor (Gianotti *et al.* 2011 and Poli *et al.* 2011).

PMOs containing chiral-single-sites

The concept of single-site PMOs can be expanded to obtain new type of ordered hybrid materials with chirality that can be used as asymmetric catalysts. This emergent topic has been explored from different approaches, being the most usual the use of bridged silsesquioxane precursors that contain chiral organic linkers which are structurally integrated into the specific PMOs. In this way, Corma *et al.* 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% enantioselectivity in the cyanosilylation of benzaldehyde (Baleizao *et al.* 2003, 2004).

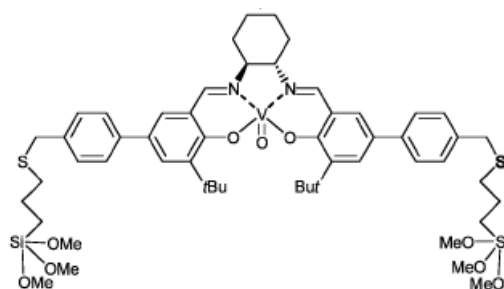


Figure 11. Bridged silsesquioxane containing vanadyl salen complex linker employed as precursor of ChiMO (Baleizao *et al.* 2003 and 2004).

Following this approach, García *et al.* prepared other attractive chiral periodic mesoporous organosilica, ChiMO, using as organic-inorganic precursor bis-silylated tartramide derived from L-(+)-dimethyl tartrate (Sharpless and Kagan ligand) (Figure 12). The organization achieved was the characteristic of M41S materials. It was also remarkable that around 12% of silicon atoms were functionalized by the chiral linkers. This chiral PMO was successfully used to catalyze the asymmetric oxidation of thioanisole, obtaining 70 % sulfoxide yields with induced enantiomeric excess of 31 %, after 24 h of reaction. The heterogeneity of the chiral builder was confirmed by reutilization of the ChiMO, supporting the effective heterogeneization of a chiral tartrate derivative organocatalyst (García *et al.* 2008).

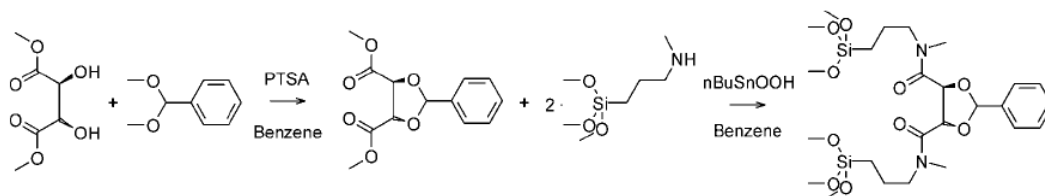


Figure 12. Synthesis of bis-silylated chiral tartramide monomer to obtain chiral PMOs (García *et al.* 2008).

PMOs which 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 to prepare organized mesoporous chiral hybrid materials with large surface ($>600 \text{ m}^2\text{g}^{-1}$) (Figure 13). The chirality of the surfaces was effectively probed by adsorption of chiral gases on the mesoporous solids (Kuschel *et al.* 2008).

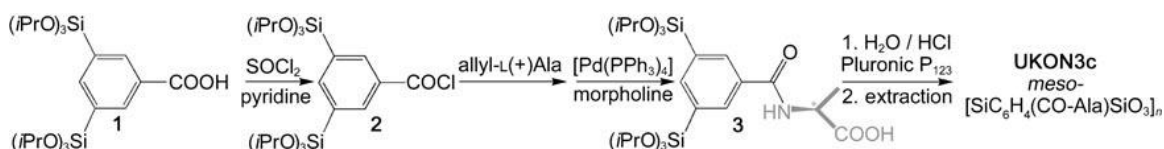


Figure 13. Synthesis of a PMO material with L-(+)-alanine introduced into the framework (Kuschel *et al.* 2008).

Also within the UKON family materials, a novel chiral mesoporous organosilica 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 center to the chiral building blocks allows to use the hybrid material as 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 homogenous 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 *et al.* 2010).

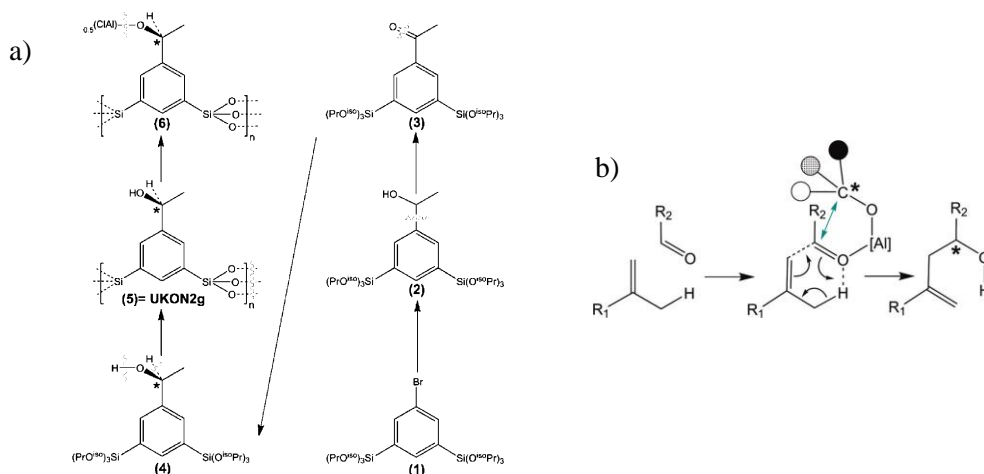


Figure 14. a) Synthesis of mesoporous organosilica containing chiral pore walls.; b) Asymmetric carbonylene scheme reaction (Kuschel *et al.* 2010).

Interesting approaches to directly generate chiral PMOs 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 permitted, for 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).

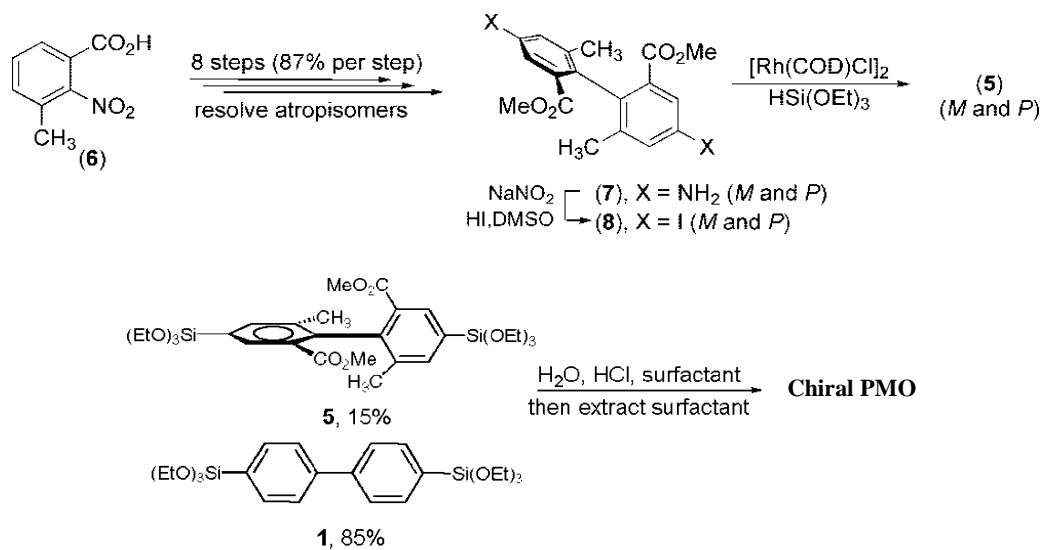


Figure 15. Synthesis route to prepare first the chiral monomer and second the derived PMOs (MacQuarrie *et al.* 2008).

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 (BTEE) 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.

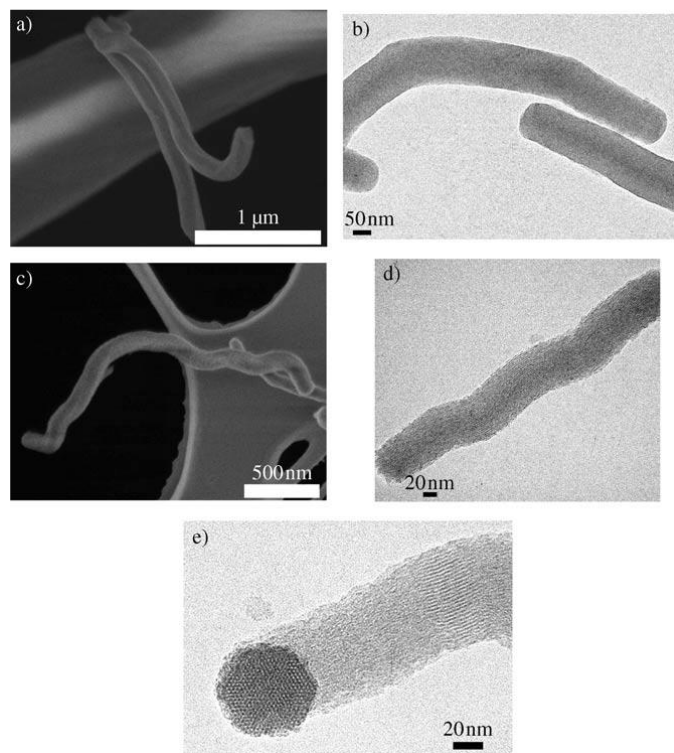


Figure 16. SEM (a and c) and TEM (b and d) micrographs of PMOs obtained with BTEE and BTEB precursors, respectively; TEM image (e) of sample containing aryl groups taken with a [100] incidence (Meng *et al.* 2007).

4. Coordination polymers or Metal-Organic Frameworks (MOFs)

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 certain extent in catalysis acting as stable single-site active materials (Li *et al.* 1999; Lebedev *et al.* 2005; Corma *et al.* 2010). Depending if the active sites in the MOFs are part of the structural nodes or linkers, or they are generated by post-synthesis modifications in the metalorganic frameworks, it is possible to classify MOF catalysts into three principal groups: (1) MOFs directly used as catalysts where the metal nodes or organic bridges exhibit catalytic activity, (2) MOFs in where active organic molecules or metallic nanoclusters are occluded or supported into the channels or cavities and (3) chemically modified MOFs by post-synthesis treatments by grafting a homogeneous catalysts counterpart onto the metalorganic frameworks, or by covalent post-modification of organic builders.

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 centers, each building 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 (Gándara *et al.* 2008; Lu *et al.* 2008; Llabrés *et al.* 2007), 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 metalorganic frameworks could perform as Lewis acid catalysts, as evidenced by Brown *et al.* who hydrothermally synthesized a new extended infinite MOF [Cu(H₂btec)(bipy)] (H₄btec = 1,2,4,5-benzenetetracarboxylic acid, bipy = 2,2'-bipyridine) (Figure 17). In this hybrid material each Cu(II) center 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 (H₂btec²⁻). The [Cu(bipy)]²⁺ moieties are bridged by H₂btec²⁻ 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 (TBHP) as oxidant. [Cu(H₂btec)(bipy)] demonstrated higher turnover frequencies (TOF) for cyclohexene conversion than for styrene, but with high selectivity towards epoxidation in both cases (Brown *et al.* 2009).

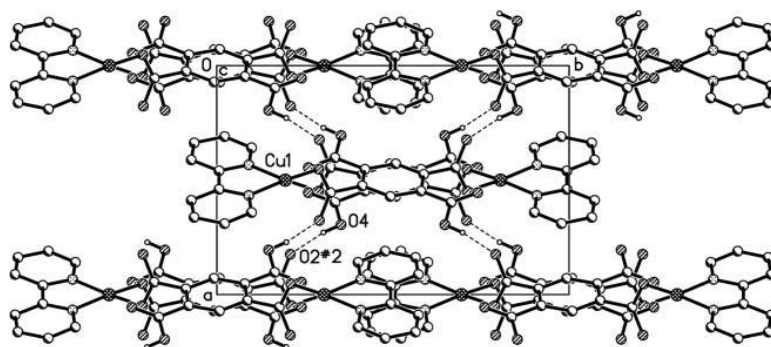


Figure 17. Scheme of [Cu(H₂btec)(bipy)] shown down the *c* axis (Brown *et al.* 2009).

Following with the catalytic activity of Cu-MOFs, recently Corma *et al.* have described the preparation of copper-containing metalorganic framework as catalysts, such as [Cu(2-pymo)₂], [Cu(im)₂], [Cu₃(BTC)₂] and [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, being those containing CuN₄ more active than CuO₄ centers. Remarkably, these Cu-MOF catalysts allowed to perform a one-pot two-step process in where the azide is formed *in situ* and reacted immediately with phenylacetylene to form the 1,4-triazole (Figure 18) (Luz *et al.* 2010).

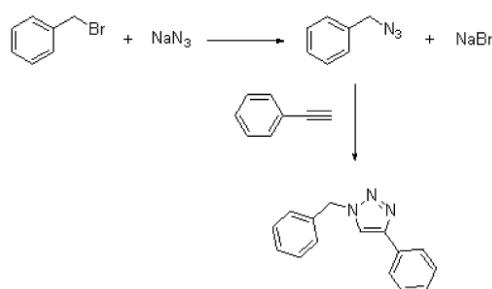


Figure 18. Formation of triazole compounds, from azide intermediates, using Cu-MOF catalysts (Luz *et al.* 2010).

Novel metalorganic frameworks featuring both Lewis acidity and shape selectivity properties have been recently presented (Gándara *et al.* 2009). Specifically, a scandium metal organic framework 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 where 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.

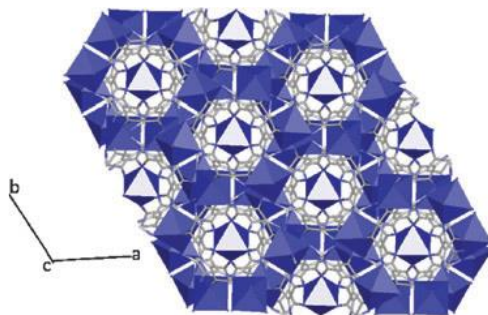


Figure 19. Polyhedral representation of the new $\text{Sc}_2(\text{C}_4\text{O}_4)_3$ MOF viewed along the c axis (Gándara *et al.* 2009).

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.* 2006). Recently, metalorganic frameworks have been prepared with non-coordinated amino groups, IRMOF-3 (IsoReticular Metal-Organic Framework), 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% 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 1-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 was 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 due 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 results that demonstrated the occurrence of

benzaldimine intermediate in the reaction mechanism (Gascón *et al.* 2009). Moreover, leaching of the active sites was observed, being those an intrinsic part of the organic linker.

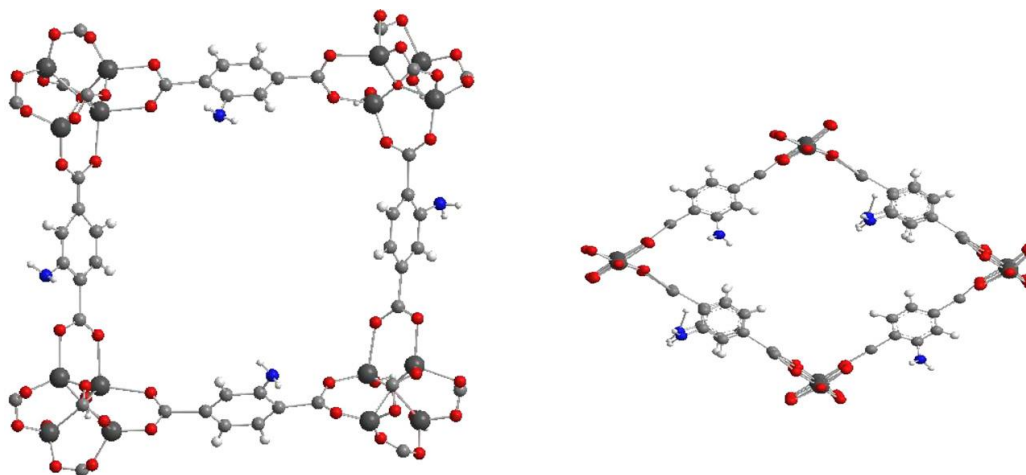


Figure 20. Structure of the synthesized MOFs: (left) IRMOF-3, (right) amino-MIL-53(Al). (Oxygen atoms in red, carbon atoms in light gray, nitrogen atoms in blue, and Zn (left) and Al (right) in dark gray (Gascón *et al.* 2009).

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 metalorganic environment. This method is currently used to heterogenize different organocatalysts to avoid the major drawbacks of homogenous catalysts in terms of catalyst separation and recycling. Within this approach, quaternary alkylammoniums salts such as Me_4NCl , Me_4NBr , Et_4NBr , Pr_4NBr , Bu_4NBr were occluded inside MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$, (BDC = benzene-1,4-dicarboxylate)) and the resulting materials revealed excellent catalytic performance for the coupling reaction of CO_2 with propylene oxide (PO) to produce propylene carbonate (PC). The reasons for the high catalytic activity of the MOF-5/ nBu_4NBr is the high surface area and accessibility to the active site, and the synergic effect of the couple MOF-5 and $\text{n-Bu}_4\text{NBr}$ to catalyze the reaction even at low CO_2 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/ Bu_4NBr catalytic system revealed also high activity and selectivity for the cycloaddition of CO_2

with other epoxides, such as glycidyl phenyl ether, epichlorohydrin and styrene oxide (Song et al. 2009).

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 $[\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_n\text{XM}_{12}\text{O}_{40}] \cdot (\text{C}_4\text{H}_{12}\text{N})_2$ ($X = \text{Si, Ge, P, As}$; $M = \text{W, Mo}$), were obtained by one-step hydrothermal synthesis of copper nitrate, benzene tricarboxylate (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 metal-organic framework (MOF) host (Figure 21). These materials demonstrated the 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).

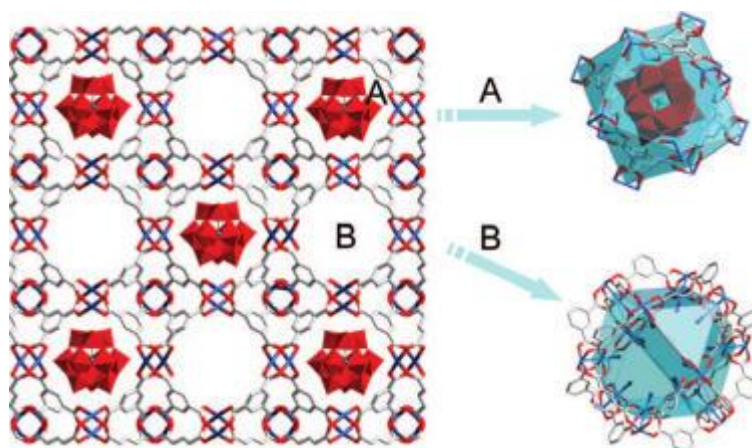


Figure 21. View of a (001) sheet with two kinds of pores, A and B, in **MOF-PMO**. The Cu-BTC framework and Keggin polyanions are represented by wireframe and polyhedral models. Blue, red, and gray represent Cu, O, and C, respectively (Sun et al. 2009).

Post-modified Metal-Organic Frameworks

Finally, additional post-synthesis treatments of MOFs have been carried out in order to covalently anchor different homogeneous organocatalysts onto the organic builders which are hence perfectly stabilized and integrated into the metalorganic framework. This methodology open 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, sulphonic 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) 8Am = 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 pK_a of the attached pyridine group being similar to that of aniline as precursor.

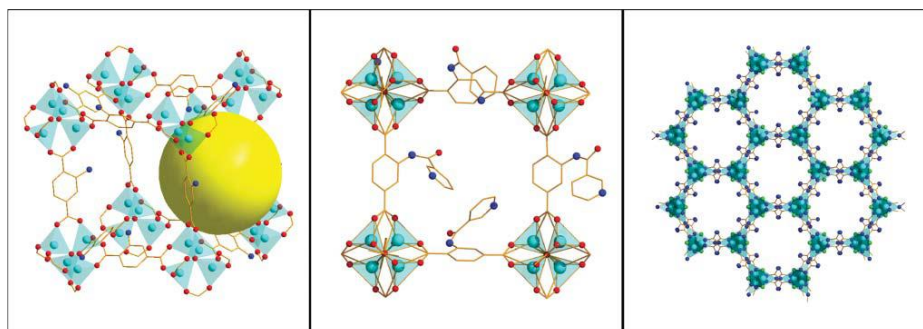


Figure 22. Diagram of IRMOF-3 (left), functionalised IRMOF-3 (middle) and ZnF(Am₂TAZ) (right) frameworks. The yellow balls indicate the size of the pore openings (Savonnet *et al.* 2009).

The catalytic performance of these modified MOFs was superior to the non-modified MOFs analogues for aza-Michael reaction, probably due to the higher hydrophilicity of the former. The resultant catalysts were also more active than their homogeneous counterparts due 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 metalorganic frameworks previously grafted with salicylaldehyde molecules (Figure 23a). The Au(III)-containing MOF was highly active and selective for 3D coupling and cyclization reactions in liquid phase. Importantly, the catalyst was fully recyclable, without leaching or modification during the reaction. More specifically, the

later was the multi-reaction coupling of N-protected ethynylaniline, amine, and aldehyde catalyzed 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 metalorganic frameworks, 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.* 2010).

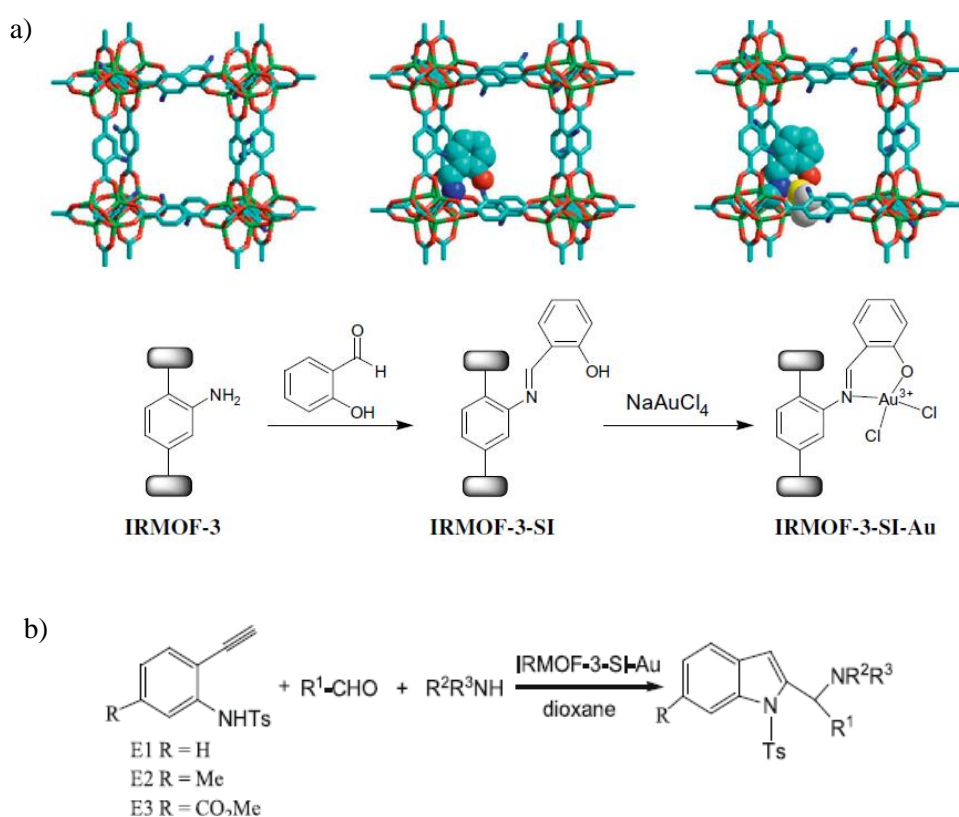


Figure 23. a) Post-synthesis modification procedure for obtaining MOFs containing Au(III) Schiff base complex. Zn: green; O: red; C: light blue; N: deep blue; Au: yellow; Cl: white. H atoms are omitted; b) multi-component coupling reaction scheme of N-protected ethynylaniline, amine, and aldehyde catalyzed by IRMOF-3-SI-Au catalyst (Zhang *et al.* 2009).

Conclusions

Different single-site catalysts based on PMOs, MOFs and supported silica materials have been presented. They show that the integration of homogenous active compounds into the defined and structured matrixes can increase the performance of molecular catalysts. Indeed, the presence of single-site heterogenized active phases in organized solids allows to obtain highly specific catalysts, with the advantages of recyclability and separation associated to heterogeneous catalysis. Definitively, the presence of single isolated sites into the framework of hybrid organic-inorganic structured materials bridges the gap between homoneneous 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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